Low Interface Energies Tune the Electrochemical Reversibility of Tin Oxide Composite Nanoframes as Lithium-Ion Battery Anodes

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Supporting Information

ABSTRACT: The conversion reaction of lithia can push up the capacity limit of tin oxide-based anodes. However, the poor reversibility limits the practical applications of lithia in lithium-ion batteries. The latest reports indicate that the reversibility of lithia has been appropriately promoted by compositing tin oxide with transition metals. The underlying mechanism is not revealed. To design better anodes, we studied the nanostructured metal/Li2O interfaces through atomic-scale modeling and proposed a porous nanoframe structure of Mn/Sn binary oxides. The first-principles calculation implied that because of a low interface energy of metal/Li2O, Mn forms smaller particles in lithia than Sn. Ultrafine Mn nanoparticles surround Sn and suppress the coarsening of Sn particles. Such a composite design and the resultant interfaces significantly enhance the reversible Li-ion storage capabilities of tin oxides. The synthesized nanoframes of manganese tin oxides exhibit an initial capacity of 1620.6 mA h g−1 at 0.05 A g−1. Even after 1000 cycles, the nanoframe anode could deliver a capacity of 547.3 mA h g−1 at 2 A g−1. In general, we demonstrated a strategy of nanostructuring interfaces with low interface energy to enhance the Li-ion storage capability of binary tin oxides and revealed the mechanism of property enhancement, which might be applied to analyze other tin oxide composites.

KEYWORDS: manganese tin oxides, nanoframes, Li-ion batteries, anodes, first-principles calculation

1. INTRODUCTION

The rapid developments of electric vehicles and portable electronics stimulate the growing demands for high-energy-density lithium-ion (Li-ion) batteries. High-capacity materials hold promises to increase the specific energy of Li-ion batteries. Among many previously reported anodes,2–6 tin oxides have received intensive attention because of large theoretical capacity and fast charge/discharge capability. The in situ studies showed that a high capacity can be obtained via the conversion reaction of tin oxides and the alloying reaction of metallic Sn.7–11 The formation of Li1.4Sn alloy can deliver a capacity of 994 mA h g−1.10 Mössbauer spectroscopy of 119Sn revealed that the lithiation process of SnO2 first involves a minor intercalation reaction of Li2SnO2 and subsequent formation of Sn(II) and Sn(0) species via conversion reactions.12–14 The utilization of conversion reactions of lithia for lithium storage is able to further push the capacity limit of SnO2.6,15 However, the poor reversibility of lithia largely limits the practical applications of SnO2 as compared to other intercalation anode materials.16

Because of the irreversibility of lithia, tin oxides usually exhibit rapid capacity decay in a few cycles.3 Tarascon et al. reported that low-valence transition-metal oxides (MO, M = Co, Ni, Cu, or Fe) can be used as anodes via conversion reactions.17 A series of composite oxides of transition metals (M) and tin have been reported to promote the conversion reaction of lithia, for example, Co2SnO4, SnO2/C, NiO/ SnO2, and Zn2SnO4.18–21 Their experimental results demon-
strate that binary or ternary M/Sn oxides are able to increase either capacity or cycling properties to pristine SnO2. The performance improvement had been attributed to synergetic or catalytic effect.\textsuperscript{25–26} Recently, Hu et al. found that the critical approach to a reversible conversion of lithia is to create a large interface area between lithia and metallic Sn because the large interface area facilitates the atomic interdiffusion.\textsuperscript{12} On the other hand, Sn is inclined to coarsen upon long-term cycling,\textsuperscript{27–29} which leads to the formation of crack and electrical isolation of active Sn particles by the solid electrolyte interphase (SEI),\textsuperscript{30,31} as illustrated in Figure 1a. A large Sn/lithia interface area eventually reduces the cyclability of anodes if the interface stability could not be maintained upon cycling. In order to reversibly convert lithia, the nano-sized morphology of Sn particles must be retained in the lithia matrix. The dopant M in a tin oxide composite is believed to stabilize the interface or confine Sn grains, as shown in Figure 1b.\textsuperscript{15} Using in situ transmission electron microscopy (TEM) technology, Jiang et al. observed that the composite of Sn/M oxides prevents the migration and aggregation of nanoparticles during cycling.\textsuperscript{32,33} These results indicate that a composite structure can not only enhance the reversibility of lithia but also improve the cycling property of tin oxides. However, the underlying mechanism of enhancements needs to be further clarified.

