Air-stable and freestanding lithium alloy/graphene foil as an alternative to lithium metal anodes

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Developing high-capacity anodes is a must to improve the energy density of lithium batteries for electric vehicle applications. Alloy anodes are one promising option, but without pre-stored lithium, the overall energy density is limited by the low-capacity lithium metal oxide cathodes. Recently, lithium metal has been revived as a high-capacity anode, but faces several challenges owing to its high reactivity and uncontrolled dendrite growth. Here, we show a series of Li-containing foils inheriting the desirable properties of alloy anodes and pure metal anodes. They consist of densely packed Li_xM (M = Si, Sn, or Al) nanoparticles encapsulated by large graphene sheets. With the protection of graphene sheets, the large and freestanding Li_xM /graphene foils are stable in different air conditions. With fully expanded Li_x Si confined in the highly conductive and chemically stable graphene matrix, this Li_x Si/graphene foil maintains a stable structure and cyclability in half cells (400 cycles with 98% capacity retention). This foil is also paired with high-capacity Li-free V₂O₅ and sulfur cathodes to achieve stable full-cell cycling.

he emerging market of electric vehicles has stimulated intensive research on lithium-ion (Li-ion) batteries with high energy density and long cycle life^{1,2}. Conventional anodes, primarily based on graphite with a theoretical capacity of 370 mAh g^{-1} , struggle to completely fulfil the demand³. Alloy anodes with much higher theoretical capacity (for example, Si: $4,200 \text{ mAh g}^{-1}$; Sn: 990 mAh g⁻¹; and SiO: 2,670 mAh g⁻¹) have been widely recognized as promising alternatives for high energy density applications⁴. However, because of their large volume change during lithiationdelithiation, these alloy anodes may potentially suffer from mechanical disintegration of the electrode structure and instability of the solid electrolyte interphase^{5,6}. Diverse micro- and nanostructure designs have been utilized to address these problems, achieving long-term cycling with high capacity^{7,8}. Particularly, freestanding Si/C composite films were fabricated to realize lightweight electrodes with further improved electrochemical performance9-11. However, alloy anodes are free of Li and are typically paired with low-capacity Li metal oxide cathode materials ($<200 \text{ mAh g}^{-1}$), which significantly limits the energy density of Li-ion batteries^{12,13}. Generally, Li-free cathode materials (for example, sulfur: 1,672 mAh g^{-1} ; V_2O_5 : 441 mAh g^{-1}) have much higher specific capacity¹⁴⁻¹⁶. As a result, there is a strong motivation to develop a new full-cell configuration with a Li-containing anode17.

Li metal is an attractive anode to construct full cells with Li-free cathodes because of its high specific capacity of 3,860 mAh g⁻¹ and lowest electrochemical potential (-3.04 V versus the standard hydrogen electrode)^{18,19}. However, Li metal anodes raise serious safety concerns and have a low Coulombic efficiency (CE) due to their uncontrolled dendrite formation, relative infinite volume change during Li plating and stripping, and high chemical reactivity with organic electrolytes^{20–22}. Extensive works, including Li/3D matrix composites^{23,24}, electrolyte additives^{25,26}, mechanically and chemically stable interphase^{27,28} and spatial deposition control²⁹,

have significantly suppressed dendrite formation and pushed the CE in corrosive carbonate electrolytes up to 98%. However, this technology is still far from real applications.

In addition, the use of Li metal is challenging because of its demanding processing requirements. Li metal is corroded immediately on exposure to humid air³⁰. Li metal anodes with fine structures typically show improved electrochemical performance and worsened stability associated with their enlarged surface area. Coating Li microparticles with Li₂CO₃ has been employed to enhance the stability of the lithium metal, but the use of a costly dry room is necessary^{31,32}. Other coatings such as Al₂O₃ via atomic layer deposition improves the stability under ambient conditions (40% relative humidity)³⁰. However, the surface texture of Li metal changes after the air exposure for several hours. An airstable, Li-containing anode with long-term cycling stability and high CE is therefore highly desired.

