Achieving over 90% initial Coulombic efficiency and highly stable Li storage in SnO$_2$ by constructing interfacial oxygen redistribution in multilayers

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Abstract:

Among the promising high capacity anode materials, tin dioxide (SnO$_2$) represents a classic and important candidate that involves both conversion and alloying reactions toward Li storage. However, the inferior reversibility of conversion reactions usually results in low initial Coulombic efficiency (ICE, ~ 60%), small reversible capacity and poor cycling stability of electrodes. Here, we demonstrate that by carefully designing the interface structure of SnO$_2$-Mo, a breakthrough comprehensive performance with ultrahigh average ICE up to 92.6 %, large capacity of 1067 mA h g$^{-1}$ and 100 % capacity retention after 200 cycles can be realized in a multilayer Mo/SnO$_2$/Mo electrode. The amorphous SnO$_2$/Mo interfaces, which are induced by redistribution of oxygen atoms between SnO$_2$ and Mo, can precisely adjust the reversible capacity and cycling stability of the multilayers, while the stable capacities of electrodes are parabolic with the interfacial density. Theoretical calculations and in/ex-situ experimental investigation clearly reveal that oxygen redistribution in the SnO$_2$/Mo hetero-interfaces boosts the Li ions transport kinetics by inducing a built-in electric field and improves the reaction reversibility of SnO$_2$. This work provides a new understanding of the interface-performance relationship of metal-oxide hybrid electrodes and pivotal guidance for creating high performance Li-ion batteries.

Keywords: Conversion reaction; interface engineering; tin dioxide; built-in electric field; oxygen redistribution
1 Introduction

The increasing demand on higher energy density and safety for Li ion batteries (LIBs) make it extremely important to exploit new anode materials with large capacity, safe operating potentials and fast Li\(^+\) diffusion kinetics in substituting the conventional graphite anodes.\(^1\)\(^-\)\(^3\) The past considerable efforts have verified that many alloying-type metals/semiconductors (Sn, Al, Si, Ge, etc.) and conversion-type metal oxides (Co\(_3\)O\(_4\), Fe\(_2\)O\(_3\), MnO\(_2\), etc.) meet well the criteria of higher capacity and safer potentials toward Li storage but still suffer from unsatisfactory reversibility and stability.\(^4\)\(^-\)\(^5\) Among those, tin dioxide (SnO\(_2\)) anode, storing Li\(^+\) through a combination of conversion reaction (SnO\(_2\) + 4Li\(^+\) + 4e\(^-\)→Sn + 2Li\(_2\)O) and then alloying reaction (Sn + 4.4Li\(^+\)+4e\(^-\)→Li\(_{4.4}\)Sn), with a theoretical capacity of 1494 mA h g\(^{-1}\) and moderate lithiation potential range of 0.4-1.0 V vs. Li/Li\(^+\),\(^6\)\(^-\)\(^7\) has been regarded as one of the typical and important anode materials for both mechanism exploring and performance tuning toward Li storage, which could ensure larger energy density and a higher level of safety for the cells.\(^8\)\(^-\)\(^9\) However, the following mentioned two major drawbacks of metal and metal oxide anodes have seriously impeded the wide utilization of it: (1) the large initial irreversible capacity loss characterized by low initial Coulombic efficiency (ICE) mainly due to inferior reversibility of conversion reaction,\(^10\)\(^-\)\(^11\) (2) severe capacity fading and unstable electrode/electrolyte interfaces resulted from the large volume effect of active phases during continuous cycling.\(^12\)

With respect to the reverse conversion reactions, Sn is oxidized to SnO\(_2\) by obtaining O from the decomposed Li\(_2\)O. As the Li\(_2\)O and SnO\(_2\) have very similar
formation enthalpy (-598 kJ mol\textsuperscript{-1} for Li\textsubscript{2}O and -581 kJ mol\textsuperscript{-1} for SnO\textsubscript{2}),\textsuperscript{6,13} how Sn competes with Li to capture O in the electrode is the key to tuning the reversible conversions of Li\textsubscript{2}O to SnO\textsubscript{2}. In fact, it has been revealed that the grain size of Sn and its contact area with Li\textsubscript{2}O determined the amount of regenerated SnO\textsubscript{2}, and high reversibility of conversion reactions can be achieved by reducing the size of Sn to about 10 nanometers.\textsuperscript{14,15} However, the nanosized Sn grains formed in the lithiated SnO\textsubscript{2} tend to coarsen, which is driven by minimizing the interface energy between the Sn and Li\textsubscript{2}O which are immiscible, and becomes serious at room temperature due to the extremely low recrystallization temperature (~ -53 °C) of Sn.\textsuperscript{16,17} Thus, the kinetics of the reverse conversion reaction is impeded and the transformation of a fraction of Sn to Li\textsubscript{x}Sn or SnO\textsubscript{2} is also hindered within large particles.\textsuperscript{18} These suggest that both the reversibility and stability of electrochemical reactions in SnO\textsubscript{2} electrodes are very sensitive to the interface interactions among the active phases including Sn, Li\textsubscript{x}Sn and Li\textsubscript{2}O. Therefore, it is important to stabilize the nanostructure of SnO\textsubscript{2} to maintain high reversibility of conversion reaction, and this has been achieved by pinning the grain boundary with the addition of transition metals (TM: Mn, Fe, Co, etc.), which leads to a high ICE of more than 77 % and enhanced capacity retention in ternary SnO\textsubscript{2}-TM-C composites.\textsuperscript{16,18,19}

