A general prelithiation approach for group IV elements and corresponding oxides

Jie Zhao\textsuperscript{a,1}, Jie Sun\textsuperscript{a,1}, Allen Pei\textsuperscript{a}, Guangmin Zhou\textsuperscript{a}, Kai Yan\textsuperscript{a}, Yayuan Liu\textsuperscript{a}, Dingchang Lin\textsuperscript{a}, Yi Cui\textsuperscript{a,\textsuperscript{b,}*}

\textsuperscript{a} Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA
\textsuperscript{b} Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA

ARTICLE INFO

Keywords:
Prelithiation
Anode materials
Group IV elements
First cycle Coulombic efficiency

ABSTRACT

Prelithiation of anode materials is an important strategy to compensate for lithium loss as a result of the formation of a solid electrolyte interphase (SEI) at the surface of anodes in lithium-ion batteries. Conventional prelithiation reagents often present serious safety concerns due to the high flammability and unstable chemical nature. Here, we successfully developed a general one-pot metallurgical process to prelithiate group IV elements and their corresponding oxides, yielding prelithiation capacity approaching the theoretical specific capacity. As-synthesized \textit{Li}$_{22}$\textit{Z} al\textit{loys} and \textit{Li}$_{22}$\textit{Z}$_{x}$-\textit{Li$_2$O} composites \((Z = \text{Si, Ge, Sn etc})\) can serve as prelithiation reagents to increase the first cycle Coulombic efficiency of both graphite and alloy-type anode materials. Among all lithiated group IV alloys, \textit{LiGe} exhibits the best stability under ambient-air conditions, consistent with the simulation results showing the large binding energy between \textit{Li} and \textit{Ge} atoms in \textit{Li}$_{22}$\textit{Ge}$_5$ crystal. Metallurgical lithiation of \textit{ZO}$_2$ results in composites with homogeneously dispersed reactive \textit{Li}$_x$\textit{Z} nanodomains embedded in a robust \textit{Li$_2$O} matrix which effectively suppresses the oxidation process. \textit{Li}$_{22}$\textit{Z}$_x$-\textit{Li$_2$O} composites further improve the ambient-air stability because the strong binding between \textit{O} atoms in \textit{Li$_2$O} and \textit{Li} atoms in \textit{Li}$_{22}$\textit{Z}$_5$ stabilizes the reactive \textit{Li}$_x$\textit{Z}$_5$ nanodomains. These results allow us to identify the prelithiation reagents with the optimal stability in air, thereby simplifying the requirement on the industrial electrode fabrication environment.

1. Introduction

The emerging electric vehicles market has stimulated intensive research on low-cost lithium-ion (Li-ion) batteries with high energy density and long cycle life [1–3]. Currently, existing Li-ion batteries are produced in the discharged state with Li pre-stored in the cathode due to the air stability of the lithiated cathode materials [4,5]. During battery operation, organic electrolytes are not stable and decompose to form an SEI layer on the surface of electrodes at the working potential of the anode [6,7]. This irreversible formation of SEI consumes Li from cathode materials and occurs mainly during the first lithiation process, resulting in an appreciable loss of active cathode materials and low first cycle Coulombic efficiency (CE) [8,9]. The first cycle CE of commercial graphite electrodes is typically around 90% [10,11], whereas first cycle CEs for high-capacity alloy anodes including Si, Ge and Sn are usually lower than 80% due to the increased surface area of the nanostructured electrodes utilized to improve cycling performance of alloy anodes [12–14]. These low first cycle CEs impose a significant hurdle in constructing full-cells for practical applications because the Li consumption at the anode side necessitates an excess amount of cathode active material solely to compensate for the first cycle losses, leading to a reduced total energy density [15]. Moreover, cathode capacity loading is limited by coating thickness due to kinetic factors [16].