Here, we report a facile process to fabricate large-scale and freestanding Li_xM /graphene foils (M = Si, Sn, or Al) with the unique nanostructure of densely packed reactive LixM nanoparticles encapsulated by large graphene sheets (graphene refers to fewlayer (<10 layers) graphene). The volumetric capacity of the $Li_xSi/graphene$ foil is 1,800–2,000 mAh cm⁻³, approaching the theoretical value of Li metal (2,061 mAh cm⁻³)³³. With fully expanded Li_xSi confined in the graphene matrix, the foil avoids the intrinsic problems of volume expansion and dendrite growth that plague Li metal, exhibiting stable cycling (400 cycles with 98% capacity retention) at areal capacity of \sim 2.4 mAh cm⁻² in half cells. The LixSi/graphene foil is successfully paired with Li-free cathodes (V2O5 and sulfur) to achieve stable full-cell cycling. The cells are in the charged state after assembly, delivering an estimated energy density of ~500 Wh kg⁻¹. The excellent airstability of Li_xM/graphene foils is attributed to their unique structure where each LixM cluster is completely surrounded and

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Figure 1 | Schematic of the microstructure and fabrication process of the Li_xM/graphene foils. a, Schematic illustrating the unique foil structure comprising densely packed reactive Li_xM nanoparticles encapsulated by large graphene sheets. M refers to Si, Sn, or Al, but other materials that can form alloys with Li can potentially be used. This foil is highly stable in different air conditions thanks to its unique structure as well as the hydrophobicity and gas impermeability of graphene sheets. The photograph of a large Li_xSi/graphene foil shows its good flexibility and the potential to scale up to industrial fabrication. **b**, Li_xM nanoparticles were synthesized by heating a stoichiometric mixture of M nanoparticles and Li metal under mechanical stirring in an argon atmosphere. Li_xM nanoparticles were mixed with graphene sheets and SBS rubber (80:10:10 by weight) to form a slurry, which was then cast on a PET release film. After drying, it was peeled off as a large freestanding Li_xM/graphene foil.

protected by the large graphene sheets. Theoretically, the hydrophobicity^{34,35} and gas impermeability³⁶ of the graphene sheets prevent the absorption and penetration of gas molecules.

Fabrication and characterization of the Li_vM/graphene foil We have developed a scalable approach to fabricate a Li_xSi/graphene foil (Fig. 1). Similar to our previous study, Li_xSi nanoparticles were synthesized on the gram-scale, by heating a stoichiometric mixture of Li metal and Si nanoparticles under mechanical stirring in an argon glovebox³⁷. Li_xSi nanoparticles were mixed with graphene sheets and poly(styrene-butadiene-styrene) (SBS) rubber (80:10:10 by weight) in toluene to form a slurry, which was then casted on a polyethylene terephthalate (PET) release film. After drying, the Li_xSi/graphene can be easily peeled off as a large freestanding foil. Thin layers of graphene sheets were coated on the double sides of the foil to ensure that even the Li_xSi nanoparticles on the surface were fully protected. This foil preparation process is also applicable to other Li alloy forming materials, such as Al and Sn. Figure 2a shows a large Li_xSi/graphene foil (8 cm wide and 24 cm long). Supplementary Movie 1 shows the foil being rolled on a tube with a diameter of 3 mm and then being unfolded without any damage. The superior mechanical property of the Li_xSi/graphene foil is further demonstrated by the uniaxial tensile test, which shows a similar trend to a Li metal foil with much higher stress (Fig. 2d). $Li_xSi/graphene$ can also be coated on two sides of a copper foil to form an electrode similar to the one used in cylindrical cells (Supplementary Fig. 1).

