Atomic Layer Deposition of SnO₂-Based Composite Anodes for Thin-Film Lithium-Ion Batteries

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Transition metal oxides are promising anode materials for lithium-ion batteries thanks to their good electrochemical reversibility, high theoretical capacities, high abundance, and low cost. The mechanism of lithium insertion or deintercalation into or from these metal oxides can be different depending upon their lattice structure or chemical nature. Synergistic effects obtained from mixing different metal oxides with (dis)similar lithiation/delithiation mechanisms (intercalation, conversion and alloying) can significantly improve the device performances. In this research, we systematically investigate the impact on electrochemical properties of SnO₂ thin-films upon mixing with TiO₂, Fe₂O₃ and ZnO. In these pure thin-films, SnO₂ displays conversion- as well as alloying-type lithiation and serves as the host material, whereas TiO₂ represents an intercalation-type anode material, Fe₂O₃ exhibits conversion reactions and ZnO expresses alloying during lithiation-delithiation processes. Importantly, all the composite thin-films have an intermixed structure at the atomic scale, as they are precisely prepared by the atomic layer deposition method. The electrochemical properties demonstrate that the composite thin-films show better performance, either higher capacities or better cycling retentions, than the individual constituent material (SnO₂, TiO₂, Fe₂O₃ or ZnO). Overall cycling stability improves to a great extent along with a slight increase in capacity with the addition of TiO₂. The supplement of Fe₂O₃ in the SnO₂–Fe₂O₃ composite thin-films moderately improves both capacity and retention, while the SnO₂–ZnO composite electrodes demonstrate a good cyclability and stabilize at a relatively high capacity. The systematic investigation of synergistic effects on the different types (intercalation, conversion and alloying) of metal oxide composites is expected to provide guidance towards the development of composite anode materials for lithium-ion batteries.

Keywords: atomic layer deposition, synergistic effect, intercalation, conversion, alloying, thin-film, SnO₂, lithium-ion battery
INTRODUCTION

Among different electrochemical energy storages devices, lithium-ion batteries (LIBs) are popular and widely used due to their unique virtues, such as low self-discharge rate, long cycle life, high conversion efficiency, and easy to manufacture flexible designs etc. With the growing needs for high power/energy density applications such as electric vehicles, grid storages etc., new demands for LIBs are requiring. However, traditional electrodes like graphite (anode, theoretical capacity is 372 mAh g$^{-1}$) and LiCoO$_2$ (cathode, theoretical capacity is 274 mAh g$^{-1}$) are unable to satisfy anymore. Therefore, it is crucial to find new materials which can fulfill these new demands (Chen et al., 2018a; Kim et al., 2019; Pender et al., 2020).

Anode materials for LIBs can be typically divided into the categories of carbonaceous material (e.g., graphite, graphene and carbon nanotubes), silicon and metal oxides (Su et al., 2014; Qi et al., 2017; Fang et al., 2019; Roselin et al., 2019). Among others, transition metal oxides have received tremendous interests due to their high theoretical capacities, good redox reversibility and ease of synthesis (Reddy et al., 2013; Zheng et al., 2018; Fang et al., 2020). There are three mechanisms of lithium storage in transition metal oxides: intercalation, conversion and alloying. For intercalation-type anodes, the lithium ions can be reversibly inserted/removed into/from the host material without chemical deformation and slight volume deterioration. As an example, (lithium-) titanium dioxide, is a typical representative of intercalation-type materials. With the limited lithium uptake per volume and high molar mass, the intercalation-type anodes are more suitable for applications which require longer stability (Zhu et al., 2012; Yan et al., 2015; Yuan et al., 2017). For the alloying-type, metal oxide firstly irreversibly converts to metal and then reacts with lithium to form lithium-metal alloys during the charging process, the following discharging process is the reversible dealloying steps of lithium-metal to metal. Sn- and Ge-based oxides are typical belonging to the alloying-type anode (Wei et al., 2013). The lithium-metal alloying and dealloying process provides the advantage of high lithium storage capability which is certainly good for the high capacity, but the accompanying severe volume change during charge-discharge is the fatal shortcoming (Zhang, 2011; Liu et al., 2017). This issue can be solved to some extent for the conversion-type metal oxides. The formed metals during the charging process do not alloy and dealloy with lithium anymore, instead, accompanying the reduction and oxidation. The metallic nanonetwork embedded in a Li$_2$O matrix formed after the reaction can improve the overall conductivity of the electrode (Wadewitz et al., 2013; Bruck et al., 2016; Lu et al., 2018). This essential merit can effectively elucidate the pulverization problem caused by volume changes and allow capacity improvement owing to their multiple redox reaction. However, the overall improvement in capacity and stability is limited to a certain extent. A summary of typical materials corresponding to the three types of anodes, and their advantages and drawbacks are listed in Table 1.