It has been noted that adding TM not only has the effect of dramatically decreasing the Sn coarsening tendency within Li\textsubscript{2}O matrix, but also favors the combination of TM with O at the SnO\textsubscript{2}/TM hetero-interface which results in the redistribution of O and the formation of vacancy (O\textsubscript{vac}) in SnO\textsubscript{2}.\textsuperscript{18} The introduction of
$O_{\text{vac}}$ in semiconductor can reduce the band gap to enhance intrinsic conductivity, and influence the surface thermodynamics of semiconductor oxides and thus facilitate phase transition,\textsuperscript{20,21} which both promote the reversibility of conversion reactions in SnO$_2$-TM hybrids.\textsuperscript{18} Besides, recent studies have also demonstrated that strong chemical bonding within heterogeneous interfaces, especially the metal/semiconductor interfaces, could lead to internal charge redistribution and even structural changes that favor the formation of a built-in electric field, boosting interfacial charge transfer.\textsuperscript{22-24} Inspired by these, to enable a breakthrough in comprehensive performance for SnO$_2$-based anodes, i.e., achieving simultaneously high ICE, large capacity and superior cycling stability, rational constructing interfacial interactions to boost the O redistribution for forming more vacancies in SnO$_2$-TM system should be an effective way.

In this work, we carefully design the interfacial structure between SnO$_2$ and Mo to modulate the structural configuration and oxygen distribution by tuning the SnO$_2$-Mo multilayers. Most surprisingly, we find that the redistribution of O atoms occurs at the hetero-interfaces between active SnO$_2$ and inactive Mo layers, generating amorphous interface regions which can precisely adjust the reversible capacity and cycling stability. A remarkable comprehensive performance with ultrahigh average ICE up to 92.6% and superior capacity retention of 100% after 200 cycles can be achieved in a sandwiched Mo/SnO$_2$/Mo electrode. In addition, a combination of DFT calculations and in/ex-situ experimental analysis reveals the mechanism of capacity increase and fast Li$^+$ transport kinetics by SnO$_2$/Mo interfaces
with the introduction of interfacial O redistribution, which provides a new
derstanding on the interface-performance relationship of metal-oxide hybrid
electrode materials for the rational design of high-performance LIBs.

2 Results and discussion

2.1 Highly reversible, stable, and rapid charge transfer process in SnO$_2$-Mo
multilayer electrodes

The as-sputtered SnO$_2$-Mo multilayer films were directly used as binder-free
anodes for LIBs (Supplementary Fig. 1). For simplicity, all of the tested anodes are
abbreviated as listed in Supplementary Table 1, including their preparation parameters.

Fig. 1a, b present the reversible capacity and ICEs of the SnO$_2$, Mo/SnO$_2$ (MS),
SnO$_2$/Mo (SM) and Mo/SnO$_2$/Mo (MSM) films at a current density of 0.2 mA cm$^{-2}$
within 0.01-3.0 V vs. Li/Li$^+$. Compared to the pure SnO$_2$ electrode, both the reversible
capacity and ICEs can be greatly increased for the electrodes combined with Mo layer.
Notably, the symmetric sandwich structured MSM electrode exhibits the best
comprehensive electrochemical performance, achieving an ultrahigh average ICE of
92.6 %, large initial reversible capacity of 1067 mA h g$^{-1}$ (calculated based on the total
mass of the sputtered layers including Mo layers), with ~100% capacity retention after
200 cycles. In contrast, the ICEs of SnO$_2$, MS, and SM electrodes are 75.0 %, 83.9 %
and 85.8 %, respectively. To eliminate the effect of total film thickness on the stability
of large capacity, MSM/5 (5 layers) and MSM/11 (11 layers) electrodes
(Supplementary Fig. 1 and Supplementary Table 1) were tested respectively with the
same layer thickness. As displayed in Supplementary Fig. 2, both the MSM/5 and
MSM/11 electrodes, with total film thickness of approximately 700 nm and 1800 nm,
respectively (Supplementary Fig. 3), also deliver ICES greater than 90 % and maintain
stable high capacities of more than 1000 mA h g\(^{-1}\) throughout the cycles. These
consolidate that the good reversibility and stability of electrochemical reactions are
intrinsic for the SnO\(_2\)/Mo multilayer electrodes regardless of its film nature.

Obviously, the SnO\(_2\)/Mo multilayer structure greatly benefits the Li storage
performance. It is believed that the SnO\(_2\)/Mo interface plays a key role, and thus,
further interface tuning was carried out based on the MSM electrode. By taking
constant film electrode thickness, MSM-A, MSM-B and MSM-C electrodes were
prepared to have different layer numbers and consequently different interfacial
densities (Supplementary Fig. 1 and Supplementary Table 1). The interfacial density
is defined as the ratio of the total thickness of the interfaces to the total thickness of
the SnO\(_2\) layers in the electrodes, and the thickness of interface is taken as 14 nm
according to cross sectional transmission electron microscopy (TEM) observation
shown in Fig. 3 later. As shown in Fig. 1c, they exhibit different reversible capacities
although good cycling stability is maintained for all the MSM, MSM-A, MSM-B and
MSM-C electrodes. Among them, the MSM-B achieves the highest initial charge
capacity of more than 1700 mA h g\(^{-1}\) while remaining high ICE of 93.4 %
(Supplementary Fig. 4). Thus, the interfaces between SnO\(_2\) and Mo layers have
significant impacts on electrochemical reactions and Li storage capability.