The graphene sheets were prepared by exfoliation of graphite with the assistance of metal halide³⁸. A low-magnification transmission electron microscopy (TEM) image (Fig. 2b) shows overlapped and interconnected graphene sheets up to several micrometres. A double-layer graphene is clearly observed in Fig. 2c, with an average interlayer distance of 0.334 nm (Supplementary Fig. 2a). The TEM image in Supplementary Fig. 2b shows graphene sheets with 3-6 layers. Raman spectroscopy analysis also suggests multilayer graphene (Supplementary Fig. 2c)³⁹. The D to G peak intensity ratio $(I_D/I_G = 0.05)$ indicates a low concentration of defects in graphene⁴⁰. The quality of graphene is further confirmed by X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 2d), showing extremely low oxygen content. The X-ray diffraction (XRD) pattern (Fig. 2e) of the Li_xSi/graphene foil contains peaks of Li₂₂Si₅ (powder diffraction file (PDF) no. 01-077-2882), graphitic carbon (PDF no. 00-056-0159) and Li₂O (PDF no. 04-008-3420). Li_xSi nanoparticles are identifiable underneath the thin graphene sheet (Fig. 2f). The Li_xSi alloy is already in its fully expanded state, so no void space needs to be created to accommodate the volume expansion of Si. Accordingly, the Li_xSi/graphene foil can be thoroughly calendared without damaging its microstructures. After calendaring at large stress of 40 MPa, Li_xSi nanoparticles are in a densely packed state as shown in the cross-sectional SEM image (Fig. 2g).

Stability of the Li_xSi/graphene foil

Theoretically, the gas impermeability of graphene, and the hydrophobicity of graphene and the SBS rubber could improve the

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Figure 2 | **Characterization of the Li_xSi/graphene foil. a**, Photograph of a large Li_xSi/graphene foil with 8 cm width and 24 cm length. The right side of the foil is rolled around a thin tube to illustrate its good flexibility. **b**, Low-magnification TEM image of the overlapped and interconnected graphene sheets. **c**, TEM image shows a double-layer graphene sheet with an interlayer distance of 0.334 nm. The inset is an atomic-resolution image of the graphene sheet. **d**, Uniaxial tensile tests of the graphene foil, bulky paper, Li metal foil and Li_xSi/graphene foil. **e**, XRD pattern reveals the highly crystalline nature of graphitic carbon and Li₂₂Si₅. **f**,**g**, Top-view (**f**) and cross-sectional view (**g**) SEM images of the Li_xSi/graphene foil.

stability of the Li_xSi/graphene foil. A water drop placed on top of a pure graphene foil gives a contact angle of 93.1° (Fig. 3a). SBS is dissolved in toluene and then spin-coated on a Si wafer. The contact angle of 99.9° confirms the hydrophobicity of SBS. After being dispersed in the SBS/toluene solution for 2 h, LirSi nanoparticles are enwrapped by a ~40-nm-thick coating (Supplementary Fig. 3). Theoretically, graphene is impermeable to gases and robust against oxidation (Fig. 3b, top), suggesting that few-layer graphene sheets are effective anti-corrosion barriers³⁶. The hydrophobic nature repels the water molecules. Furthermore, the gas impermeability nature ensures that the graphene sheets can prevent gas penetration, even if the molecules in the air are adsorbed on the foil. The cross-sectional SEM image (Fig. 3b, bottom) shows that the Li_xSi nanoparticles aggregate to form a cluster during calendaring and that the cluster is perfectly encapsulated by the graphene sheets. Therefore, each Li_rSi cluster is entirely protected by the graphene sheets. Photographs of the Li foil and the LirSi/graphene foil exposed to ambient air (daytime relative humidity = 20-30%, night time relative humidity = 50-60%) indicate the superior stability of the Li_xSi /graphene foil (Fig. 3c). After exposure to ambient air for just 3 min, the colour of Li metal turns black. The XPS analysis (Supplementary Fig. 4) indicates the formation of Li₂CO₃ after 48 h exposure⁴¹. The colour of Li_xSi/graphene foil remains the same even after 48 h. The cross-sectional SEM images (Supplementary Fig. 5a,b) confirm that the change in thickness is negligible after exposure to ambient air for 1 day. To test whether the foil is stable for the baking process, the foil with 19-µm thickness was baked at 80 °C for 6 h in the dry room (dew point, -50 °C). The areal capacity of the LirSi/graphene foil remained almost unchanged, indicating that this foil can survive the baking process to remove residual solvent and water (Fig. 3d). To investigate the dry-air stability, the foil was stored in the dry room for two weeks and its remaining capacity was examined over time. After two weeks, it still maintained 94.3% of its original capacity, exhibiting a high areal capacity of 3.6 mAh cm⁻² (Fig. 3e). XRD confirms that there was no obvious change after dry-air exposure