The size and volume of SnO2 particles play an important role in the reversibility of the conversion step (SnO2 + 4Li+ + 4e $\leftrightarrow$ Sn + 2Li2O). A critical size of about 3 nm enables the reversible cycling of SnO2. However, the large surface area of nanoparticles usually results in the excessive SEI formation.\textsuperscript{11,34,35} Small particle sizes also lead to low packing density. It is desirable to generate a hierarchical structure in which primary particles below the critical size assemble into a secondary structure for the purposes of high packing density. Various porous structures with nano-sized SnO2 have been synthesized to simultaneously take advantage of the high activity of small particles and the high density of large hierarchical particles.\textsuperscript{36–38} Porous structures also help to alleviate the strains caused by the volume change (about 250%), which is detrimental to the anode cyclability.\textsuperscript{18,31,39} Thus, to build a better tin oxide-based anode, we have to understand the lithia reversibility fundamentally on multiple scales from atoms, interfaces, to particles and apply the underlying mechanisms to design porous nanocomposites with hierarchical structures.

Herein, we first focused on the metal/Li2O interfaces and studied how the particle sizes of metallic Mn and Sn change in the composite during lithiation (Figure 1c). Mn is inclined to form ultrafine nanoparticles because of low interface energy as compared to Sn in a lithia matrix. Ultrafine Mn can separate Sn nuclei and suppress their aggregation (Figure 1b). To realize such a design strategy, we synthesized porous manganese tin oxide nanoframes (PMNs). Benefiting from its composite structure and the porous nanoframe morphology, the PMN anode exhibits an initial capacity of 1620.6 mA h g$^{-1}$ at 0.05 A g$^{-1}$ and a high reversible capacity of 912.0 mA h g$^{-1}$ at 0.2 A g$^{-1}$ after 100 cycles. The long-term cycling results show that the PMN could deliver a capacity of 547.3 mA h g$^{-1}$ at 2 A g$^{-1}$ even after 1000 cycles.

\section{EXPERIMENTAL SECTION}

\subsection{Computation Methodology and Models.} The critical nucleation radius of metals in a lithia matrix was estimated by the classic nucleation thermodynamics according to the reference (see the Supporting Information for details).\textsuperscript{40} The interface energy of Li2O and metals (M = Mn or Sn) was calculated by the density functional theory (DFT). For a given interface of Li2O/M, the interface energy was calculated based on the following expression:\textsuperscript{41,42}

\[
\gamma_{\text{Li}_2\text{O}/\text{M}} = \frac{1}{2A} \left[ E_{\text{Li}_2\text{O}/\text{M}} - n_q E_{\text{Li}_2\text{O}} - n_M E_M + (2n_O - n_L) E_{\text{Li}} + (2n_O - n_L) \Delta \mu_{\text{Li}} \right]
\]

\textit{(1)}

where $\gamma_{\text{Li}_2\text{O}/\text{M}}$ is the interface energy of Li2O/M, $E_{\text{Li}_2\text{O}/\text{M}}$ is the total energy of the interface model, $E_{\text{Li}_2\text{O}}$ and $E_M$ are the energies of bulk Li2O and M, $n_q$ and $n_M$ are the number of Li2O and M in the interface model, $n_O$ and $n_L$ are the numbers of oxygen and lithium atoms, respectively, $\Delta \mu_{\text{Li}}$ is translated to the negative of the voltage against Li/Li', and A is the interface area. The strain energy may exist...
inside metal slabs for commensurating two phases. It was proportional to the atom number of M (n_M) in metal slabs, and the interface energy could be further estimated by fitting the following expression.

\[ \gamma_{\text{Li}_2\text{O}/\text{M}} = \gamma_{\text{Li}_2\text{O}/\text{M}}^\text{lim} + n_M \sigma \]  

where \( \gamma_{\text{Li}_2\text{O}/\text{M}}^\text{lim} \) is the fitted limit of the interface energy and \( \sigma \) is the constant related to the strain energy in metal slabs. The model building and calculation strategies could be referred to the literature.43–45