Supplementary Fig. 5 shows the differential charge capacity plots (DCPs) for the
SnO$_2$, MSM and MSM-B electrodes. There are two distinct groups of peaks, including
the peaks of Li$_x$Sn dealloying within 0.01-1.0 V and the broad peaks of reversed
conversion reaction within 1.0-2.0 V. These three electrodes in Supplementary Fig. 5
maintain similar peak intensity for the dealloying reactions. Nevertheless, compared
to pure SnO$_2$ electrode, the reversibility of conversion reaction is greatly improved for
the MSM, and it can be further enhanced in the MSM-B with a much higher
interfacial density, demonstrating that the interfacial effect plays a huge role in
adjusting the electrochemical reactions of SnO$_2$-Mo multilayers. Fig. 1d illustrates the
relationship between the capacity increase and the interfacial density of multilayers
with a constant thickness as the MSM. The fitting curve reveals that the charge
capacity increase is parabolic with the interfacial density, and it reaches the maximum
as the interfacial density reaches the optimal value (about 0.5, representing half of the
SnO$_2$ layer is interfacial status), indicating that the additional reversible capacity
should be contributed from the interfacial Li storage. Continuing to increase the
interfacial density, the reversible capacity gradually decreases until it reaches the
lowest value in MSM-E and MSM-n with an interfacial density of 1 (The electrode is
entirely interfacial). The detailed mechanism will be further discussed later. This fitted
curve clearly demonstrates the interfacial regulation on the electrochemical reactions
and Li storage, and provides pivotal guidance for creating high performance
SnO$_2$-based electrodes. Fig. 1e summarizes the electrochemical performance reported
in the representative literatures on SnO$_2$-based anodes. From the perspective of
large reversible capacity, high ICE and superb capacity retention, the MSM electrode
represents a breakthrough comprehensive performance for SnO$_2$-based anodes.$^{14, 18, 47}$

Since the interfaces in SnO$_2$-Mo electrodes have an obvious regulatory effect on
the reversible storage of Li, it must also affect the charge transfer process. To evaluate
the Li storage characteristic and the transport kinetics, the rate capabilities of the
MSM and SnO$_2$ electrodes are compared at various current rates from 0.05 to 2 mA
cm$^{-2}$, as shown in Fig. 2a. Apparently, the MSM exhibits higher capacity retention
than SnO$_2$ at any current rate. More importantly, as it switches from high rate of 2 mA
cm$^{-2}$ to 0.05 mA cm$^{-2}$ again, the capacity of MSM recovers to that in the initial cycle
at 0.05 mA cm$^{-2}$. The superior rate capability of MSM indicates the significantly
increased Li$^+$ transport kinetics within both the SnO$_2$ and Mo layers. Fig. 2b shows
the discharge/charge curves at the 1st and 50th cycle for the SnO$_2$, MSM and MSM-B.
The initial charge curves reveal that MSM has a reversible capacity 1.4 times that of
SnO$_2$, and the reversible capacity of MSM-B is up to 1.6 times that of MSM. Due to
the inactivity of the Mo layers, the additional capacity for the electrodes with greater
interfacial density should originate from the Li storage reactions at the interfaces
mainly within the potential range of 1.0-2.0 V, which will be further verified later.

Fig. 2b also reveals that the initial reversible capacities of MSM and MSM-B can
still be maintained or even slightly increased after 50 cycles, which could be
attributed to the Li storage reactions at the SnO$_2$/Mo interfaces and gradually
activation of active materials, as well as the decomposition of solid electrolyte
interphase (SEI) at high potential range above 2.0V. In contrast, the capacity of SnO$_2$
has drastically decreased. Generally, most of the capacity fading in SnO$_2$ electrode
results from the declining reversibility of the conversion reaction \( \text{Li}_2\text{O} + \text{Sn} \rightarrow \text{SnO}_2 \), which can be reflected by the variation of differential charge capacity plots (DCPs) at different cycles.\(^{14, 18}\) As shown in Fig. 2c, in the SnO\(_2\) electrode, the dealloying peaks of \( \text{Li}_x\text{Sn} \) around 0.5 V gradually shift to higher potentials due to increasing polarization resulted from the coarsening of Sn and \( \text{Li}_x\text{Sn} \) phases. Furthermore, the complete disappearance of DCP peaks within 1.0-2.0 V after 50 cycles suggests dramatically declining reversibility of conversion reactions in the SnO\(_2\) electrode. In contrast, for the MSM, as shown in Fig. 2d, both the potential positions and integral intensities of these DCP peaks remain stable even after 200 cycles, demonstrating the outstanding reversibility and stability of the alloying and conversion reactions.

### 2.2 Phase and structural characterization for the interfaces and O redistribution in MSM electrode

Fig. 3a displays the grazing incidence X-ray diffraction (GI-XRD) patterns taken from the MSM with different incident angles, exhibiting structural information along the film depth. The phase constituents of each layer were tested by adjusting the grazing angle. Fig. 3b displays the comparison of GI-XRD patterns with the same incident angle of 2\(^{\circ}\) for the MSM, MSM-A, MSM-B and MSM-C. Obviously, the diffraction peaks gradually weaken and broaden towards a lower angle as the SnO\(_2\)/Mo interfacial density increased, implying the increased amorphous components and defects such as oxygen vacancies,\(^{48, 49}\) and another distinguishable diffraction
peak at 44° could be MoO$_x$.

