Nanocrystalline Li–Al–Mn–Si Foil as Reversible Li Host: Electronic Percolation and Electrochemical Cycling Stability

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ABSTRACT: When a metallic foil (Li metal or LiAl) with initial Li inventory (LiInv) is used as the anode in lithium-ion batteries, its metallurgical damage state in the presence of organic liquid electrolyte and cycling electrochemical potential is of great interest. While LiAl foil operates at a voltage that eliminates LiBCC dendrite, the state-of-health (SOH) of LiAl anode can still degrade quickly in full-cell cycling. To analyze the causes, we decompose SOH = SOHe × SOHi × LiInv, where SOHe is SOH of electronic percolation within the anode, SOHi is SOH of Li percolation from cathode to the anode interior, and LiInv is the amount of cyclable lithium in a full cell, all normalized such that 1 means perfectly healthy, and 0 means dead. Any of the three (SOHe, SOHi, LiInv) dropping to zero would mean death of the full cell. Considering the poor performance of pure Al foil due to rapid evolution of the anode foil by measuring the in-plane electronic conductance (CI) losses. To counter this problem, such MP method is more effective than the previous expensive and complicated electrochemical prelithiation and external chemical lithiation paradigms.

Yet, despite the initially enhanced LiInv, SOH of LiAl anode still degrades in full-cell cycling. When drastic phase transformation occurs from Al FCC ↔ LiAlCubic with volume change up to ~100%, it is a bona fide “chemomechanical shock” and would render much change of the original foil structure. Since grain boundaries (GBs) support faster diffusion than the bulk, the initial invasion of Li always

Aluminum may be a competitive anode candidate for lithium-ion batteries (LIBs), given its low cost, high theoretical capacity (993 mAh g⁻¹ for LiAl), and moderate electrochemical potential that inhibits the formation of LiBCC dendrites even at high rates. Dense free-standing LiAl foil, as a variation of the popular pure LiBCC metal foil with starting Lithium inventory (LiInv), attracts our attention considering its excellent electronic conductivity and dendrite-free deposition. Previous attempts at utilizing Al foil anode demonstrated a rapid drop in LiInv due to cumulative Coulombic inefficiency (CI ≡ 1-CE) losses. To counter this problem, metallurgical prelithiation (MP) of pristine Al foil at room temperature has been proven to be effective. Because LiAl foil is less reactive toward electrolyte and air, which is hugely advantageous for industrial processing, the free-standing LiAl foil is quite competitive in terms of large-scale production, and such MP method is more efficient than the previous expensive and complicated electrochemical prelithiation and external chemical lithiation paradigms.

Supporting Information

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goes along the GB, inducing phase transformations along the way. This imposes a challenge for original grain-to-grain compatibility, making GB sliding and even cracking the main mechanism to accommodate drastic deformation and geometric incompatibility. As local GB sliding is unavoidable, the GB free-volume and GB "complexion" that govern further electronic and mass transport will change. Fundamentally, for the half-cell reaction
to proceed in later battery cycling, global Li+ ionic (electrolyte) and electronic (metallic) transport must be guaranteed; otherwise, a grain cannot stay electrochemically active. Unlike in the slurry coating case, we do not have explicit binders or conductive agents, so GBs effectively play the role of conductive binders that mechanically hold adjacent grains together and allow electrons to hop across. Generally speaking, the GB "electrochemical complexion" could change in the following gradations during battery cycling: (a) with GB sliding there can be more free volume and accelerated Li atomic diffusivity, a little liquid electrolyte can seep in, forming patches of SEI, but still thin enough that electron can tunnel across, in which case the local electronic conductivity degrades but is still nonzero, (b) a big enough divide has opened up with lots of electrolyte infow, so that electron tunneling is no longer possible and this GB is no longer conductive electronically, and ultimately (c) all the grain boundaries surrounding one grain or cluster of grains have achieved (b) status, so this grain cluster can no longer be electrochemically active for (1). Note that the GB electrochemical complexities on average evolve in the direction of local electronic conductivity (SOHe) with cycling. If the liquid electrolyte has dried out, there will also be Li/Li+ conductivity ↓↓, and SOH↓s to zero. Such SOH failure could be reversed once new liquid electrolyte is injected to provide percolating Li+(electrolyte) transport. In contrast, SOHe drops to zero when the metal fragments into pieces, cutting off supply of e− (metallic), and SOHe failure would not be easily repairable as it involves the damage of solid components. Therefore, experimentally, SOHe should be tracked carefully in situ (by for instance in-plane electronic measurements, see below), in particular for binder-free and conductive-agent free foil electrodes, where GBs play the dual role of binders and conductive agents to active regions in (1).