Prelithiation is a common way to improve the first cycle CE of Li-ion batteries. Cathode prelithiation was previously achieved by the addition of Li-rich compounds such as \textit{Li}_2\textit{NiO}_2 [17], \textit{Li}_6\textit{CoO}_4 [18], metal/\textit{Li$_2$O} composites [19], and metal/LiF composites [20]. However, prelithiation capacities of these materials are generally lower than 1000 mAh/g, \textit{Li$_2$O} and \textit{Li$_3$N} powders exhibit much higher specific capacities (> 1400 mAh/g), but the use of these additives is accompanied with the evolution of \textit{O}$_2$ and \textit{N}$_2$ gas, respectively [21–23]. In terms of anode prelithiation, Si nanowires and Sn-C electrode were electrochemically lithiated by directly shorting with Li metal [24,25]. Choi’s group further improved this electrochemical lithiation approach in a controlled manner by shorting silicon monoxide with Li metal in the presence of an optimized circuit.
resistance and simultaneously monitoring the voltage between both electrodes [26]. Microscale stabilized lithium metal powder (SLMP, FMC Lithium Corp) [27–29], and a polymer protected Li metal layer [30] have been also effectively employed to compensate for the first cycle irreversible capacity loss of various anode materials including graphite and Si. Recently, we demonstrated that metallurgically synthesized Li$_x$Si nanoparticles (NPs) can serve as a high-capacity prelithiation reagent to effectively increase the 1st cycle CE of anode materials [31]. Li$_2$O and artificial-SEI coatings have been utilized to increase the stability of Li$_x$Si NPs in air with low humidity level (< 10% relative humidity (RH)) [32]. Furthermore, metallurgically lithiated SiO$_2$ developed a unique composite structure of homogeneously dispersed reactive Li$_x$Si nanodomains embedded in a robust Li$_2$O matrix which was found to further improve ambient-air stability (~ 40% RH) [33]. Group IV elements such as Ge and Sn also have relatively high specific capacities (1640 mAh/g for Ge, and 993 mAh/g for Sn) and similar volumetric capacities to Si (2574 mAh/cm$^3$ for Si, 2275 mAh/cm$^3$ for Ge, and 2111 mAh/cm$^3$ for Sn), making them also suitable for pre-storing Li [15,34–36]. As such, the strategy of embedding active lithium alloys in a robust Li$_2$O matrix is also attractive for other group IV elements and is predicted to stabilize the lithiated group IV alloys.

Herein, we developed a one-pot metallurgical process to synthesize Li$_{22}Z_5$ alloys (Z = Ge and Sn) and Li$_{22}Z_5$-Li$_2$O composites by using Z and 2O$_2$ as the source materials, respectively. Both Li$_{22}Z_5$ alloys and Li$_{22}Z_5$-Li$_2$O composites are reactive enough to predissolve various anode materials such as graphite and Sn, thereby achieving high 1st cycle CEs of >100%. Among all lithiated group IV alloys, Li$_x$Ge NPs exhibits the best stability under ambient-air conditions, consistent with the simulation results showing that Ge atoms in the cubic Li$_{22}Ge_5$ crystal have the strongest bonding with Li atoms. Li$_{22}Ge_5$-Li$_2$O compositions further enhanced the air stability over their corresponding Li$_{22}Z_5$ alloys thanks to the strong bonding between O atoms in Li$_2$O and Li atoms in Li$_{22}Z_5$.