The cross-sectional morphology of different SnO$_2$-Mo multilayers with obvious columnar crystal feature was visually confirmed by scanning electron microscope (SEM) and TEM images in Supplementary Figs. 6-9. Specifically, Fig. 3c shows the cross-sectional structure of the MSM sample prepared by focused ion beam (FIB), which consists of two layers of Mo and one layer of SnO$_2$. The high-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns demonstrate the detailed structural information on each layer and the interface (Fig. 3d-f). The lattice fringes and diffraction rings reveal that most Mo and SnO$_2$ are polycrystalline. Nevertheless, there are some amorphous components around the columnar Mo grains, as depicted in Fig. 3d. Meanwhile, from the HRTEM and fast Fourier transform (FFT) images for the interface between SnO$_2$ and Mo layers (Fig. 3f), it is revealed that there is an amorphous region along the SnO$_2$/Mo interface with a width of about 14 nm. Moreover, as shown in Supplementary Fig. 9g, amorphous products are more prominent in the MSM-B with greater interfacial density, which is consistent with the results in Fig. 3b. By comparing energy-dispersive X-ray spectroscopy (EDS) mapping and line scan of Sn, Mo, and O elements for the MSM electrode, as shown in Fig. 3g, it can be found that Mo layer and SnO$_2$ layer have obvious mutual diffusion across the interface in the MSM. O shows a high content in the Mo layer, although it mainly exists in the SnO$_2$ layer. For MSM-B with higher interfacial density (Fig. 3h), O is more uniformly distributed across the multilayers, meaning the even more evident diffusion of O. These indicate that increasing the interfacial density among
SnO$_2$ and Mo layers can induce obvious O redistribution and thus amorphous region formation, which could be the main reason for the great enhancements in the capacity, reversibility and cycling stability of the MSM and MSM-B electrodes.

Such a redistribution of O could result in the phase transformation at the SnO$_2$/Mo interfaces. The detachment of O atoms from the lattice of SnO$_2$ definitely also introduces abundant defects, i.e. O$_{\text{vac}}$. To further verify that, the chemical information at the interfaces of MSM and the presence of O$_{\text{vac}}$ were analyzed using X-ray photoelectron spectroscopy (XPS). Fig. 4a, b show the XPS spectra for Sn and Mo elements at the up side of interface in MSM, the two peaks in Mo 3d XPS spectrum confirm the presence of MoO$_3$, while the valence band spectrum of Sn belongs to SnO. Similarly, for the down side of interface (Fig. 4c, d), the Mo3d XPS spectrum can be fitted into six peaks, corresponding to Mo, MoO$_2$ and MoO$_3$, respectively, and the valence band spectrum of Sn can be assigned to the combination of SnO and SnO$_2$. The existence of SnO and MoO$_2$ as well as MoO$_3$ in the MSM electrode reveals a significant redistribution of O and the resulting O$_{\text{vac}}$ in SnO$_2$ layer.

The presence of the O$_{\text{vac}}$ in MSM is further proved by O 1s XPS spectra in Supplementary Fig. 10. The peaks at 530.3 eV and 531.7 eV are attributed to the Metal (M)–O and the O$_{\text{vac}}$, respectively.$^{20,50}$ Thus, the O redistribution and O$_{\text{vac}}$ here due to interfacial effects reflects the charge transfer and structural change in MSM, leading to the generation of the amorphous interfaces and the amorphous MoO$_x$ products in Mo layers, and affecting the electronic and structural behaviors of MSM electrode, thereby modifying its reaction kinetics and therefore improving the Li
storage capabilities.

To verify the specificity and superiority of the O redistribution and in situ formed amorphous interfaces in the MSM, MoO$_3$-SnO$_2$ multilayers with the highest valence state of Mo and Sn elements were also assembled (Supplementary Table 2 and Supplementary Fig. 11). As expected, there is no amorphous interface between MoO$_3$ and SnO$_2$ layers. And thus, the MoO$_3$/SnO$_2$/MoO$_3$ sandwitched electrode has a lower ICE of 77\% and a charge capacity retention of 61.4 \% after 50 cycles, which is close to the pure SnO$_2$ and much inferior to those of the MSM electrode.

2.3 Theoretical calculations to understand O distribution-boosted reaction kinetics

Density functional theory (DFT) calculations were performed to understand the interfacial structure in MSM. Crystal structures of SnO$_2$ and Mo as well as SnO$_2$/Mo hetero-interface viewed along [001] direction are shown in Fig. 4e and Supplementary Fig. 11. Three models based on the contact types are established for calculating the interfacial formation energy, and model 2 shows the lowest value of -0.367 eV Å$^{-2}$, demonstrating the most stable interface state (Supplementary Table 3). According to the calculated Bader charge (Supplementary Table 4), the distribution of valence states at the hetero-interface for Sn and Mo are plotted in Fig. 4f. The presence of SnO, MoO$_2$ and MoO$_3$ with Bader charge in range of 2.8-4.5 eV, theoretically confirms the obvious interdiffusion process of O at the hetero-structure.