We expect porosity (p) evolution of the foil to be a key factor controlling SOHe, which can be independently estimated (see below), in particular right after the chemomechanical shock:

from mechanical prelithiation. We will show that such chemomechanical shock induces ultrananocrystallization of the LiAlCubic product phase on the right-hand side, which will have profound effect on subsequent electrochemical cycling.
Porosity, which characterizes damage and SOHe, will be shown to be significantly improved by minor addition of dopants (1−2 wt % Mn, Si) before MP that refines the initial Al_{FCC} grain size and provides more GB network for Li diffusion and stress relaxation to accommodate the chemomechanical shock and nanocrystallization. These intriguing relationships provide valuable insights for designing long-lived foil anodes.

In subsequent electrochemical cycling, all three factors (SOHe × SOHi × LiInv) of the foil anode are indispensable. They are indeed the critical concerns of any full-cell electrode, whether it is powder slurry, alloy foil, or pure Li_{BCC} foil. Particularly, in foil systems, the evolution of GB electrochemical complexion needs to reach a fine balance between increasing SOHi and decreasing SOHe to make full use of LiInv. We find that coarse-grained pure Al foil after MP is incapable to achieve this kind of gentle balance, as we applied a facile roll-to-roll MP process (Figure S1a). Li$_x$Al foil (characterized by XRD in Figure S1b) is fragile and tends to disintegrate into fragments (Figure S1c) right after MP, with larger porosity and damaged electronic percolation from the
AlMnSi alloy, which was chosen as the starting material. We expect that these doping elements precipitate out in the form of second-phase nanoparticles, which have a well-known Zener pinning and grain refinement effect in polycrystalline materials by pinning down the motion of GBs. Transmission electron microscopy (TEM) was adopted to characterize its microstructure. As shown in Figure 1a, some precipitates with a size of ~100 nm (marked with yellow arrows) are located at the GBs in AlMnSi foil. In pure Al foil, in contrast, only a few dislocations were found in Figure S2. The grain size of AlMnSi is reduced to ~10 μm thick LiBCC foil in the middle. Because of mechanical pressure and resulting reaction heat, MP readily proceeded, consuming the LiBCC foil with mechanical peeling, and one of them is shown in Figure 2f. Electron backscattered diffraction (EBSD) imaging of the pure Al foil before MP is shown in Figure S1f, where only several ~50 μm sized grains and GB network could be observed. Note that such coarse grain size is comparable to the foil thickness (40 μm) itself; thus, phase transformation could easily propagate along one coarse GB all the way to the bottom to penetrate the foil during MP, bringing about greater risk of cutting off “(metallic) transfer in one swoop. Thus, this result compels us to explore a better chemomechanical shock accommodation strategy (better "shock absorber") to maintain good LDD and a healthy SOHe in foil systems.

In this work, commercially available AlMnSi alloy, which is doped with 1–2 wt % Mn and Si, was chosen as the starting material. We believe the unacceptably large porosity (close to 30%, as shown next) of MPed LiAl foil results from insufficient GB sliding systems that failed to relieve the phase transformation stress generated during chemomechanical shock (2). Electron backscattered diffraction (EBSD) imaging of the pure Al foil before MP is shown in Figure S1f, where only several ~50 μm sized grains and GB network could be observed. Note that such coarse grain size is comparable to the foil thickness (40 μm) itself; thus, phase transformation could easily propagate along one coarse GB all the way to the bottom to penetrate the foil during MP, bringing about greater risk of cutting off “(metallic) transfer in one swoop. Thus, this result compels us to explore a better chemomechanical shock accommodation strategy (better "shock absorber") to maintain good LDD and a healthy SOHe in foil systems.