(Supplementary Fig. 6a,b). Nanoscale Li alloy is extremely unstable in ambient air, losing most of its capacity within just several hours (Fig. 3f inset). With the protection of the graphene sheets, the Li_xSi/graphene foil exhibits excellent stability even in air with a high humidity level (20-60% relative humidity). After being exposed to ambient air for 3 days, the foil still exhibits a high areal capacity of 3.1 mAh cm^{-2} (Fig. 3f). The XRD pattern reveals small peaks belonging to LiOH (PDF no. 00-032-0564), which is related to H₂O contamination in the humid air (Supplementary Fig. 6c). Rietveld refinement quantitative analysis confirms that Li22Si5 remains the main component. With a lower amount of graphene, the foil $(Li_xSi:graphene:SBS = 90:5:5 \text{ by weight})$ exhibits a large capacity drop (42%) after exposure to the ambient air for the same time (Supplementary Fig. 7). The air stability of the LirSi/graphene foil increases the possibility for safe handling and simplifies the requirements on the industrial battery fabrication environment.

Electrochemical performance of the Li_xSi/graphene foil

The first-cycle delithiation capacities of Li_xSi/graphene foils with thicknesses of 19 and 42 μm were 3.8 and 8.3 $mAh\ cm^{-2}$ in half cells, respectively (Fig. 4a and Supplementary Fig. 8). Based on the foil thickness and areal capacity, the volumetric capacity is ~2,000 mAh cm⁻³, close to the theoretical value of $Li_{22}Si_5$ (2,240 mAh cm⁻³) and Li (2,061 mAh cm⁻³)^{4,33}. The experimental values for Si anodes reported in the literature are generally lower than 1,300 mAh cm⁻³ due to the low tap density of nanostructured Si and void space created to accommodate the volume expansion⁸. The specific capacity of the Li_xSi/graphene foil is \sim 1,600 mAh g⁻¹ based on the mass of LirSi. The foils with thicknesses of 12 and 19 µm are used to evaluate the long-term cycling performance (Fig. 4b). From the 4th to the 400th cycle at a current density of 1 mA cm^{-2} , the capacity retention of the 19-µm-thick foil is ~98%, showing an areal capacity of 2.4 mAh cm⁻². There are two characteristics that allow for such superior cycling performance. The first is the high conductivity of graphene sheets $(1,400 \text{ S cm}^{-1})$. The second is that Si is already in its fully lithiated

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Figure 3 | Stability of the Li_xSi/graphene foil. a, Images showing the contact angle of a water drop: 93.1° on a graphene foil and 99.9° on a SBS-coated Si wafer. **b**, Top: a schematic illustrating the use of large graphene sheets to prevent the penetration of gas molecules in the air. Bottom: cross-sectional view SEM image confirms that Li_xSi nanoparticles aggregate to form a cluster during calendaring and that the cluster is well encapsulated by large graphene sheets in the hybrid foil. **c**, Photographs of the Li metal and Li_xSi/graphene foil exposed to ambient air for different durations. **d**, The areal capacity of a Li_xSi/graphene foil before and after baking at 80 °C for 6 h in the dry room (dew point, -50 °C). **e**, The areal capacity retention of a Li_xSi/graphene foil in the dry room for two weeks. The inset shows the trend of capacity decay of the Li_xSi/graphene foils and Li_xSi/Li₂O nanoparticles (black) with varying durations. For each exposure time, eight cells were fabricated and tested for the Li_xSi/graphene foil exposed to ambient air for three days. The inset shows the trend of capacity retention of the Li_xSi/graphene foil exposed to ambient air for three days. The inset shows the trend of capacities. **f**, The areal capacity retention of the Li_xSi/graphene foil exposed to ambient air for three days. The inset shows the trend of capacity decay of Li_xSi/Li₂O nanoparticles (black) with varying durations. For each exposure time, eight cells were foil (red) and Li_xSi/Li₂O nanoparticles, respectively. The error bars indicate the standard deviation of the remaining capacities. **f**, The areal capacity retention of the Li_xSi/graphene foil exposed to ambient air for three days. The inset shows the trend of capacity decay of Li_xSi/graphene foil (red) and Li_xSi/Li₂O nanoparticles (black) with varying durations. For each exposure time, eight cells were fabricate the standard deviation of the remaining capacities the standard deviation of the remaining capacities.