2. Materials and methods

2.1. Synthesis of Li$_x$Z alloys and Li$_x$Z-Li$_2$O composites

Ge and GeO$_2$ nanoparticles (Sigma Aldrich) were the first ground to obtain fine powders by planetary ball milling operated at a grinding speed of 400 rpm for 24 h. SnO$_2$ nanoclusters were prepared via a bio-inspired hydrothermal method in the presence of tri(hydroxymethyl) aminomethane (THAM, Sigma Aldrich) [37]. 0.27 g of Na$_2$SnO$_3$·3H$_2$O (Sigma Aldrich) and 0.2 g of THAM were first dissolved into 35 ml of distilled H$_2$O, and then transferred into a 40 mL Teflon-lined stainless-steel autoclave. The autoclave was kept at 120 °C for 1 h. Finally, the obtained white sample was washed with deionized water and pure ethanol. The starting materials including Ge NPs, GeO$_2$ NPs, Sn NPs (Sigma Aldrich) and SnO$_2$ nanoclusters were dried under vacuum for 48 h and then heated to 120 °C in the argon glovebox (O$_2$ level < 1 ppm, and H$_2$O level < 0.1 ppm) for 12 h to remove trapped water and oxygen. A mixture of ball-milled Ge NPs and Li metal (99.9%, Alfa Aesar) (1177:500 mg, which is determined by the chemical reaction in Supplementary information, Fig. S1) was heated at 250 °C under mechanical stirring inside a tantalum crucible at 200 rpm for 2 days and then quenched to obtain the crystalline phase of Li$_{22}Ge_5$ in the argon glovebox. Under similar conditions, GeO$_2$ NPs or SnO$_2$ nanoclusters were reacted with molten Li to form Li$_2$Ge-10Li$_2$O or Li$_x$Sn-10Li$_2$O composite, respectively. The weight ratio of starting materials to Li metal is also determined by the chemical equation in Supplementary information, Fig. S1. The synthesis condition of Li$_x$Sn alloy is slightly different because of the low melting point of Sn compared with other staring materials. The alloying temperature should be maintained between the melting points of Li metal and Sn (180°C and 232°C, respectively) to ensure the preservation of the morphology of Sn NPs.

2.2. Electrochemical characterization

Sn NPs, graphite, carbon black (Super P, TIMCAL, Switzerland), and polyvinylidene fluoride binder (PVDF, Kynar HSV 900) were dried under vacuum for 24 h to remove trapped water. To prepare the working electrodes, various materials were dispersed uniformly in tetrahydrofuran (THF, Sigma Aldrich) to form a slurry (Anode materials and mass ratio are based on specific cells). The slurry was then cast onto a thin copper foil and dried under vacuum. Coin-type 2032 cells were assembled in an argon glovebox using Li metal as counter/reference electrode. The electrolyte is 1.0 M lithium hexafluorophosphate (LiPF$_6$) in 1:1 v/v ethylene carbonate/diethyl carbonate (BASF, LP 40). Cyclic voltammetry measurements were carried out on a BioLogic VMP3 system. Galvanostatic cycling was carried out using an MTT 8 Channel battery tester and a 96-channel battery tester (Arbin Instruments). The total mass loading of Li$_x$Z NPs or Li$_x$Z-Li$_2$O composites based anode was 2.0–3.0 mg/cm$^2$ and the typical mass loading of the graphite based anode was ~ 5 mg/cm$^2$.