For the MSM electrode, due to the inactive Mo layer toward Li storage, the
redistribution of O is vitally important for Li\textsuperscript{+} successfully passing through the Mo layer to SnO\textsubscript{2} layer. As illustrated in detail in Fig. 4g, in the hetero-interface region, O from SnO\textsubscript{2} diffuses into the Mo layers through the interfaces and the gaps between the columnar crystals, thus, O aggregates at the SnO\textsubscript{2}/Mo interfaces and the grain boundaries of Mo. A gradient distribution of O content appears in the Mo layers, that is, it gradually increases from the outside to the interface (Fig. 4g1). The redistribution of O results in the loss of O to generate SnO\textsubscript{x} (1\textless x\textless 2) for the SnO\textsubscript{2} at the interfaces, and the capturing of O to generate MoO\textsubscript{x} (4\textless x\textless 6) for Mo at the interfaces and the boundaries of columnar crystals, thus forming amorphous interfaces composed of SnO\textsubscript{x} and MoO\textsubscript{x}, and the gradient distribution of active MoO\textsubscript{x} in Mo layers toward Li storage (Fig. 4g2). Therefore, as displayed in Fig. 4g3, owing to the driving force of the concentration difference of O, Li\textsuperscript{+} can diffuse into the MSM easily through the favorable pathway provided by the active MoO\textsubscript{x} which surrounds the metal Mo with good electronic conductivity. Moreover, the presence of SnO\textsubscript{x} with numerous O\textsubscript{vac} in the SnO\textsubscript{2} layer could contribute to improved electrical conductivity and reversibility of conversion reaction, leading to high ICE.\textsuperscript{18,51}

Changes in the internal structural characteristics inevitably affect the charge transfer behaviors of MSM. The in-situ formed heterojunctions formed by the metal oxide semiconductors could induce a built-in electric field (E) between the interface and SnO\textsubscript{2} layer. The calculated electrostatic potential for SnO\textsubscript{2}, SnO, MoO\textsubscript{2} and MoO\textsubscript{3} at the interface are shown in Fig. 5a. Since the work function (W\textsubscript{f}) of the SnO\textsubscript{2} (7.36 eV) is larger than that of all other oxides, electrons transfer from the interface (SnO,
MoO$_3$ and MoO$_2$) to SnO$_2$ across the heterojunctions.$^{52,53}$ Therefore, the $E$ is generated within MSM, pointing from the interface to SnO$_2$ layer.$^{42,54}$ Under the $E$, the barrier for the diffusion of Li$^+$ in the bulk of SnO$_2$ also changes accordingly (Fig. 5b, c). Along the direction of $E$ (A→B→C), the diffusion barrier decreases from 0.16 eV to 0.13 eV(A→B) and 0.08 eV to 0.05 eV(B→C), which is beneficial for the insertion of Li$^+$ and the inflow of electrons in MSM. The electrons/ions transfer pathway and detailed mechanism of boosted charge transfer in MSM are illustrated in Fig. 5d. When the battery is discharged (lithiation), an additional junction barrier electric force, pointing to SnO$_2$ from the interface, facilitates the rapid insertion of Li$^+$, and this effect is strongest near the interface.$^{54,55}$ As clearly revealed by in-situ TEM observation shown in Supplementary Video 1, the process of Li$^+$ quickly passing through the outer Mo layer to the SnO$_2$ layer has been found. After full lithiation, the Li$_x$Sn, Mo and Li$_2$O products from SnO$_x$ and MoO$_x$ lead to a Li$^+$ rich region in the micro-domain of SnO$_2$ layer and a Li$^+$ poor region at the interface. Thus, a new $E$ builds with a direction from SnO$_2$ layer to the interface, promoting the following Li$^+$ extraction process. These theoretical calculations offer a thorough insight into the interfacial effects of electrode materials for LIBs. Due to the charge transfer driving force originating from the hetero-interface, MSM electrode exhibits high-rate capability and low resistance toward Li$^+$ insertion and extraction, as displayed in Fig. 2a.
2.4 In/ex-situ characterizations to reveal the interfacial effect on highly reversible and stable conversion reactions

Another important aspect that needs to be understood is how the SnO2/Mo interfaces contributed to the additional reversible capacity and highly reversible and stable conversion reactions in MSM electrode. From the in-situ XRD analysis for the SnO2 electrode, as shown in Fig. 6a, the gradually disappearing of SnO2 and appearing of Sn in conversion reaction and then appearing of LixSn phases during alloying reactions happened along with the discharge from 3.0 V to 0.01 V. However, the clearly observed diffraction peak of Sn as recharged to 3 V indicates poor reversibility of the conversion reaction. For the MSM multilayers in the initial cycle, as shown in Fig. 6b, the Sn and LixSn phases which generated in the conversion and alloying reactions are basically undetectable, suggesting their ultrafine grain size which homogenously dispersed within the Li2O, which leads to the largely reversible conversion between SnO2 and Sn/Li2O in the repeated cycles in MSM. Besides, the diffraction of Mo weakens and shifts to lower 2θ values when discharging, and increases and shifts to the original 2θ values when charging. Obviously, the variation of Mo peak throughout the cycle in MSM is much more obvious than that in the pure Mo (Supplementary Fig. 13), and agrees with the GI-XRD results as the interfacial density increases (Fig. 3b). Therefore, the variation of Mo peak can be used to track the evolution of the interfaces, and the interfaces should expand during the Li⁺ insertion process and partially recover during the Li⁺ extraction process, indicating the interfacial Li storage characteristic. Further tracking of the Mo peak in the subsequent
cycles (Fig. 6c, d) demonstrates that the interface remains stable after the 10th cycle.