and expanded state. The morphology change of individual Li_xSi clusters during cycling is indicated by the cross-sectional SEM images (Fig. 4c). A LixSi cluster (~5 µm) is encapsulated by graphene sheets. Void space is created during the delithiation process, which accommodates further volume expansion of the subsequent lithiation process. Therefore, the foil avoids the intrinsic problems of volume expansion that plague alternatives such as Li metal or unlithiated Si. The Li_xSi/graphene foil is in the fully charged state and discharged directly to deliver high capacity at the first cycle. Therefore, there is no first cycle CE. The CE of the following cycles is defined as delithiation capacity over lithiation capacity. The second cycle CE is 98.7%, and the CE of the later cycles reaches a high value of 99.92%. The improved early and later cycle CE is ascribed to several characteristics. In the foil, the Li_xSi cluster is enwrapped in graphene sheets, which is chemically and structurally similar to graphite anodes. LixSi nanoparticles are packed densely in a cluster form and encapsulated by graphene sheets to lower the surface accessible to the electrolyte and therefore reduces the side reactions.

The excellent performance of the $Li_xSi/graphene$ foil in half cells makes it possible to be used in full cells. We paired our $Li_xSi/graphene$ foil with a traditional LiFePO₄ cathode (LiFePO₄:conductive carbon (Super P):polyvinylidene fluoride (PVDF) = 70:20:10 by weight). Figure 4d shows the voltage profiles of foil-LiFePO₄ and Li-LiFePO₄ cells between 2.5 and 3.8 V. The voltage drop of the full cell is due to the higher voltage plateau (~0.4 V) of Li_xSi . The full and half cells show similar capacities of 132.2 mAh g^{-1} and 130.6 mAh g^{-1} at 1 C (the capacity and rate are both based on the mass of LiFePO₄). The rate capability was tested at various rates from 0.2 to 20 C (Fig. 4e). At low rate, the capacities of LiFePO₄ in full and half cells are similar. Compared with half cells, LiFePO4 in the full cell exhibits higher capacity especially at a high rate (~91.7 mAh g^{-1} at 10 C and 84.0 mAh g^{-1} at 20 C). Both cells exhibit stable cycling for 200 cycles at 1 C (Supplementary Fig. 9). The average CE of the full cell is 99.92%, slightly higher than the half cell (99.84%). After cycling, cells were dissembled to check the morphology of the Li_xSi/graphene foil and the Li counter electrode. As shown in Supplementary Fig. 10, Li metal cracks and the superficial Li even peels off after 200 cycles, due to the uncontrolled Li stripping/plating. The magnified SEM image shows massive dendrite formation on the Li metal. The morphology of the LixSi/graphene foil remains almost the same. The XPS spectra before and after sputtering confirms that the solid electrolyte interphase formed on the Li metal is thick and mainly consists of Li₂CO₃ and LiF (Supplementary Fig. 11)^{41,42}. In contrast, XPS performed on the foil mainly detects signals from the electrolytes. The Li_xSi/graphene foil can also be paired with a V₂O₅ cathode $(V_2O_5 \text{ nanosheets:Super P:PVDF} = 70:20:10 \text{ by weight})$, exhibiting stable cycling performance at a capacity around 365 mAh g^{-1} at 1 C (the capacity is based on the mass of V_2O_5 in the cathode; $1 \text{ C} = 441 \text{ mAg}^{-1}$ of V₂O₅; the mass ratio of anode to cathode is 1:4; Supplementary Fig. 12). With an average voltage of 2.5 V, the estimated energy density is $\sim 510 \text{ Wh kg}^{-1}$.