3. Results and discussion

3.1. Density functional theory simulation

To study the stability of different Li$_x$Z alloys (Z = Si, Ge and Sn) in ambient-air conditions, we performed density functional theory (DFT) simulations to calculate the interaction between Z atoms and Li atoms in the cubic Li$_{22}Z_5$ crystal. The binding energy (E$_b$) of Li with Si, Ge, and Sn was obtained using CASTEP simulation package in the framework of DFT. Although Li alloyed with group IV elements to form the Li-richest alloys with the same formula, the crystal structures are slightly different. For simplicity, we selected the similar simulation fragments of Li$_x$Si$_{10}$ pseudo-tetrahedron from cubic Li$_2$Si$_{10}$, Li$_x$Ge$_{10}$ pseudo-tetrahedron from cubic Li$_2$Ge$_{10}$, and Li$_x$Sn$_{10}$ octahedron from cubic Li$_2$Sn$_{10}$ (Li$_{12}$Sn$_8$) as shown in Fig. 1a. Li was calculated to have a binding energy of ~2.98 eV with Ge, which is higher than that of the other two species (Si: ~0.80 eV, Sn: ~2.15 eV). According to this definition, a more negative value of E$_b$ indicates a stronger binding or a more energetically favorable reaction. Based on the DFT simulation results, Li$_{22}Ge_5$ is the most thermally stable alloy in the crystalline Li$_{22}Z_5$ family. Previously, we performed DFT simulations to calculate the interaction energy between O atoms in Li$_2$O and Li atoms in Li$_2$Si$_{10}$ [33]. The binding energies between O atoms of Li$_2$O and surface Li atoms of Li$_{22}Si_5$ are much larger than the binding energy between Li and Si atoms in Li$_2$Si$_5$ crystal. In Li$_x$Si$_{10}$Li$_2$O composites, Li$_x$Si$_{10}$ nanodomains are uniformly embedded in a robust Li$_2$O matrix, providing more binding between O in Li$_2$O and Li in Li$_{22}Si_5$ which effectively stabilizes the Li in Li$_{22}Si_5$ nanodomains. It is anticipated that this effect is also applicable to other Li$_x$Z-Li$_2$O composites improving their stability beyond that of pure Li$_x$Z alloys.

3.2. Synthesis and characterizations of Li$_x$Z alloys and Li$_x$Z-Li$_2$O composites

To confirm the DFT results, Li$_x$Z alloys and Li$_x$Z-Li$_2$O composites were synthesized. Ge NPs and GeO$_2$ NPs were used as the starting materials to form the Li$_x$Ge alloy and Li$_x$Ge-Li$_2$O composite, respectively. A mixture of ball-milled Ge NPs and Li metal (1177:500 mg) was heated at 250 °C under mechanical stirring inside a tantalum crucible at 200 rpm for 2 days and then quenched to obtain the crystalline phase of Li$_{22}Ge_5$ in an argon glovebox (Fig. 1b). Under the same conditions, ball-milled GeO$_2$ NPs were reacted with molten Li to form the Li$_x$Ge-Li$_2$O composite. Scanning electron microscopy (SEM) was utilized to characterize the morphology of the Ge and GeO$_2$ NPs before and after lithiation. After ball milling, the size of Ge NPs is in the range of 40–220 nm, while that of GeO$_2$ NPs is in the range of 110–370 nm as shown in Fig. 2a and d. The sizes of the derived Li$_x$Ge alloy and
LixGe-Li2O composite were larger than those of the starting materials because of the volume expansion and some degree of particle aggregation during the metallurgical process (Fig. 2b and e). The size distributions of Ge and GeO2 NPs before and after thermal lithiation are shown in Supplementary information, Fig. S2. X-ray diffraction (XRD) confirms the crystalline nature of ball-milled Ge powder (PDF no. 00–004-0545) and a small portion of GeO2 (PDF no. 00–036-1463) resulting from the high-energy ball-milling process in air (Fig. 2c, upper). XRD confirms the complete transformation of Ge in both Ge powder and the intrinsic oxide GeO2 to crystalline Li22Ge5 (PDF no. 01–081-6059) during the thermal alloying process (Fig. 2c, bottom). The small peaks of Li2O (PDF no. 00–012-0254) come from the conversion of the small amount of intrinsic oxide GeO2. XRD (Supplementary information, Fig. S3) also shows the complete formation of crystalline Li22Ge5 and Li2O during the thermal alloying process of GeO2 powder and molten Li. The only difference is the much higher percentage of Li2O in the final product. Kapton tapes covered the XRD samples to suppress side reactions in the air, contributing the broad background of XRD patterns.