Even though the three types of metal oxide have their advantages, their shortcomings of either low capacity or tremendous volume changes together with the poor electronic conductivity make it hard to undertake the task of a good battery material individually. A strategy to effectively combat the bad impacts is using two different phases while react towards lithium at two different electrochemical potentials (vs. Li/Li$^+$) in one composite electrode. Regarding this aspect, the hybrid AO$_x$-BO$_y$ (A, B are different metal) electrodes are expected to sequentially alleviate the volume expansion and provide a highway for charge transfer in the two phases, guiding to a high reversible capacity and rate performance compared with pure phases. There are literatures reporting a synergistic effect of two different metal oxides leading to a significant improvement in cyclability and capacity (Wu et al., 2015; Zhao et al., 2016). SnO$_2$ is a well-studied material and it exhibits a typical conversion and following alloying reaction mechanism towards lithium (Chen and Lou, 2013; Zhao et al., 2015b; Zoller et al., 2019). There are many
researches on the synergistic effect between SnO₂ and another metal oxide, like SnO₂–CuO (Cheong et al., 2018), SnO₂–TiO₂ (Yi et al., 2016), SnO₂–Fe₂O₃ (Kint et al., 2019), SnO₂–ZnO (Zhao et al., 2019), SnO₂–Co₃O₄ (Zhao et al., 2015a) and SnO₂–In₂O₃ (Kim et al., 2007) etc. as composite anode material for LIBs.

In this report, SnO₂–TiO₂, SnO₂–Fe₂O₃, and SnO₂–ZnO composite thin-films intermixed at the atomic scale were precisely prepared by the atomic layer deposition (ALD), and were used as model electrodes to systematically investigate their evolved electrochemical properties. Here ALD provides the advantages of precise thickness and composition control of the thin-film electrodes, which in turn allows for the investigation of the transport process of lithium ions through the active material without the interference of polymeric binder and carbon black as used in conventional composite electrodes (Ha et al., 2012). Thin-film electrodes react with lithium fast and effectively which encourage the cyclic voltammetry curve with higher resolution and thus can be used to analyze more details of the peak and furtherly deconvolute overlapping reactions (Ferraresi et al., 2018).

Three typical representative substances which exhibit a different reaction mechanism as pure thin-films (intercalation-type TiO₂, conversion-type Fe₂O₃ and alloying-type ZnO) have been mixed with SnO₂ material. The precisely controlled compositions were verified by X-ray photoemission spectroscopy (XPS), surface morphologies measured with atomic force microscopy (AFM), synergistic effect mechanisms were mainly investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), cycling stability and rate capability.

### EXPERIMENTAL

The thin-film samples were prepared in a home-built high vacuum ALD system (base pressure is below 5 × 10⁻⁶ mbar) (Xie et al., 2007; Musschoot et al., 2009; Dendooven et al., 2010). Tetrakis(dimethylamino)tin(IV) (TDMASn, 99.9%, Sigma Aldrich) and H₂O was used to deposit SnO₂, where TDMASn bubbler heated to 45°C, and the corresponding conveyer tube to the chamber held at 50°C (Zhao et al., 2019). To deposit TiO₂ and ZnO, tetrakis(dimethylamido)titanium (TDMAT, 99.99%, Sigma Aldrich) and diethyl zinc (DEZn, 95%, Strem Chemicals) were chosen as metal sources respectively, and H₂O used as the co-reactant. TDMAT, DEZn and H₂O were kept at room temperature and all the conveyer tubes were kept at 50°C (Deng et al., 2015). Tert-butyl ferrocene (TBF, 98%, Strem Chemicals) and oxygen plasma was used to deposit Fe₂O₃ (Ramachandran et al., 2014). The TBF bubbler was kept at 75°C, and the conveyer tube to the chamber was heated to 85°C. The parameters for generating oxygen plasma are as follows: the input oxygen pressure is 1 × 10⁻² mbar, a radio frequency remote plasma source at a frequency of 13.56 MHz and the output power is 200 W. The substrate temperature was held at 150°C for all the depositions. The ALD of SnO₂–MOₓ composites were conducted by using the supercycles based sequence of n × (x SnO₂ + y MOₓ) (M = Ti, Fe or Zn), where x is the cycle number of
ALD SnO₂, y is the cycle number of ALD MOₓ, and n represents the supercycle repetition number. The value of x and y was chosen to achieve atomic scale intermixing rather than multilayer deposition, as illustrated in Figure 1A.