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Figure 4 | Electrochemical performance of the Li_x**Si**/graphene foil. **a**, First-cycle areal delibilitation capacities of Li_xSi/graphene foils with thicknesses of 19 and 42 μ m. **b**, Half-cell cycling performance of Li_xSi/graphene foils with thicknesses of 12 and 19 μ m at 0.1 mA cm⁻² for the first three cycles and 1 mA cm⁻² for the following cycles. The orange curve is the cycling performance of a pure graphene foil at the rate of C/5 (1 C = 372 mA g⁻¹ of carbon). The Coulombic efficiency is plotted for the foil with the thickness of 19 μ m only (purple). **c**, Schematics and the corresponding cross-sectional view SEM images of the foil before and after being cycled and stopped at the delibilitated and lithiated states. **d**, The voltage profiles of Li_xSi/graphene foil-LiFePO₄ full cell and Li-LiFePO₄ (LiFePO₄: Super P:PVDF = 70:20:10 by weight) half cell within a potential window of 2.5-3.8 eV. The capacity and rate are both based on the mass of LiFePO₄ in the cathode. **e**, Rate capability of Li_xSi/graphene foil-LiFePO₄ and Li-LiFePO₄ cells at various rates from 0.2 to 20 C (1 C = 170 mA g⁻¹ of LiFePO₄).



Figure 5 | **Characterization of the sulfur electrode and the sulfur batteries. a**, SEM image of the graphitic carbon-encapsulated sulfur composites. **b**, TEM image of the graphitic carbon-encapsulated sulfur composite. Inset shows the magnified graphitic carbon lattice fringes. **c**, The voltage profiles of Li_xSi/graphene foil-S and Li-S cells at a rate of 0.5 C ($1 C = 1.67 A g^{-1}$ of S; the capacity is based on the mass of graphitic carbon-encapsulated S in the cathode; the mass ratio of anode to cathode is 1.8:1). **d**, Cycling performance of Li_xSi/graphene foil-S and Li-S cells at a rate of 0.5 C. The Coulombic efficiency is plotted on the right *y* axis. **e**, XPS spectra of C 1s (left) and S 2*p* (right) performed on Li metal (top) and the Li_xSi/graphene foil (bottom) cycled in the sulfur batteries for 50 times.

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Characterization of the sulfur batteries

SEM of the graphitic carbon-encapsulated sulfur composite indicates sulfur can permeate into the graphitic carbon cage by capillary force and the composite maintains the original morphology of the cage (Fig. 5a). TEM confirms that the sulfur particles are well encapsulated by the graphitic carbon shell (>20 layers; Fig. 5b). The XRD pattern shows sharp and strong sulfur diffraction peaks (PDF no. 00-08-0247; Supplementary Fig. 13a). The broad peak between 23° and 30° is ascribed to the graphitic carbon cage. Figure 5c shows the voltage profile of the LixSi/graphene foil-S cell between 1.3 and 2.6 V, which shows a specific capacity of 1,086 mAh g^{-1} with an average voltage of ~1.8 V (the capacity is based on the mass of graphitic carbon-encapsulated S in the cathode). The mass ratio of anode to cathode is 1.8:1. Therefore, the estimated energy density is around 490 Wh kg⁻¹. There are two discharge voltage plateaus at 2.1 and 1.7 V, which agree with the Li-S discharge plateaus (2.4 and 2.1 V) and Li-Si (0.4 V) in half cells⁴³. The foil-S cell (Fig. 5d) demonstrates excellent cycling stability at 0.5 C and maintains a capacity of 858 mAh g^{-1} after 110 cycles with a CE of 99.5%, higher than that of the half cell (98.8%), indicating its great potential to replace Li metal in sulfur batteries (1 C = 1,672 mA g^{-1} of S). In the Li-S cell, the highly soluble polysulphides can easily diffuse from cathode to anode, and form a deposit of Li₂S₂/Li₂S on the Li metal, which is confirmed by the XPS spectrum of S 2p (Fig. 5e)^{38,42}. The counts of $\rm Li_2S_2$ and $\rm Li_2S$ peaks are highly suppressed for the foil, which indicates that the protective action of the chemically stable graphene sheets minimizes the shuttle effect significantly. The relatively lower peaks of O-C=O and SO_3^{2-} confirms that the decomposition of Li salt is also suppressed in the foil-S cell. Without passivation with the LiNO₃ additive, the foil-S cell loses 57% capacity after 110 cycles and consistently exhibits lower CE, which confirms the necessity of the LiNO₃ additive in the foil-S cells (Supplementary Fig. 13b).