2.2. Synthesis of PMNs, Bulk MnSnO_3, SnO_2, and MnO. In a typical synthetic route of PMNs, about 0.01 mol of MnCl_2·4H_2O and 0.01 mol of SnCl_4 were dissolved in 100 mL deionized water under vigorous stirring until the solution turned transparent. About 80 mL NaOH (1 M) was slowly dropped into the solution to form brown precipitates and stirred for 1 h. The precipitates were separated by centrifugation and washed with deionized water. After being dried in air at 50 °C for 12 h, the obtained powder was annealed in Ar gas at 400 °C for 4 h with a ramp rate of 4 °C min⁻¹. Bulk MnSnO_3 powders were prepared by the hydrothermal treatment of the aqueous solution of 0.225 M NaOH, 0.015 M SnCl_4·4H_2O and 0.015 M MnCl_2·4H_2O at 120 °C for 2 h. The PMN powders were dispersed in 30 mL deionized water containing 6 mL HNO_3 and then transferred into a 50 mL Teflon-lined stainless steel autoclave. After heating at 150 °C for 4 h, the resultant SnO_2 nanoparticles were centrifuged, washed, and dried at 60 °C. MnO nanoparticles were synthesized by mixing 0.1 M MnCl_2·4H_2O and 1 M NaOH directly. After centrifuging and washing, the precipitates were annealed in forming gas (95% Ar and 5% H_2) at 400 °C for 4 h.

2.3. Materials Characterization. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX 2500 V with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALab MKII X-ray photoelectron spectrometer with Mg Kα X-ray as the excitation source. A Zeiss Ultra 55 field-emission scanning electron microscope was used for morphology observation and energy-dispersive X-ray spectroscopy (EDX) measurement. High-resolution TEM (HRTEM) images were recorded on a FEI Tecnai G² 20 microscope at 200 kV. Nitrogen adsorption isotherms were measured on a Micromeritics ASAP 2020M + C instrument.

2.4. Electrochemical Measurement. The slurries of 70% active material, 20% acetylene black, and 10% polyvinylidene fluoride in N-methyl pyrrolidone were cast on a copper foil to form an anode laminate. The mass loading of active materials was controlled at ~2 mg cm⁻². The obtained samples were assembled into coin cells (CR2032) with a lithium foil as the counter electrode in an Ar-filled glovebox. The electrolyte was 1 M LiPF_6 in a 1:1 (volume ratio) mixture of ethylene carbonate and dimethyl carbonate. Cyclic voltammogram (CV) curves were measured in the range of 0.01 to 3 V at varied scan rates. Electrochemical impedance spectroscopy (EIS) spectra were obtained between 100 kHz and 100 mHz with a potentiostat (BioLogic VSP, France) at 3 V. Galvanostatic charge/discharge curves were measured with a CT2001A test system (Land Electronic Co., China) between 0.01 and 3 V.

3. RESULTS AND DISCUSSION

According to the classical nucleation theory, the critical nucleation size is proportional to the interface energy of Li_2O/metals (see the Supporting Information). To estimate the interface energy of Li_2O/Sn and Li_2O/Mn using the DFT calculation, we build the interface models by sandwiching a metal slab between Li_2O slabs to satisfy the periodic boundary conditions as shown in Figure 1d,e. To commensurate the lattice parameters of metal and oxide, metal slabs were appropriately strained (see details in the Supporting Information). The induced strain energy was proportional to the number of metal atoms. Three models were built for each interface by varying the thickness of metal slabs. Figure 2a,d shows the linear regression of interface energy with respect to the number of Sn or Mn atoms. From the intercepts, one can deduce that the interface energy of Li_2O/Sn with the most stable configuration was estimated to be 4.1 J m⁻², whereas the Li_2O/Mn model has an interface energy of 3.2 J m⁻². By using eq SI-2, the critical nucleation size for Mn in a lithia matrix was calculated to be 0.18 nm, which is much lower than that of Sn (0.40 nm).