Thin-films were deposited on Si (100) substrates for growth characterizations. In-situ spectroscopic ellipsometry (SE) was used to monitor the thickness of the thin-film in between ALD cycles using a Woollam M-2000 spectrometer fitted directly onto the ALD reactor. X-ray reflectometry (XRR) was used to measure the thickness and density of the as-deposited thin-films, in which XRR was performed on a Bruker D8 diffractometer with Cu Ka (λ = 0.154 nm) radiation. Surface morphologies and roughness were characterized by atomic force microscopy (AFM, Bruker Dimension Edge system) in tapping mode and scanning electron microscopy (SEM, Quanta 200 F FEI). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific™ with Al Ka (λ = 0.834 nm) X-rays generated at 15 kV and 70 W. C 1 s assigned at 284.6 eV was used to calibrate the binding energy.

Electrochemical characterizations were conducted in an argon-filled glovebox (H₂O < 1 ppm, O₂ < 1 ppm) with a home-built potentiostat/galvanostat (Dobbelaere et al., 2017) connected to a three-electrode set (Figure 3A). The thin-films deposited on the Si-20 nm SiO₂-40 nm TiN substrates were used as the electrodes for electrochemical tests. Lithium ribbon (99.9%, Sigma-Aldrich) was used as counter and reference electrode, and 1 M LiClO₄ in propylene carbonate (PC, 99%, io-li-tec) was used as Li⁺ electrolyte. The CV was measured at a scan rate of 1 mV s⁻¹ from 0.1–3.0 V (vs. Li/Li⁺). The EIS was conducted at the frequency from 100 KHz to 10 mHz m = ρ × V = ρ × s × t was used to calculate the mass (m) of active materials, where the contact area (s) is 1.05 cm², while the density (ρ) and the thickness (t) were obtained from XRR results.

RESULTS AND DISCUSSIONS

Atomic Layer Deposition Growth and Characterizations of Thin-Films

Three thin-film materials were prepared, i.e., SnO₂ intermixed with TiO₂, Fe₂O₃ and ZnO respectively, at a ratio of 1:1, labeled as SnO₂–TiO₂, SnO₂–Fe₂O₃, and SnO₂–ZnO. The ALD process sequence was 120 × (SnO₂ + 2TiO₂) for SnO₂–TiO₂, 120 × (SnO₂ + 4Fe₂O₃) for SnO₂–Fe₂O₃, and 80 × (2SnO₂ + 3ZnO) for SnO₂–ZnO. Figure 1B displays the thickness as a function of supercycle number from in-situ SE, and the results show that the thickness is 27.3, 25.6 and 31.1 nm for 120 cycles of SnO₂–TiO₂, 120 cycles of SnO₂–Fe₂O₃ and 80 cycles of SnO₂–ZnO, respectively. Figure 1C shows the recorded XRR curves of the three thin-films where no fundamental differences can be found in the thickness profile. All samples exhibit clear Kiessig fringes, which is indicating a smooth surface. The simulation results indicate thicknesses of 28, 25 and 30 nm which are in line with the in-situ SE result, roughness of 0.62, 0.97 and 0.51 nm, and densities of 5.2, 5.6 and 5.9 g cm⁻³ for the SnO₂–TiO₂,
SnO$_2$–Fe$_2$O$_3$ and SnO$_2$–ZnO thin-films respectively. The surface morphologies were obtained from AFM in tapping mode. The corresponding three-dimensional surface morphologies of the as-deposited composite thin-films are shown in Figures 1D–F. The surface topography of all three thin-films were found to be smooth, homogeneous with uniform grains. The root mean square (RMS) roughness values are 0.89, 1.10 and 0.65 nm obtained for SnO$_2$–TiO$_2$, SnO$_2$–Fe$_2$O$_3$ and SnO$_2$–ZnO thin-films, respectively, which are well in agreement with the XRR results. Table 2 summarizes the thickness, density, and roughness values obtained from the in-situ SE and XRR data fittings.