The variation of the SnO$_2$/Mo interfaces in MSM has also been directly revealed by in-situ TEM observation (Supplementary Video 1). As shown in Fig. 6e, f, and Supplementary Figs. 14 and 15, the interface zone becomes wider and more distinct during the initial 10 cycles and then reaches its steady state. Therefore, the variation of the SnO$_2$/Mo interfaces observed by in-situ XRD and in-situ TEM demonstrates the interfacial Li storage characteristic, which could be the absorption of Li at the interfaces that contributes to the extra storage capacity in the MSM electrodes.$^{56, 57}$

The contribution of interfacial storage can be further enhanced by increasing the interfacial density in the MSM-A and MSM-B multilayers. However, as the Mo and SnO$_2$ layers become much thinner (such as MSM-C, D) and the interfacial density is too high, the Li adsorption energy should be enhanced due to the ultra-high interfacial effect.$^{58, 59}$ It has been previously revealed that the interfacial Li adsorption helps to increase the additional storage capacity in Li$_2$S/graphene composites before the amount of adsorbed Li atoms reaches 2.$^{58}$ The high Li adsorption energy should hinder the Li$^+$ diffusion process, and the absorbed Li at the interfaces is difficult to detach during the delithiation process, leading to the increased irreversible capacity and decreased ICE (Supplementary Fig. 16). Besides, more oxygen in SnO$_2$ should redistribute to Mo in the multilayers with higher interfacial density, finally forming MoO$_x$ and SnO$_x$ multilayers rather than original metal/semiconductor heterogeneous interfaces. In this case, the driving force from concentration difference of O for fast ion diffusion and the internal interfacial charge redistribution should be weakened,
resulting in inferior reversibility and stability of lithiation and delithiation reactions.

In contrast, in the SnO\textsubscript{2} or MS electrodes without or just with limited SnO\textsubscript{2}/Mo interface, poor structural stability and instantaneous collapse of active layer during lithiation can be also found by in the in-situ TEM observation (Supplementary Video 2). These further consolidate that the Li storage behaviors at the SnO\textsubscript{2}/Mo interfaces are responsible for the relationship between the capacity increase and interfacial density, as displayed in Fig. 1d.

To investigate the interfacial effect on the promotion of highly reversible Li storage, the composition distribution of Li in the depth direction (perpendicularly to the current collector) in the MSM during the 1st cycle was investigated by time-of-flight secondary ion mass spectrometry (TOF-SIMS), as displayed in Fig. 6g and Supplementary Fig. 17. The depth profiles of Li as discharged to 0.01 V, charged to 1V and 3V (Fig. 6g), indicate that a large and almost equal amount of Li can be released during the processes of dealloying and reverse conversion reactions, meeting well with the theoretical capacity proportion of these two reactions (771 vs. 784 mA h g\textsuperscript{-1}), demonstrating the fully reversible reactions in the MSM.

It is noted that XRD and TEM are hard to clarify the existence of Li\textsubscript{2}O and the regenerated SnO\textsubscript{2} which are usually amorphous. Thus, spectrum methods were conducted to characterize the reversible conversion between Li\textsubscript{2}O and SnO\textsubscript{2}. Since Li\textsubscript{2}O turns into Li\textsubscript{2}CO\textsubscript{3} when exposed to air, the variation of Li\textsubscript{2}CO\textsubscript{3} could evaluate the variation of Li\textsubscript{2}O in the electrodes. As shown in Fig. 6h, the Fourier transform infrared spectrometer (FTIR) spectra of the MSM electrode clearly reveal the
generation and disappearance of Li$_2$O during the discharge/charge reactions. Li$_2$O starts to generate when discharged to 0.6 V and its content reaches the maximum at 0.01 V, indicating the completed conversion reaction. On the contrary, during the charging process, Li$_2$O gradually diminishes and then disappears at 2 V, indicating that Li$_2$O is completely reacted with Sn again and converted to SnO$_2$. The regenerated SnO$_2$ is further proven by surface-enhanced Raman spectrum (SERS) collected from the MSM electrode as shown in Supplementary Fig. 18. These fully confirm that the reversibility and stability of the conversion reaction in SnO$_2$ is greatly promoted in the MSM electrode with amorphous interfaces caused by O redistribution, which is responsible for the demonstrated high round-trip efficiency, increased capacity and superior cycling stability in the SnO$_2$-Mo multilayers.