Figure 2b,e presents the partial density of states (PDOS) of the middle and interface atoms in Li_8O_5Mn_10 and Li_16O_10Sn_10.
respectively. With the O 2p orbital in the middle of Li₂O slabs as the references, one can see that the interface O 2p states in Li₁₆O₁₀Sn₁₀ shift toward the Fermi energy; however, the energy level of the interface O 2p state is lowered in Li₈O₅Mn₁₀. Figure 2c,f shows that the electrons are accumulated along the M–O bonds and most at the oxygen atoms, indicating the strong ionicity of M–O bonds. Thus, the downshift of the interface O 2p orbital in Li₈O₅Mn₁₀ is induced by the relatively strong electrostatic potentials, indicating the strong Li₂O/metal interaction at interfaces as compared to that in Li₁₆O₁₀Sn₁₀. The difference on interface energies can also be inferred from the bond energy. As shown in Table S1, the Mn–O bond energy (2.46 eV) in MnO is stronger than those of Sn–O bonds in SnO (1.43 eV) and SnO₂ (1.54 eV). Such a strong affinity of Mn to O implies a low Li₂O/Mn interface energy as compared to that of Li₂O/Sn. Table 1 lists the calculated interface properties of Li₂O/Sn and Li₂O/Mn. The work of separation (W sep) is the work required to reversibly separate the interface into two free surfaces and thus a measure of the interface bond strength.⁴⁶ ⁴⁷ The calculated W sep of Li₂O/Mn is 6.7 J m⁻², which is larger than that of Li₂O/Sn (4.9 J m⁻²), indicating the strong bond strength between Li₂O and Mn slabs. It can be inferred from the above calculation and analyses that the strong affinity between Li₂O and Mn leads to the small nucleation size.

Table 1. Calculated Interface Properties of Li₂O and Mn/Sn

<table>
<thead>
<tr>
<th>interface</th>
<th>Li₂O/Mn</th>
<th>Li₂O/Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>work of separation (J m⁻²)</td>
<td>6.7</td>
<td>4.9</td>
</tr>
<tr>
<td>interface energy (J m⁻²)</td>
<td>3.2</td>
<td>4.1</td>
</tr>
<tr>
<td>critical nucleation size (nm)</td>
<td>0.18</td>
<td>0.40</td>
</tr>
</tbody>
</table>

On the basis of the calculation results, we design a composite material of manganese tin oxides. Figure S4a shows the TEM image of the uniform precursor MnSn(OH)₆ nanocubes. These nanocubes exhibit a uniform rectangular morphology with a side length of 20–25 nm. A lattice fringe spacing of 0.392 nm confirms the (200) crystallographic plane of MnSn(OH)₆. The selected area electron diffraction (SAED) of one nanocube in Figure S4c confirms that these nanocubes are single crystals of MnSn(OH)₆ (JCPDS card no. 72-0007). After heat treatment, the precursors were dehydrated to form porous MnSnO₃ nanoframes (Figure 3a). The phase composition was confirmed by the XRD patterns in Figure 3g. The reduced intensity and increased peak width indicate the low crystallinity of dehydrated PMNs as compared to MnSn(OH)₆. Figure 3b presents the HRTEM image of a PMN. It shows that the nanoframe consists of crystalline grains and porous interiors. The multiple rings in the SAED pattern (Figure 3c) agree with MnSnO₃ (JCPDS card no. 85-0615). It confirms that PMNs are polycrystalline. Figure 3d–f presents the TEM images of the control samples of bulk MnSnO₃, SnO₂, and MnO, respectively. The XRD patterns are given in Figure S5. The XPS analysis (Figure 3h) shows that the binding energies of Mn 2p₁/₂ and Mn 2p₃/₂ are around 641.9 and 653.6 eV, respectively, indicating the existence of divalent Mn.⁴⁸ The XPS signals of Sn 3d₅/₂ (486.7 eV) and Sn 3d₃/₂ (495.1 eV) (Figure 3i) agreed with Sn⁴⁺ in MnSnO₃.²⁰ Figure 3j shows that the Brunauer–Emmett–Teller (BET) surface area of the PMNs is 69.1 m² g⁻¹ and the main pore size is around 4 nm.

To test whether the porous structure and nano-sized grains of PMNs are favorable for high-capacity Li-ion battery anodes, we assembled them with lithium into half cells, tested their electrochemical properties, and compared them with bulk MnSnO₃ and SnO₂ anodes. Figure 4a shows the CV curves of...
PMNs. In the first cycle, PMNs exhibit an irreversible peak at 0.95 V, which is attributed to the formation of SEI.49 Three reduction peaks at 1.08, 0.5, and 0.06 V in the second cathodic scan are correlated to the multiple-step reduction reactions of metallic Sn/Mn and sequential Sn alloying process upon lithiation.50,51 Two main peaks around 0.55 and 1.17 V during the oxidation scan are ascribed to the dealloying reactions of LixSn and the formation of MnO, respectively.52,53 A broad hump at 1.25−2.0 V implies the reoxidation of Sn via the reversible reaction of lithia in PMNs. The galvanostatic charge/discharge profiles in Figure 4b show a high initial capacity of 1620.6 mA h g⁻¹. It decreases to 1247.0 mA h g⁻¹ in the second cycle. The overall lithiation profile is a slope without a distinct plateau around 1.0 V that is usually shown by large SnO₂ particles.54 The capacity below 1.25 V is around 1164.8 mA h g⁻¹. Upon delithiation, there is about 567.8 mA h g⁻¹ capacity above 1.25 V, indicating the possible formation of tin oxides. The XPS spectra in Figure 4c show that the Sn 3d signals of a lithiated sample could be deconvoluted into three components, which are attributed to Sn(IV/II) oxides and metallic Sn, respectively.9,55,56 The oxide signals may result from superficial oxidation. After delithiation, there are two typical spin–orbit splitting peaks of Sn 3d₅/₂ (486.7 eV) and 3d₃/₂ (495.1 eV), indicating that Sn is reoxidized to Sn(IV). It explains the extra capacity above 1.25 V.