Finally, we would like to emphasize that the whole foil preparation process is applicable to other materials. LixM was synthesized by heating a mixture of M nanoparticles and Li metal under an inert atmosphere. Although M refers to Sn and Al (and Si in our previous example), other materials that form alloys with Li can be potentially used. The Li_xM /graphene foil is prepared via vacuum filtration of a suspension of Li_xM and graphene sheets in toluene. The slurry coating and peeling-off approach mentioned above is also suitable. The XRD pattern of the Li_xSn/graphene foil indicates that it is made of Li₂₂Sn₅ (PDF no. 01-081-6569) and graphitic carbon (Supplementary Fig. 14). The XRD pattern of the $Li_xAl/graphene$ foil confirms the existence of Li_3Al_2 (PDF no. 04-007-1619) and graphitic carbon. The Li_xSn/graphene foil and $Li_{x}Al/graphene$ foil deliver high areal capacities of 2 mAh cm⁻² and 2.5 mAh cm⁻², respectively (Supplementary Fig. 15). The Li_xM/graphene foils exhibit stable cycling at C/20 for the first three cycles and at C/2 for the following cycles (1C = 990 mA g^{-1} of Sn for the Li_x Sn/graphene foil, $1C = 2.2 \text{ A g}^{-1}$ of Al for the Li_xAl/graphene foil). The excellent cycling stability is attributed to the similar structure of fully expanded Li_xM being confined in the highly conductive graphene matrix (Supplementary Fig. 16a). After exposure to ambient air for three days, the Li_xSn/graphene and Li_rAl/graphene foils exhibit high capacity retention of 91% and 88%, respectively (Supplementary Fig. 16b).

Conclusions

In this work, we have developed a facile process to fabricate largescale and freestanding $\text{Li}_x M/\text{graphene}$ anodes with the unique foil structure comprising densely packed $\text{Li}_x M$ nanoparticles encapsulated by large graphene sheets. M refers to Si, Sn, and Al, but other materials that can form alloys with Li can potentially be used. With its long-term cyclability and high CE in half cells, the $\text{Li}_x Si/\text{graphene}$ foil has been successfully paired with high-capacity Li-free cathodes (sulfur and V_2O_5) to achieve stable full-cell cyclability. The Li_xM/graphene foil is highly stable in different air conditions due to its unique structure in which each Li_xM cluster is completely surrounded and protected by the large graphene sheets. The air-stability could be further improved by atomic layer deposition of oxides or fluorides on the double sides of the foils. By addressing the electrochemical and environmental stability simultaneously, our Li-containing anodes should be attractive alternatives to Li metal anodes.

Methods

Methods and any associated references are available in the online version of the paper.

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Author contributions

J.Z., G.Z. and Y.C. conceived the concept. J.Z. and G.Z. carried out the synthesis and performed materials characterization and electrochemical measurements. J.X., Y.J., L.L., Y.L., P.-C.H. and J.W assisted in the synthesis and characterization of electrode materials. K.L. conducted stress-strain tests. K.Y. and H.-M.C. provided important experimental insights. J.Z., G.Z., K.Y., Y.L., H.-M.C. and Y.C. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.