3 Conclusions

To summarize, we assembled the SnO$_2$-Mo multilayers with adjustable interfaces and tunable oxygen distribution, and established a model to quantify the regulating effect of SnO$_2$/Mo interfaces on the stability and reversibility of conversion between SnO$_2$ and Sn/Li$_2$O.Benefiting from the multifaceted interfacial effects on the structural stability, Li storage capacity and reaction kinetics, Mo/SnO$_2$/Mo exhibits good cycling stability and accelerated charge-transfer kinetics, realizing a breakthrough performance with high average ICE of 92.6 % and large capacity of 1067 mA h g$^{-1}$ remained 100 % after 200 cycles. Furthermore, we clarified that the redistribution of oxygen between SnO$_2$ and Mo layers helps to form SnO$_2$/Mo
amorphous interfaces, thereby providing additional reversible capacity and promoting the highly reversible and rapid conversion reaction in lithiated SnO$_2$. This work based on interface engineering and modulation of oxygen distribution provides a novel fundamental strategy to design highly reversible and stable conversion-type electrode materials for large capacity Li storage.

4 Experimental

4.1 Preparation of multilayer thin film electrodes

All multilayer thin film electrodes were deposited on Cu foil substrates (6*6 cm$^2$) using a KYKY JGB-560 magnetron sputtering system. The targets of SnO$_2$, Mo and MoO$_3$ have a diameter of 60 mm and a thickness of 5 mm. Under optimized conditions, in a typical deposition, a radio frequency magnetron (power 120 W, 2.0 Pa Ar as the working gas) was used during deposition after a base pressure of 1.0 *10$^{-4}$ Pa was achieved. The various multilayer thin films, namely, SnO$_2$, SnO$_2$-Mo and SnO$_2$-MoO$_3$, were comparatively investigated as anodes for LIBs.

To prepare the sample for surface enhanced Raman spectroscopy (SERS) measurement, colloid of Au nanoparticles was deposited on the surface of the SnO$_2$ and Mo/SnO$_2$/Mo electrodes.

4.2 Materials characterization

X-ray diffraction (XRD) was performed with a PANalytical X'Pert Pro Alpha-1 diffractometer using Cu Ka radiation. The microstructure was characterized using a
Carl Zeiss Supra 40 field emission scanning electron microscope (SEM) and a high-resolution transmission electron microscope (TEM, JEOL JEM-2100F) operating at 200 kV. The compositions of the layers were determined with an energy-dispersive spectrometer (EDS) attached to the TEM. X-ray photoelectron spectroscopy (XPS) was performed with a PerkinElmer PHI 5000c XPS system using the C 1s peak at 284.8 eV as a reference. TOF-SIMS measurements were conducted on a TOF-SIMS spectrometer (TESCAN GAIA3 model 2016 UHR SEM). The TOF-SIMS measurements were conducted in positive mode. A pulsed 30 keV Ga$^+$ ion beam was used in the high current mode for depth profiling. The SERS measurement was conducted with a laser Raman spectrometer (Raman, Horiba) at an excitation wavelength of 532.0 nm. The accurate component analysis was conducted by an Escable 250 X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA). FTIR spectra were obtained by a Nicolet iS50FTIR spectroscopy, equipped with attenuated total reflectance technique. The measurement worked in the range of 4000-700 cm$^{-1}$.

For the ex-situ measurement of electrochemically tested electrodes, the samples were carefully stored and transferred to minimize air exposure. The reacted film electrodes at different states were prepared by discharging/charging to a controlled cutoff voltage. These electrodes were removed from the electrochemical cells, rinsed with DMC and dried under vacuum in the ante-chamber of an argon filled glove box.
4.3 In-Situ Examinations

In-situ XRD analysis was conducted with a PANalytical X’Pert Pro Alpha-1 diffractometer using Cu Kα radiation and investigated by a homemade cell that was sealed by Be foil as the X-ray penetrator, accompanied with the lithiation/delithiation process. The 2θ range of each scan started from 25° to 45° with step increment of 0.02° at step size of 0.26°. In-situ TEM measurement was performed on a JEOL 1400 TEM. The MSM electrode was displayed on an Au rod as the working electrode, while a small film of Li metal was scratched on a W wire as the counter electrode. A thin layer of Li₂O was expected to form as the solid electrolyte during the charge transfer process. When physical contact between the two electrodes was encountered, a potential bias of ±3 V versus Li/Li⁺ was applied to drive the diffusion of Li⁺.

4.4 Electrochemical measurements

CR2016 coin-type half-cells were assembled in a glove box with Li metal foil as the counter electrode and a polyethylene membrane as the separator. The electrolyte was a solution of 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:2, and 10 wt% fluoroethylene carbonate (FEC) was added. The electrochemical performance of the different film electrodes was measured by galvanostatic charge–discharge cycling using a multi-channel battery test system (LAND CT2001A) at various current densities, and cutoff potentials of 0.01 V for discharging and 3.0 V or 1.0 V for charging.
4.5 Computational Method

Our SnO$_2$/Mo heterostructure models consist of a slab of Mo deposited on top of a SnO$_2$ surface. According to previous reports, the (110) surface of rutile SnO$_2$ (space group P4$_2/mnm$) is the most stable, so we selected the (110) surface of SnO$_2$ to match with the (110) surface of cubic Mo (space group Im$ar{3}$m).