To understand how the particle size influences reactions above 1.25 V, we intentionally synthesized bulk MnSnO₃ (∼200 nm) and SnO₂ (∼5 nm) and measured their CV curves under the same conditions as used for PMNs. Bulk MnSnO₃ has a nanocube morphology (Figure 3d), and SnO₂ nanoparticles are generally aggregated (Figure 3e). It could be clearly seen from Figure 4d that bulk MnSnO₃ delivers a minor current density at 1.25−2.0 V as compared to PMNs and no significant peaks appear above 1.25 V. It implies that only a small portion of bulk MnSnO₃ is cyclable above 1.25 V probably because the existence of Mn helps to enhance the conversion of tin back to its oxide. The enhancement is not as significant as PMNs because the large particle size (Figure 3d) of bulk MnSnO₃ may lead to the incomplete conversion. It is interesting to note that pure SnO₂ shows an oxidative peak with a tail at 1.35 V in the first scan (Figure 4g). In contrast to bulk MnSnO₃, the small size of SnO₂ (5 nm) enhances the delithiation step above 1.25 V and exhibits the peaks in the first oxidative scan. Thus, lithiated SnO₂ is able to be partially delithiated back to its oxide states. However, the two oxidative peaks of SnO₂ above 1.25 V disappear in the following cycles, and the current density decreases to even lower values than bulk MnSnO₃. It indicates that the reversibility of SnO₂ above 1.25 V degrades with cycles. By comparing the CV curves and morphologies of three samples, it may be inferred that because of large particle sizes, the long distance for atom migration limits the delithiation and reformation of Sn/Mn oxides, leading to poor cycling reversibility above 1.25 V. Because PMNs have the advantages of small grain sizes as SnO₂ does and the enhancement effect of Mn/Sn binary oxides, PMNs are able to demonstrate good reversibility to oxides and gain extra capacity.

Figure 4e presents the SAED pattern and rotational integral of a delithiated PMN, which are indexed to the composite of SnO₂ and MnO, instead of MnSnO₃. The HRTEM image in Figure S6 shows the phase separation of SnO₂ and MnO, which is not reoxidized back to PMNs. It should be noted that the composite of SnO₂ and MnO differs from a simple mechanical mixture because the composite is formed by the electrochemical reaction, yielding a good dispersion of nanosized SnO₂ and MnO grains, which is of vital importance to the
reversibility of composite anodes. The SAED pattern of the delithiated SnO$_2$ anode in Figure 4f shows that the main rings are related to metallic Sn. In conjunction with the CV analysis, it appears that there are two distinct cycling models for PMN and SnO$_2$, respectively. The PMN anode forms a composite with nano-sized SnO$_2$ and MnO grains, which could be cycled via both alloying and conversion reactions as illustrated in Figure 4h. However, the SnO$_2$ anode is mainly charged/discharged via alloying reactions after the second cycle as illustrated in Figure 4i. The difference on cycling models result from the Mn doping and nanoframe structure, which will be further studied later.

Figure 5a shows the rate properties of PMNs, bulk MnSnO$_3$, and SnO$_2$ at varied current densities. The PMN anode delivers higher capacities at both low and high current densities than bulk MnSnO$_3$ because of the smaller grain size. SnO$_2$ shows higher specific capacities at low current densities than bulk MnSnO$_3$ because of its relatively high theoretical capacities. The decreased capacity retention of SnO$_2$ at high current densities may be due to the capacity delivered by the conversion reaction, which decays significantly with cycling as indicated by the CVs in Figure 4g. The EIS analysis in Figure 5b may also explain the difference on cycling models result from the Mn doping and nanoframe structure, which will be further studied later.