Li22Sn5 alloy was obtained at similar synthesis conditions as Li22Ge5 alloy by using Sn NPs as the starting material. The only difference is the alloying temperature should be maintained between the melting points of Li metal and Sn to ensure the preservation of the morphology of Sn NPs. Both SEM (Fig. 2f) and TEM (Supplementary information, Fig. S4a) images confirm that the Sn NPs have sizes less than 200 nm. After metallurgical lithiation, the shape of the NPs is retained, whereas the particle sizes are larger due to volume expansion and some aggregation (Fig. 2g and Supplementary information, Fig. S4b). XRD confirms the transformation from Sn (PDF no. 00-004-0673) to Li22Sn5 (PDF no. 01-081-6569) after thermal alloying with molten Li (Fig. 2h). The small amount of Li2O again arises from the intrinsic monoxide SnO (PDF no. 04-005-4541) in Sn NPs. The hydrothermal-synthesized SnO2 nanoclusters are uniform both in size (~ 50 nm) and shape as confirmed by SEM and TEM (Fig. 2i and Supplementary information, Fig. S5a). The magnified TEM image (Supplementary information, Fig. S5b) shows that the clusters are composed of ultrafine crystallites with size of 10 nm. The lattices with plane spacing of 3.34 nm and 2.64 nm are observed, corresponding to the SnO2 (110) and (101) lattice planes, respectively. The monodisperse SnO2 nanoclusters were utilized as the precursor for the LixSn-Li2O composite. After thermal lithiation, the morphology of SnO2 nanoclusters was preserved, whereas the size of the clusters slightly increased to 75 nm because of volume expansion (Fig. 2j). XRD of lithiated SnO2 shows the same final products as lithiated Sn NPs with a higher percentage of the Li2O phase (Supplementary information, Fig. S6).

3.3. Electrochemical characterizations of LixZ alloys and LixZ-Li2O composites

To study the electrochemical properties of the LixZ alloys and LixZ-Li2O composites, half cells were fabricated with Li metal as a counter electrode. LixZ alloys or LixZ-Li2O composites were mixed with Super P and PVDF (65:20:15 by weight) in THF to form a slurry, which was then drop cast on a thin copper foil and dried under vacuum. Because of the high reactivity of LixZ alloys and LixZ-Li2O composites, solvents with higher polarity were avoided. To measure the prelithiation
capacities of the Li₅Ge alloy and Li₅Ge-Li₂O composite, the electrodes were charged to 1.5 V directly at a slow rate of C/20 (1 C = 1640 mA/g for Ge and 1126 mA/g for GeO₂). The prelithiation capacities were 1335 mAh/g and 892 mAh/g based on the masses of Ge and GeO₂ in the electrode, respectively (Fig. 3a). Similarly, charged to 2 V at a rate of C/20, the Li₅Sn alloy and Li₅Sn-Li₂O composite electrodes had extraction capacities of 910 mAh/g and 695 mAh/g, approaching the theoretical specific capacities of Sn and SnO₂, respectively (The specific capacity is estimated on the basis of the mass of Sn or SnO₂ in the electrode. 1 C = 990 mA/g for Sn and 782 mA/g for SnO₂. Fig. 3b). The voltage profile of the lithiated SnO₂ electrode exhibits the same plateaus as that of the lithiated Sn electrode, reflecting the same active

Fig. 2. (a, b) SEM images of Ge NPs (a) before and (b) after thermal lithiation. (c) XRD patterns of Ge NPs before (upper) and after lithiation (bottom). (d, e) SEM images of GeO₂ NPs (d) before and (e) after thermal lithiation. (f, g) SEM images of Sn NPs (f) before and (g) after thermal lithiation. (h) XRD patterns of Sn NPs before (upper) and after lithiation (bottom). (i, j) SEM images of SnO₂ nanoclusters (i) before and (j) after thermal lithiation. Scale bar, 500 nm.
material compositions of the electrodes. Consistently, the cyclic voltammetry (CV) profile of the lithiated SnO2 electrode shows the typical shape of a Sn electrode (Supplementary information, Fig. S7) [38].