The XRD patterns of the composite thin-films and binary oxide reference thin-films are shown in Figure 2A. All the patterns clearly reveal (although with the existence of Si background) the amorphous structure except for the ZnO reference film which shows diffractions of (002) and (101) indicating a polycrystalline nearly 1:1 atomic ratio between SnO$_2$ and MO$_x$ in the SnO$_2$ laminate structure and uniform mixing between SnO$_2$ and MO$_x$. The calculated atomic concentration values indicate a peak so of Sn, Ti, Fe, Na and O elements, while no other impurities are observed. The calculated atomic concentration values indicate a nearly 1:1 atomic ratio between SnO$_2$ and MO$_x$ in the SnO$_2$–MO$_x$ composite thin-films, as shown in Table 2. From the XPS depth profiles in Figure 2C, the Fe content in SnO$_2$–TiO$_2$, Fe content in SnO$_2$–Fe$_2$O$_3$ and Zn content in SnO$_2$–ZnO are almost unchanged throughout the respective thin-film, indicating there is no bilayer or laminate structure and uniform mixing between SnO$_2$ and MO$_x$ has been achieved. The binding energy of the Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ peaks for SnO$_2$–TiO$_2$ are centered at 456.5 and 459.7 eV, as displayed in Figure 2D, where the splitting between Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ was 5.8 eV indicating the presence of Ti$^{4+}$ (Li et al., 2015a). In Figure 2E, Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ are centered at 710.3 and 723.5 eV demonstrating the trivalent state of iron present in SnO$_2$–Fe$_2$O$_3$ thin-films (Gu et al., 2017). Figure 2F shows peaks aligned at 1020.8 and 1043.9 eV which corresponding to the Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ of Zn$^{2+}$ (Zhao et al., 2019). Based on the above results, it can be summarized that 25–30 nm thick, uniform, smooth and atomically intermixed SnO$_2$–TiO$_2$, SnO$_2$–Fe$_2$O$_3$ and SnO$_2$–ZnO composite thin-films were grown successfully with an atomic ratio of SnO$_2$/MO$_x$ at ~1:1.

**Electrochemical Characterization of SnO$_2$**

To evaluate the synergistic effect between SnO$_2$ and MO$_x$, the electrochemical studies of a pure SnO$_2$ thin-film was performed as a reference. Figure 3B shows the initial three cycle CV curves where five distinct cathodic peaks can be observed during lithiation and three anodic peaks during delithiation. In the early stage of lithiation from 1.5 to 0.8 V, multiple reactions lead to the formation of intermediate Li$_2$SnO$_3$ and metallic Sn phases (corresponding to Eqs 1 and 2). Further lithiation to the range between 0.6 and 0.4 V results in another intermediate Li$_8$SnO$_6$ and metallic Sn phases (Eqs 3 and 4). At the potential of ~0.25 V, the accumulated metallic Sn alloyed to Li$_x$Sn phases (Eq. 5). Above 1.5 V, Sn is partially re-oxidized to SnO$_2$, and then repeats in the following cycle. Two intermediate phases, Li$_5$SnO$_6$ and Li$_8$SnO$_6$, were detected during lithiation of the thin-film SnO$_2$ electrode. These results match very well with the reported SnO$_2$ thin-film model electrodes (Ferraresi et al., 2018).

It is worth mentioning that the reaction mechanisms of SnO$_2$ with Li$^+$ usually differ between the thin-film based electrodes and the slurry-based conventional electrodes. This is mainly because of the existence of conductive additives and binders in the latter (Wen et al., 2007; He et al., 2013; Jahel et al., 2014; Xie et al., 2015). Conventional SnO$_2$ slurry electrodes exhibit two obvious cathodic peaks around 0.87 and 1.18 V, attributed to the Li$_2$O formation and electrolyte decomposition, and other redox peaks appear at 0.15 and 0.56 V are linked to the multistep Li$_x$Sn$_y$ formation. The multistep conversion and alloying mechanism of the SnO$_2$ thin-film electrode makes it obtain a theoretical capacity of 1,491 mAh g$^{-1}$, in which 711 mAh g$^{-1}$ comes from the irreversible conversion reaction and 783 mAh g$^{-1}$ from the reversible alloying step. The evolution of SnO$_2$ thin-films during lithiation can be summarized as follows (Kim et al., 2014; Ferraresi et al., 2018):

$$2\text{SnO}_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{SnO}_2 + \text{Li}_x\text{SnO}_3$$

$$\text{SnO} + 0.67\text{Li}^+ + 0.67\text{e}^- \rightarrow 0.67\text{Sn} + 0.33\text{Li}_2\text{SnO}_3$$