Figure 5b shows Nyquist plots of PMNs, bulk MnSnO$_3$, and SnO$_2$. The semicircle diameter in the Nyquist plots of Figure 5b is related to the resistance of interface charge transfer. A small semicircle diameter of PMNs indicates that the nano-sized SnO$_2$ and MnO grains enable the low resistance and facilitates the interface charge transfer, leading to the enhanced rate properties as compared to bulk MnSnO$_3$. Figure 5c presents the cycling properties of three samples at a low current density of 0.2 A g$^{-1}$. All three samples suffer a capacity decay in the first few cycles. After 100 cycles, PMNs deliver a relatively stable capacity of 912.0 mA h g$^{-1}$, whereas bulk MnSnO$_3$ and SnO$_2$ only retain 383.2 and 223.1 mA h g$^{-1}$, respectively. To differentiate the conversion and alloying reactions of tin oxides, we separated the total capacity at 1.25 V. Figure 5d presents the separate capacities contributed by conversion and alloy reactions. The PMN sample shows higher capacities for either conversion or alloying reactions than bulk MnSnO$_3$ and SnO$_2$ because PMNs have the small grain size and porous frame structure. The capacity contributed by the conversion reaction of tin oxides gradually decreases on all three samples during cycling. Figure 5e shows the long-term cycling properties at 2 A g$^{-1}$. The PMN anode shows an initial capacity of 1173.0 mA h g$^{-1}$ with an initial Coulombic efficiency (CE) of 65%. After 35 cycles, the capacity decreases to 716.0 mA h g$^{-1}$ and the CE increases to 99.7%. Although bulk MnSnO$_3$ and SnO$_2$ show comparable capacities initially, they degrade rapidly with the cycle numbers. After 1000 cycles, PMNs are still able to deliver a capacity of 547.3 mA h g$^{-1}$. Figure 5f shows the texture and morphology images of pristine and cycled PMN. The uniform distribution of Mn and Sn indicates that there is no segregation of Sn or Mn, which may explain the good cyclability of PMNs. Figure 5g shows the TEM images and EDX elemental mapping images of pristine and cycled PMN. As anode material, PMNs are able to increase the cyclability of tin oxides and the mechanism result from the unique structure.

The nanoframe structure is able to provide the short diffusion length for Li ions in both solid and electrolyte phases. A short Li-ion diffusion length will affect the reaction mechanism and kinetics of PMNs. Figure 6a shows the CV curves of PMNs at varied scan rates from 0.1 to 0.6 mV s$^{-1}$. The current response (i) obeys a power law relationship with respect to the scan rate (v): $i(v) = a v^{b}$ (59) Both a and b could be determined by the slope and intercept from Figure 6b. In the range of 0.1−0.4 mV s$^{-1}$, the b-values for cathodic and anodic peaks are 0.74 and 0.93, respectively, suggesting that the kinetics is mainly surface-controlled. When the scan rate increases over 0.4 mV s$^{-1}$, the b-values of cathodic and anodic peaks decrease to 0.58 and 0.66, respectively, indicating that the kinetics is diffusion-controlled. The capacity contributions from capacitive and diffusion-controlled charge could be quantified on the basis of the relationship: $i(v) = k_1 v^{1/2} + k_2 v^{1/2}$, where $k_1$ and $k_2$ correspond to the current contributions from the surface capacitive effects and the diffusion-controlled intercalation process, respectively. The shaded region in Figure 6c shows the capacitive contribution at 0.3 mV s$^{-1}$. A close examination of capacity contributions at varied scan rates (Figure 6d) allow us to conclude that with the increase of scan rates, the percentage of capacitive contribution increases and the lithiation/delithiation reactions gradually turn to be diffusion-controlled. A large portion of capacitive contribution indicates that nanoframes provide rapid kinetics for Li-ion storage.