Because of their low potential and high capacity, LixZ alloys and LixZ-Li2O composites are reactive enough to be used as prelithiation regents to increase the 1st cycle CE of different anode materials, such as graphite and Sn. In Fig. 3c, the blue voltage profile of a graphite control cell reveals a plateau between 0.2 and 0.7 V, corresponding to SEI formation during the first lithiation process. As a result, the 1st cycle CE of the graphite control cell is only 87.4% as measured in the voltage window of 0.005–1.5 V. To confirm the prelithiation effect, LixZ alloy was mixed with graphite flakes and PVDF at a certain ratio in a slurry to form the working electrodes. On the addition of organic electrolytes, LixZ alloy was spontaneously activated, providing additional Li ions to the anode for SEI formation and partial lithiation of the active anode materials. After cell assembly, it takes about 6 h for the potential of electrodes to reach a steady state. With the addition of LixSn NPs, the open-circuit voltage (OCV) of graphite/LixSn cell (graphite flakes:LixSn:PVDF = 75:15:10 by weight) is decreased to 0.4 V, significantly lower than the 1.4 V of the control cell, indicating partial prelithiation of the graphite flakes. The capacity of LixSn NPs compensates the irreversible capacity loss of the graphite in the first cycle, increasing the 1st cycle CE from 77.7% to 100.3%. With the relatively higher specific capacity, a smaller amount (12 wt%) of LixGe NPs is needed for prelithiation of graphite flakes to reach a similar 1st cycle CE of 100.6%. With the addition of LixZ NPs, graphite/LixZ cells exhibit consistent higher capacity and stable cycling at C/20 for the first three cycles and C/5 for the following cycles (1 C = 372 mA/g of graphite). The capacity is based on the total mass of graphite flakes and Z in LixZ NPs (Fig. 3d). Both as-synthesized LixGe and LixSn alloys are in nanoparticle form and tend to be embedded in the interparticle spaces between microscale graphite flakes. Since LixGe and LixSn NPs are already in their fully expanded states, they will not squeeze graphite flakes during lithiation and delithiation, contributing to the stable cycling of graphite/LixZ cells. Aside from intercalation-type graphite anodes, prelithiation using LixZ NPs is also applicable to high-capacity alloy-type anodes such as Sn. Prelithiation of Sn NPs with LixSn NPs (mass ratio 60:20) shows consistent results, increasing 1st cycle CE from 77.7% to 94.1% (Supplementary information, Fig. S8).