$$1.33\text{Li}_5\text{SnO}_6 + 2\text{Li}^+ + 2\text{e}^- \rightarrow 0.67\text{Sn} + 0.67\text{Li}_2\text{SnO}_3$$

$$0.67\text{Li}_8\text{SnO}_6 + 2.67\text{Li}^+ + 2.67\text{e}^- \rightarrow 0.67\text{Sn} + 4\text{Li}_2\text{O}$$

$$\text{Sn} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Sn}$$

**Synergistic Effect Between SnO$_2$ and TiO$_2$**

To unveil the influence of TiO$_2$ anode material, which belongs to intercalation-type in its bulk form, intermixed into the SnO$_2$ matrix on the lithiation/delithiation process, the electrochemical performance of SnO$_2$–TiO$_2$ composite thin-films were investigated. Figure 4A shows the CV curves of a pure TiO$_2$ reference thin-film in the initial three cycles where redox pair peaks assigned at 1.6 and 2.2 V corresponding to the Li$^+$ insertion and extraction into or from TiO$_2$ (Eq. 6). The overlap of the CV curves show the excellent Ti$^{4+}$/Ti$^{3+}$ reversibility during the charge-discharge process (Ban et al., 2013).

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**TABLE 2 |** The thickness, density, roughness and XPS composition of SnO$_2$–TiO$_2$, SnO$_2$–Fe$_2$O$_3$, and SnO$_2$–ZnO composite thin-films by ALD.

| Sample          | ALD deposition | Thickness (nm) | Density (g cm$^{-3}$) | Roughness (nm) | XPS composition (at %) |
|-----------------|----------------|---------------|----------------------|----------------|------------------------|
|                 | In-situ SE     | XRR AFM       |                      |                |                        |
| SnO$_2$–TiO$_2$ | 120 × (SnO$_2$ + 2TiO$_2$) | 27.3          | 5.2                  | 0.62           | 22 26 52               |
| SnO$_2$–Fe$_2$O$_3$ | 120 × (SnO$_2$ + 4Fe$_2$O$_3$) | 25.6          | 5.6                  | 0.97           | 15 31 54               |
| SnO$_2$–ZnO     | 80 × (2SnO$_2$ + 3ZnO) | 31.1          | 5.9                  | 0.51           | 21 22 57               |
\[
\text{xLi}^+ + \text{TiO}_2 \leftrightarrow \text{Li}_x \text{TiO}_2
\]  \hspace{1cm} (6)

Figure 4B displays the CV curves of the SnO$_2$–TiO$_2$ composite thin-film electrodes. In the first cathodic sweep, the first sharp peak around 1.6 V can be assigned to the lithium insertion into TiO$_2$. The huge peak around 0.9 V is probably related to the reductive transformation of SnO$_2$ to Sn/SnO (corresponding to Eqs 1–3). At very low potential, the peak located at 0.2 V is believed due to the formation of Li$_x$Sn alloys (Eq. 5). During the anodic process, the broad peaks centered around 0.6 and 1.7 V correspond to the multi-step dealloying reactions from Li$_x$Sn to Sn followed by oxidation of Sn to SnO$_2$, respectively. Furthermore, the anodic peak at 2.45 V is most likely linked to the Li$^+$ extraction from Li$_x$TiO$_2$. Notably, both sharp cathodic peaks around 0.9 and 1.6 V disappeared from the second cycle and a new broad peak appeared at around 1.3 V instead. The broad peak possibly resulted from the combination of Li$_x$TiO$_2$ and Li$_x$SnO$_2$ formation. Those differences between SnO$_2$ and SnO$_2$–TiO$_2$ suggest the obvious influence of TiO$_2$ intermixing with SnO$_2$, which would certainly affect the cycling performance. As expected, in Figure 4C the SnO$_2$ reference electrode displayed an initial capacity as high as 2,260 mAh g$^{-1}$, but it continuously and rapidly declined to 879 mAh g$^{-1}$ after 50 cycles. On the other hand, the TiO$_2$ reference thin-film electrode delivered an initial capacity of 516 and 468 mAh g$^{-1}$ after 50 cycles, exhibiting a capacity retention of 90.7%, which reflects the advantages of its cycling stability due to the insertion/extraction reaction mechanism. For the SnO$_2$–TiO$_2$
composite electrode, the first discharge capacity is 1,270 mAh g\(^{-1}\), followed by capacity fading during the initial cycles, yielding a capacity of 1,177 mAh g\(^{-1}\) that remained stable until the 50th cycle almost without any decay. In addition, in terms of rate performance (Figure 4D), as expected, the SnO\(_2\) electrode showed worst capacity retention followed by SnO\(_2\)–TiO\(_2\) and TiO\(_2\). There is an obvious synergistic effect between SnO\(_2\) and TiO\(_2\), as the incorporation of TiO\(_2\) avoids the dramatic capacity fading observed for the SnO\(_2\) reference, while the presence of SnO\(_2\) in the intermixed layer enhanced the capacity with respect to the TiO\(_2\) reference (Chen et al., 2018b).