To further elucidate why PMNs improved the cycling properties, we conducted the ex situ TEM analysis on three partially lithiated anodes of PMNs, SnO$_2$, and MnO, respectively. Figure 7a shows the TEM image of cycled PMN particles. The diffraction rings in Figure 7b could be indexed to metallic Sn and Mn. The diffusive background is attributed to the amorphous Li$_2$O matrix. The lattice fringes in the HRTEM image of Figure 7d could be visualized as the
crystallized Sn and Mn, as circled by the dashed line. Figure 7b,e shows that Sn particles in the lithiated SnO2 anode have a spherical shape with relatively large diameters as compared to the Sn particles in Figure 7d. The TEM images of the MnO anode in Figure 7c,f indicate that metallic Mn particles are much smaller than Sn in Figure 7b. The diffraction patterns and rotational integration plots in Figure 7h,i agree with the conversion mechanism in the reactions of SnO2 + 4Li+ + 4e \rightarrow Sn + 2Li2O and MnO + 2Li+ + 2e \rightarrow Mn + Li2O.

The differences of metal (Sn and Mn) particle size in Figure 7d−f seem to imply the important mechanism of metal nucleation and growth in a lithia matrix upon electrochemical cycling. Figure 8 shows the statistical results of the particles size of Sn and Mn upon the HRTEM images. It indicates that Sn usually exhibits large particles with an average diameter of about 25 nm in the partially lithiated SnO2 anode. By contrast, Mn particles show the average diameter around 5 nm in the...
MnO anode. Grain coarsening should be avoided to build better Sn-based anodes because the large particles lead to poor cycling properties. It is interesting to note that in the lithiated PMN anode, Mn shows the same particle size as it does in a MnO anode and Sn particles exhibit a reduced average particle size. It indicates that Mn may suppress the Sn particles to grow as large as Sn does in the pure SnO2 anode. The experimental results basically corroborate our first-principles calculation. The thermodynamic mechanism of the good cyclability of PMN anodes is attributed to the relatively small nucleation size of Mn as compared to Sn and the suppression of Sn growth by ultrafine Mn.

After nucleation, the growth of metal nuclei depends on the mobility of metal atoms at the interface and lithia matrix. Sn has an extremely low recrystallization temperature because of the large atom radius and low melting point (~506 K).52,53,60 Mn migrates slowly in lithia because of the high melting points (1519 K) and the strong M–O affinity. Thus, the nano-sized Sn prefers growing large particles at room temperatures as compared to Mn. Beaulieu and Dahn reported that the liberated Sn atoms could react with Mn to form Sn2Mn in a Sn–Mn–C anode.61 A reformation of Sn–Mn–Sn alloy was not observed in our PMN anode. The strong Mn–O affinity on the interfaces may impede the Sn–Mn alloying process in lithia. Thus, Mn and Sn nanoparticles precipitated out of the lithia matrix as their own metallic phases. The ultrafine Mn nanoparticles were well-dispersed around Sn and limited the coarsening of Sn particles. This synergistic effect may explain why the average size of Sn particles in cycled PMNs is smaller than that in cycled SnO2 (Figure 8). In general, the nanoframe and composite structures are able to modulate the nucleation and growth of metal nanoparticles to achieve a homogeneous distribution of resized Sn particles, which in turn improves the overall conversion reaction and obtains a high capacity as well as a better cycling capability.

4. CONCLUSIONS

Through the first-principles calculations of the Li2O/M (M = Sn or Mn) interfaces, we found that because of the low interface energy, Mn in PMNs shows a small critical nucleation size during lithiation. Ultrafine Mn nanoparticles could separate Sn nuclei and suppress the aggregation or growth of Sn particles, leading to ideal homogeneous mixtures of metallic Sn/Mn embedded in a lithia matrix. According to the calculated mechanism, we proposed a porous nanoframe structure of Mn/Sn binary oxide via a simple coprecipitation and heat treatment route. Because of Mn/Sn synergistic effects and nano-sized grains, the nanoframes are able to activate the conversion reaction of lithia, whereas the porous structures accommodate the volume change. The lithia reversibility and electrode cyclability were significantly improved. The PMN anode exhibits an initial capacity of 1620.6 mA h g\(^{-1}\) at 0.05 A g\(^{-1}\) and could even deliver a capacity of 547.3 mA h g\(^{-1}\) even after 1000 cycles at 2 A g\(^{-1}\). The results of this work provide a high-performance anode material and help the in-depth understanding of property enhancement, which may be applied to other composite oxide systems.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b11062.

Critical nucleation size, interface energy estimation, interface model of Li2O/M (M = Mn or Sn), top view of interfaces, M–O bond energy calculation, crystal structure used for the calculation, and lattice parameters used for calculation and summary of calculated energies (PDF)

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