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Methods

Preparation of the Li_xM/graphene foils. M represents Si, Al, Sn and other materials that can form alloys with Li. M nanoparticles (Si nanoparticles (100 nm, MTI Inc.), Al nanoparticles (50 nm, MTI Inc.) and Sn nanoparticles (<150 nm, Sigma-Aldrich)) were dried under vacuum for 48 h to remove trapped water. LixM was prepared by mechanically stirring a stoichiometric mixture of M nanoparticles and Li metal foil at 250 °C for 48 h in a glove box filled with argon (H2O level <0.1 ppm and O₂ level <1.0 ppm). The synthesis temperature of Li_xSn is slightly different, maintained between the melting points of Li metal and Sn to ensure the preservation of the morphology of the Sn nanoparticles. The graphene sheets were fabricated by an intercalation-expansion-exfoliation method, in which graphene sheets were exfoliated via a graphite intercalation compound with negligible oxidation as described in ref. 38. The Li_xM alloy was mixed with graphene sheets and SBS (Kraton D1161) rubber (80:10:10 by weight) in anhydrous toluene to form a slurry, which was then cast on a commercial PET release film. After drying, it was peeled off as a large freestanding Li_xM/graphene foil. Li_xM/graphene foils were also prepared via vacuum filtration of a suspension of Li_xM and graphene sheets (80:20 by weight) in anhydrous toluene. In case there were unprotected LixM nanoparticles on the surface of the foil, thin layers of graphene sheets were coated on the double sides of the foil to further enhance the protection. After drying, a pressure of 40 MPa was applied to the foil and held for 0.5 h. The whole foil preparation process was performed under argon atmosphere.

Electrochemical testing. For the Li_xM/graphene foil half cells, the working electrodes were assembled in 2032-type coin cells with Li metal (Alfa Aesar) as the counter electrode. The electrolyte was 1.0 M LiPF₆ in 1:1 v/v ethylene carbonate/ diethyl carbonate (BASF, LP40) with 10 vol% fluoroethylene carbonate and 1 vol% vinylene carbonate. After a cell was assembled, it took about 6 h for the electrode to

reach equilibrium as determined by the stabilized voltage of the cell. For the fabrication of the LiFePO4 cathode, a LiFePO4 slurry (LiFePO4 (MTI Inc.):Super P (TIMCAL):PVDF (Kynar HSV 900)) = 70:20:10 by weight) was coated onto an Al foil and dried under vacuum. The total mass loading was $\sim 10 \text{ mg cm}^{-2}$. In the foil -LiFePO₄ cell, the mass ratio of anode to cathode is 1:5. For the fabrication of the V₂O₅ cathode, a V₂O₅ slurry (V₂O₅ nanosheets:Super P:PVDF = 70:20:10 by weight) was coated onto an Al foil and dried under vacuum. For the fabrication of the graphitic carbon-encapsulated sulfur electrodes, a sulfur slurry (graphitic Cencapsulated S:Super P:PVDF = 70:20:10 by weight) was coated on an Al foil and dried under vacuum. The mass loading of the sulfur cathode was $\sim 1 \text{ mg cm}^{-2}$. The electrolyte was 1.0 M lithium bis-trifluoromethanesulphonylimide in 1:1 v/v 1,3-dioxolane/1,2-dimethoxyethane with 0.4 M LiNO3 additive. In the foil-S cell, the mass ratio of anode to cathode is 1.8:1. Galvanostatic cycling was carried out using an MTI 8-channel battery tester and the voltage depends on the specific cell. For the full-cell performance, rate and capacity are both based on the mass of active cathode materials. After assembly of the LixSi/graphene foil-S cell, the cell was in the charged state. For the calculation of the CE, the first discharge capacity was ignored. The second CE = capacity_{2nd discharge}/capacity_{1st charge} \times 100%.

Characterizations. Powder X-ray diffraction was performed on a PANalyticalX'Pert with Ni-filtered Cu K α radiation. XPS analysis was performed on PHI Versa Probe 5000 (Physical Electronics). SEM images were taken using a FEI XL30 Sirion SEM. The TEM images were acquired using FEI Titan 80–300 environmental TEM at an acceleration voltage of 80 kV. The stress–strain tests were performed on TA Instrument Q800 dynamic mechanical analyser.

Data availability. The data that support the plots within this paper and other finding of this study are available from the corresponding author upon reasonable request.