**Synergistic Effect Between SnO\(_2\) and Fe\(_2\)O\(_3\)**

In the next attempt, we investigated the effects of atomically intermixing conversion-type Fe\(_2\)O\(_3\) into a SnO\(_2\) matrix. The CV curves of a pure Fe\(_2\)O\(_3\) reference thin-film electrode are presented in Figure 5A. During the first lithiation process, three cathodic peaks are observed at 1.62, 0.98 and 0.76 V, respectively, corresponding to the following three lithiation steps (Wang et al., 2017):

\[
x\text{Li}^+ + \text{Fe}_{2}\text{O}_3 + xe^- \rightarrow \text{Li}_x\text{Fe}_{2}\text{O}_3 \\
(2-x)\text{Li}^+ + \text{Li}_x\text{Fe}_{2}\text{O}_3 + (2-x)e^- \rightarrow \text{Li}_2\text{Fe}_{2}\text{O}_3 \\
4\text{Li}^+ + \text{Li}_x\text{Fe}_{2}\text{O}_3 + 4e^- \rightarrow 3\text{Li}_2\text{O} + 2\text{Fe}
\] (7, 8, 9)

At the initial stage of lithiation at 1.62 V, a small amount of lithium can react with Fe\(_2\)O\(_3\) to form Li\(_x\)Fe\(_2\)O\(_3\) (Eq. 7). With further lithiation to 0.98 V, Li\(_x\)Fe\(_2\)O\(_3\) transformed to Li\(_2\)Fe\(_2\)O\(_3\) (Eq. 8). At around 0.76 V, the sharp and intense peak corresponds to the complete conversion to metallic Fe (Eq. 9). In the anodic polarization process, several broad overlapping peaks are observed corresponding to the progressing oxidation of metallic Fe to Fe\(^{2+}\) and further to Fe\(^{3+}\). Figure 5B shows the CV behavior of the SnO\(_2\)–Fe\(_2\)O\(_3\) composite thin-film electrode, which is closely analogous to a combination of the CV behaviors of pure Fe\(_2\)O\(_3\) (Figure 5A) and pure SnO\(_2\) (Figure 3B). In the first cycle, there are three reduction peaks at 1.15, 0.93 and 0.31 V, and three oxidation peaks at 0.46, 1.05, and 1.97 V, respectively. The rather weak reaction peak at 1.15 V is assigned to the refoundation of Li\(_x\)Fe\(_2\)O\(_3\) and further reaction to Li\(_2\)Fe\(_2\)O\(_3\) (Eqs 7 and 8). The sharp reduction peak around 0.93 V is attributed to the coinciding reduction reactions of SnO\(_2\) to Sn/SnO and Fe\(^{2+}\) to Fe, and the formation of Li\(_2\)O. The peak at 0.31 V ascribes to the formation of a series of Li\(_x\)Sn alloys. The delithiation reactions can be described by the following: the oxidation peaks at 0.46 and 1.05 V during the initial charge process can be attributed to the multi-step conversion of the Li\(_x\)Sn alloy to Sn, the oxidation peak at 1.97 V can be attributed to the oxidation of Fe to Fe\(^{3+}\) (Li et al., 2015b). From the cycling performance, we can see that the SnO\(_2\)–Fe\(_2\)O\(_3\) composite thin-film electrode achieves a discharge capacity of 1,580 mAh g\(^{-1}\), while pure Fe\(_2\)O\(_3\) shows a discharge capacity of 1,062 mAh g\(^{-1}\) after 50 cycles at 1 C (Figure 5C). The composite electrode holds 70.2% of the initial capacity after 50 cycles outperforming both the pure SnO\(_2\) (38.9%) and Fe\(_2\)O\(_3\) (54.3%) electrode. Figure 5D shows the further investigations of rate capabilities of all three electrodes. Among all, the pure Fe\(_2\)O\(_3\) has the worst rate capability, while for the SnO\(_2\)–Fe\(_2\)O\(_3\) composite electrode, although the specific capacity gradually decreases with the increase in current density, the capacity is always maintained higher than both SnO\(_2\) and Fe\(_2\)O\(_3\) at every delivered rate from 1 to...
FIGURE 5 | CV curves of (A) conversion-type Fe$_2$O$_3$ and (B) SnO$_2$–Fe$_2$O$_3$ composite electrodes. The comparison of SnO$_2$, Fe$_2$O$_3$ and SnO$_2$–Fe$_2$O$_3$ electrode: (C) cycling performance at 1 C and (D) rate performance from 1 to 100 C.