3.4. Air-stability of LixZ alloys and LixZ-Li2O composites

The stability of LixZ alloys and LixZ-Li2O composite was tested under different air conditions to confirm the DFT simulation results. To compare their dry-air stability, different LixZ alloys were stored in a dry room (dew point = −50 °C) for 5 days. The remaining capacity of LixSn NPs exposed to dry air over many days were studied by charging the LixSn NPs electrodes to 2 V at a low rate of C/20 (Fig. 4a). After 5 days’ exposure, LixSn NPs exhibit a high capacity of 845 mA/h/g, corresponding to a capacity retention of 93%. Among the LixZ alloys, LixGe shows the best dry-air stability with negligible (6.5%) capacity decay after 5 days of exposure, consistent with the simulation results indicating that...
Ge atoms in the Li$_{22}$Ge$_5$ crystal has the strongest bonding with Li atoms which stabilizes active Li. The trend of capacity decay of lithiated Si (black), Sn (purple) and Ge (red) NPs, which loses 33% capacity after 5 days (inset of Fig. 4a). To further challenge the stability of Li$_x$Ge, Li$_x$Ge NPs was exposed to ambient air (~40% RH) for 6 h, exhibiting a high extraction capacity of 947 mAh/g (30% capacity loss, Fig. 4b). Although the specific capacity is relatively lower, Li$_x$Ge-Li$_2$O NPs exhibit superior ambient-air stability with a higher capacity retention of 85% (15% capacity loss) compared to bare Li$_x$Ge NPs. The capacity retentions of lithiated Z NPs and their corresponding oxides in ambient air after various durations were studied as shown in Fig. 4c. Similar to the trends in dry air conditions, the capacity decay of Li$_x$Ge and Li$_x$Sn NPs is much slower than that of Li$_x$Si NPs, because of the stronger binding between Li atoms and Ge or Sn atoms in the corresponding cubic crystals. No new peaks are present in the XRD pattern of Li$_x$Sn NPs exposed to ambient air for 2 h (Fig. 4d). The XRD pattern reveals small peaks belonging to Li(OH)•H$_2$O (PDF no. 04-010-4336), and the intensity of Li$_x$Sn peaks drops significantly after being exposed to ambient air for 6 h. Consistently, Li$_x$Sn NPs show a high extraction capacity of 707 mAh/g after 2 h of exposure and only 45% capacity retention after 6 h (Supplementary information, Fig. S9). It is necessary to notice that Li$_x$Z-Li$_2$O composites consistently exhibit superior ambient-air stability as compared with bare Li$_x$Z NPs. Similar to the Li$_x$Si-Li$_2$O composite, thermal lithiation of ZO$_2$ results in a composite with homogeneously dispersed reactive Li$_x$Z nanodomains embedded in a robust Li$_2$O matrix, providing more binding between O atoms in Li$_2$O and Li atoms in Li$_x$Z$_5$, which effectively stabilizes the Li in Li$_x$Z nanodomains. Usually, Li$_x$Z$_5$ alloys have a thin coating of Li$_2$O, that serves as a passivation shell slowing down the corrosion reaction in the air [31]. However, the highly robust and crystalline Li$_x$O matrix formed at high temperature is dense enough to prevent side reactions in the air compared with Li$_2$O coating formed at room temperature. For core-shell structure, any pinhole will provide a pathway for inner Li$_x$Z to react with the air and thus, reduce the capacity. In the Li$_x$Z$_5$-Li$_2$O composites, Li$_x$Z$_5$ nanodomains are uniformly embedded in a robust Li$_2$O matrix, such that each Li$_x$Z$_5$ nanodomain has localized Li$_2$O protection. Even if some Li$_x$Z domains are inactivated by the presence of pinholes on the surface, the inner Li$_2$O still serves as a localized anti-corrosion layer to prevent inner Li$_x$Z domains from additional corrosion.

4. Conclusions

In conclusion, we have developed a general prelithiation approach to obtain Li$_x$Z$_5$ alloys (Z = Ge and Sn) and Li$_x$Z$_5$-Li$_2$O composites using Z and ZO$_2$ as starting materials, respectively. This approach is general applicable to Z and oxides with complex nanostructures. Because of their high capacity and low chemical potential, both Li$_x$Z$_5$ alloys and Li$_x$Z$_5$-Li$_2$O composites are reactive enough to prelithiate graphite and alloy-type anode materials. Among all lithiated group IV alloys, Li$_x$Ge alloy exhibits the best ambient-air stability, consistent with the simulation results showing the large binding energy between Li and Ge atoms in Li$_x$Ge$_5$ crystal. Li$_x$Z$_5$-Li$_2$O composites consistently exhibit better ambient-air stability than their correspond-
ing $\text{Li}_{22}\text{Zn}$ alloys due to the strong binding between O atoms in the $\text{Li}_2\text{O}$ and Li atoms in $\text{Li}_2\text{Zn}$ which stabilizes the reactive $\text{Li}_{22}\text{Zn}$ nanodomains. These guiding principles point out the prelithiation reagents with the best air stability, simplifying requirements for industrial battery fabrication environments, which in turn, can decrease battery manufacturing costs.

Acknowledgements

We acknowledge the support from the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, Battery Materials Research Program of the U.S. Department of Energy.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2017.06.013.

References