All calculations were performed by using the projector augmented wave (PAW) method within density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP). Generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE) formula was employed for evaluating the electron exchange correlation energy. The DFT-D3 method of Grimme was used to describe the weak dispersion forces. The energy cutoff for the plane waves was set to 500 eV. Brillouin-zone integrations were approximated by using special k-point sampling of Monkhorst-Park scheme [MP76] with a k-point mesh resolution of $2\pi \times 0.03 \, \text{Å}^{-1}$. The structural parameters were fully optimized until the energy on each atom was less than $10^{-5}$ eV and the forces on each atom were less than $0.01$ eV/Å. The ab initio molecular dynamics (AIMD) simulations were performed in supercell models and only the gamma point was used for the Brillouin zone sampling to keep the computational cost at a reasonable level. The time step was set to 2fs. The NVT ensemble using Nosé-Hoover thermostat was adopted. For Li$^+$ diffusion into the SnO$_2$ surface, the climbing image nudged elastic band (CI-NEB) method was used in supercell models.
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Author contributions

R.H., M.Z. and X.L. conceived the idea and designed the experiments. X.L., H.Z., L.T. and X.X. conducted the material preparation, electrochemical measurements and materials characterization. X.L. performed the ex-situ measurements and the data analysis. X.L., J.C. and X.Y. performed in-situ experiments and participated in data analysis. X.Z. and S.W. performed the theoretical calculations. X.L., J.C. and J.H. wrote the paper with assistance from coauthors.

Competing interests

The authors declare no competing interests.
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Fig. 1 Highly reversible and stable Li storage properties of SnO$_2$-Mo electrodes in half cells.

(a) Comparison of charge capacity. (b) Summary of the ICEs from every five cells for SnO$_2$, SM, MS and MSM electrodes. (c) Cycling performance of MSM-A, MSM-B and MSM-C electrodes in the initial 50 cycles. (d) The relationship between normalized capacity increase and interfacial density. The charge capacity of each electrode is taken from the 5th cycle. The dotted lines represent the capacity increase calculated from the fitting curves. (e) The reversible capacities, capacity retentions after 200 cycles and ICEs of SnO$_2$-based anodes for LIBs reported in the recent literatures, including the pure SnO$_2$, SnO$_2$-C, SnO$_2$-Ms, SnO$_2$-MOs, SnO$_2$-MSs. The red sphere represents the average electrochemical performance of the MSM electrode.
Fig. 2 Comparison of the rate capabilities and reaction reversibility for the SnO$_2$ and MSM electrodes. (a) Rate capabilities of SnO$_2$ and MSM electrodes. (b) Charge–discharge profiles of SnO$_2$, MSM and MSM-B electrodes at the 1st and 50th cycles. (c, d) Differential charge capacity vs. voltage curve of SnO$_2$ and MSM electrodes at the 1st, 10th, 20th, 50th, 100th and 200th cycles.
Fig. 3 GI-XRD and FIB-TEM characterizations of the structure and cross-sectional morphology of MSM, MSM-A, MSM-B and MSM-C. (a) GI-XRD patterns of MSM with the incident angle of 0.3°, 0.5° and 2.0°. (b) GI-XRD patterns of MSM, MSM-A, MSM-B and MSM-C with the incident angle of 2°. (c-g) TEM observation of MSM. (c) Typical FIB-TEM image of cross-sectional morphology. (d, e) HRTEM images of the Mo and SnO$_2$ layers, insets in (d) and (e) are the corresponding SAED images. (f) HRTEM image at the interface between Mo and SnO$_2$ layers, and FFT images of corresponding regions. (g, h) EDS mapping and line-scan images of Sn, Mo and O elements for MSM and MSM-B.
Fig. 4 XPS analysis and DFT calculations of valence states and charge distributions at the interfaces of MSM. (a-d) XPS spectra at the interfaces of MSM. (a) Mo 3d at the up side of interface in MSM. (b) Valence band Spectrum of Sn 3d at the up side of interface in MSM. (c) Mo 3d at the down side of interface in MSM. (d) Valence band Spectrum of Sn 3d at the down side of interface in MSM. (e) Crystal structure of Mo, SnO$_2$ and the interface viewed along [001] direction. (f) Distribution of valence states of Sn and Mo atoms at the hetero-interface in MSM. (g) Schematic showing the redistribution of O and the rapid transfer process of electrons/ions in MSM.
Fig. 5 DFT calculations of the Li\textsuperscript{+} transfer dynamics boosted by induced electric field effect

(E). (a) Calculated electrostatic potential of SnO\textsubscript{2}, SnO, MoO\textsubscript{3}, and MoO\textsubscript{2}, respectively. (b) Crystal structure of SnO\textsubscript{2} with three Li\textsuperscript{+} intercalated at A, B, and C sites. (c) Calculated diffusion barrier of Li\textsuperscript{+} from A→B and B→C along the electric field. (d) Schematic diagram of the effect of $E$ and the mechanism of boosted charge transfer within MSM.
Fig. 6 In/ex-situ observations of morphology and phase evolution of MSM electrode during lithiation/delithiation processes. (a-d) Contour plots of in-situ XRD patterns against the voltage for the SnO$_2$ and MSM electrodes. (a) SnO$_2$ electrode during the 1st cycle. (b-d) MSM electrode during the 1st cycle (b), 2nd cycle (c) and 10th cycle (d). (e, f) In-situ TEM observation of MSM electrode at the fully delithiated status in the 1st cycle (e) and 10th cycle (f). (g) TOF-SIMS characterization for Li/Sn depth profiles as discharged to 0.01 V, charged to 1V and 3V in the 1st cycle. (h) Ex-situ FTIR spectra at seven different states during the 1st cycle, namely OCP, discharged to 1.5V, 0.6V and 0.01 V, recharged to 1V, 2V and 3.0 V.