FIGURE 6 | CV curves of (A) alloying-type ZnO and (B) SnO$_2$–ZnO composite electrodes. The comparison of SnO$_2$, ZnO and SnO$_2$–ZnO composite electrode: (C) cycling performance at 1 C and (D) rate performance from 1 to 100 C.
100 °C, especially significantly superior to Fe₂O₃. The obtained capacity from the SnO₂–Fe₂O₃ composite electrode is significantly higher than that of the pure SnO₂ or Fe₂O₃ reference electrode.

**Synergistic Effect Between SnO₂ and ZnO**

ZnO is known for exhibiting an alloying-type reaction mechanism towards lithium. Hence, ZnO-incorporated SnO₂ composite thin-films were prepared subsequently to explore the synergistic effect of two atomically intermixed anode materials with similar alloying-based mechanism. Figure 6A shows CV curves of pure ZnO thin-film electrode. The peak at 0.6 V in the first cathodic sweep aligned to the reduction of ZnO to Zn (Eq. 10), and the peaks at 0.4 and 0.12 V correspond to the multi-phase formation of LiₓZn alloys (Eq. 11). In the anodic sweep, several small peaks at 0.3, 0.47 and 0.61 V can be linked to the multi-dealloying steps from LiₓZn to Zn, the peak at 1.4 V is most probably due to the re-oxidation of Zn (Lu et al., 2017; Zhao et al., 2019).

$$2Li^+ + ZnO + 2e^- \rightarrow Zn + Li_2O \quad (10)$$

**TABLE 3** The theoretical, initial charge-discharge capacity, Coulombic efficiency, the discharge capacity after 50 cycles at 1°C and the retention rate of all the investigated thin-film electrodes.

| Material     | Theoretical (mAh g⁻¹) | Initial discharge (mAh g⁻¹) | Initial charge (mAh g⁻¹) | Initial Coulombic efficiency (%) | Discharge after 50 cycles (mAh g⁻¹) | Retention (%) |
|--------------|-----------------------|----------------------------|--------------------------|----------------------------------|-------------------------------------|---------------|
| SnO₂         | 1,491                 | 2,260                      | 1,908                    | 84.4                             | 879                                 | 38.9          |
| TiO₂         | 396                   | 516                        | 488                      | 94.6                             | 468                                 | 90.7          |
| Fe₂O₃        | 1,007                 | 1,956                      | 1,723                    | 88.1                             | 1,062                               | 54.3          |
| ZnO          | 978                   | 2,092                      | 1,808                    | 86.4                             | 730                                 | 34.9          |
| SnO₂–TiO₂    | 626.2                 | 1,270                      | 1,177                    | 92.7                             | 1,126                               | 88.7          |
| SnO₂–Fe₂O₃   | 896.8                 | 2,252                      | 2,016                    | 89.5                             | 1,580                               | 70.2          |
| SnO₂–ZnO     | 849.3                 | 2,386                      | 2,169                    | 90.9                             | 1,795                               | 75.2          |

**FIGURE 7** SEM images of the morphology before and after cycling for the (A1,A2) SnO₂, (B1,B2) SnO₂–TiO₂, (C1,C2) SnO₂–Fe₂O₃, and (D1,D2) SnO₂–ZnO electrode. (E) EIS of the electrodes before and after cycling. (F) Schematic illustration of SnO₂ and the effect of atomically intermixing SnO₂ with MOₓ on the lithiation mechanism.
\[ x\text{Li}^+ + \text{Zn} + x^e \rightarrow \text{Li}_x\text{Zn} \]  

The CV curves of the SnO$_2$–ZnO composite thin-film electrode are shown in Figure 6B. During the first cathodic scan, a sharp reduction peak around 0.98 V is observed which could be explained as the combination of the reduction of SnO$_2$ and ZnO to Sn and Zn, respectively. The peaks at 0.55 and 0.22 V probably correspond to the formations of Li$_x$Sn and Li$_x$Zn, respectively. During the first anodic scan, a peak at 0.54 V and a broad peak around 1.12 V are clearly distinguishable which could be attributed to multi-step dealloying reactions. The other two peaks at higher voltages (1.30 and ~2 V) are probably due to stepwise re-oxidation from Sn to SnO$_2$ and Zn to ZnO. As observed in the cycling performance in Figure 6C, both the pure ZnO and SnO$_2$ thin-film electrodes suffer from significant capacity decay. However, the SnO$_2$–ZnO composite anode delivers a reversible capacity of 1,795 mAh g$^{-1}$ after 50 cycles and exhibits 75.2% capacity retention with respect to the first cycle, which is much superior than that of 38.9% and 34.9% obtained from pure SnO$_2$ and ZnO, respectively. The SnO$_2$–ZnO composite electrodes also exhibit an impressive rate capability. Figure 6D shows the rate capability behavior over 80 cycles from 1 to 100 C. The discharge capacities reach to 2,325, 1,992, 1,847, 1,642, 1,504, 1,209, and 743 mAh g$^{-1}$ at 1, 2, 5, 10, 20, 50, and 100 C, respectively. Even after cycling at high rate of 100 C the capacity could return to 2,089 mAh g$^{-1}$ when the current density returned back to 1 C. The SnO$_2$–ZnO composite electrodes offer a higher capacity than that of pure SnO$_2$ and Fe$_2$O$_3$ at every rate condition. Apparently, composite thin-film electrodes not only improve the capacity but also help in achieving improved cycling stability and rate performance.

**Discussion on the Lithium Storage Mechanism**

Table 3 lists a comparison of the details of capacities, Coulombic efficiencies and retention rates of all the investigated thin-film electrodes (pure references and composites). The charge capacity achieved in all the cases are higher than the theoretical capacity, which is due to the extremely thin films of active materials achieved by ALD (Mattelaer et al., 2015; Kint et al., 2019; Zhao et al., 2019; Li et al., 2020). The composite thin-films (SnO$_2$–TiO$_2$, SnO$_2$–Fe$_2$O$_3$, and SnO$_2$–ZnO) show better electrochemical properties, either higher capacity or better retention rate than their individual counter parts (SnO$_2$ and TiO$_2$, Fe$_2$O$_3$, or ZnO). With the addition of TiO$_2$, although the SnO$_2$ obtained smaller capacity, a significant improvement in cycling stability is observed in SnO$_2$–TiO$_2$ composite thin-film electrode. As for the SnO$_2$–Fe$_2$O$_3$ composite thin-film electrode, both the capacity and stability are moderately improved. In the case of SnO$_2$–ZnO composite thin-film electrode, notably, after few initial cycles of dropping, the capacity stabilizes and after 50 cycles it eventually offers the highest capacity among all the electrodes.

**CONCLUSIONS**

We have exploited the benefits of ALD to fabricate uniform, smooth and well atomically intermixed SnO$_2$–TiO$_2$, SnO$_2$–Fe$_2$O$_3$ and SnO$_2$–ZnO composite thin-film model electrodes to evaluate their electrochemical performance as anode materials for LIBs. Cycling stability discloses the effect of synergy on battery capacity performance. All the composite thin-films (SnO$_2$–TiO$_2$, SnO$_2$–Fe$_2$O$_3$ and SnO$_2$–ZnO) show better electrochemical properties, either higher capacity, better retention or improved rate capability as compared to the individual components (SnO$_2$, TiO$_2$, Fe$_2$O$_3$ and ZnO). With the addition of TiO$_2$, the composite...
thin-films achieve lower overall capacity but obtain excellent cyclability. With incorporation of Fe₂O₃ in the composite thin-films, both the capacity and retention are improved, but both have moderate effect. With regards to the addition of ZnO, the composite thin-films can be stabilized at higher capacity than the bare components after a capacity drop in the few initial cycles. The SnO₂–ZnO composite thin-film electrodes eventually obtain the best comprehensive performance amongst the tested materials. This work reports a systematic study of the synergistic effects between two different types of metal oxide and can hopefully provide a useful guidance for the development of better composite anode materials for thin-film rechargeable batteries.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

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AUTHOR CONTRIBUTIONS

CD conceived the original idea and supervised the writing. BZ did all the experiments and data analysis, plotted the figures, wrote the original draft. AD and JD revised the manuscript.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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