Compared to the severely damaged LiAl foil (Figure S1d), SEM of the nanocrystalline LiAl,AlMnSi foil is shown in Figure S5. Some nanoscale pores can be seen on the surface, but they are clearly different from the deep and long cracks in pure LiAl (Figure S1d). Most of the ultrananocrystalline LiAl/LiAl GBs in LiAl,AlMnSi are not cracked, providing no electrolyte ingress access, but aid Li transport by the extra free volume inside. We then quantitatively measure the porosity or total “free-volume” that is caused by the chemomechanical shock of AlMnSi and pure Al during MP. First, presuming no porosity is generated during MP, and no lateral expansion, the theoretical thickness is calculated. From ab initio calculations (materialsproject.org), LiBCC (mp-135) has volume per Li atom of 20.121 Å³, AlFCC (mp-134) has volume per Al atom of 16.472 Å³, and LiAlCubic (mp-1067) has volume per LiAl of 32.103 Å³, almost double that of AlFCC and which is the basis for the shock. Therefore, to absorb 25 μm worth of LiBCC at least (16.472/20.121) × 25 μm = 20.47 μm worth of AlFCC is needed for the reaction, forming 39.887 μm worth of LiAlCubic and leaving 40 − 20.47 = 19.53 μm of unreacted AlFCC (as-received AlMnSi/Al foil is 40 μm thick). The ideal thickness of the LiAl,AlMnSi and LiAl foils is supposed to be 39.887 + 19.53 = 59.4 μm after the reaction if no porosity and no lateral expansion are involved.

Then the actual apparent thicknesses of LiAl,AlMnSi and LiAl samples are measured and shown in Table S3. The total apparent thickness is decomposed into the apparent reacted layer thickness and the unreacted layer thickness: ttotal = treact + tunrea. Independent measurements are performed at different locations of the foil to not only obtain the average E[t] but also the standard deviation σ[t] (the value behind the ± in Table S4). Note that when measuring treact and tunrea, 20 random spots were selected (Figure S6). Additionally, however, we notice there actually can be some lateral areal expansion (Table S5) during MP, meaning there can be sample-wide plastic deformation in both in-plane x, y and out-of-plane z. We therefore define

\[ \alpha \equiv \frac{\text{area}(\text{after MP})}{\text{area}(\text{before MP})} \]

and find \( \alpha = 1.228 \) for pure LiAl, but it is very close to 1.0 in LiAl,AlMnSi (Table S5). We can then calculate the porosity within the apparent reacted layer

\[ p \equiv \frac{E[t_{\text{total}}] - 59.4 \mu m/\alpha}{E[t_{\text{react}}]} \]

as the unreacted layer is clearly still fully dense and find that \( P_{\text{LiAl}} = 18.1 \mu m/66.5 \mu m = 27.2\% \), which is a huge amount of porosity, approaching that of slurry coatings (even though we profess to make a foil anode, in Figure S1). In contrast, \( P_{\text{LiAl,AlMnSi}} = 5.6 \mu m/50.6 \mu m = 11.0\% \), which is much less damaging, considering not all free volume belong to open pores, and much of the 11.0% could be trapped inside the ultrananocrystalline LiAl/LiAl GBs that facilitate Li GB diffusion but do not allow liquid electrolyte invasion.

Cross-sectional SEM in Figure 2b shows that in LiAl,AlMnSi, the total thickness increases to \( E[t_{\text{total}}] = 65.0 \mu m \) after MP, with a \( E[t_{\text{react}}] = 50.6 \mu m \) apparent reacted layer, and \( E[t_{\text{unrea}}] = 14.4 \mu m \) AlMnSi layer. Note that MP could be controlled by tuning the mechanical pressure, and the electrochemically retrievable LiFv generally increases as mechanical pressure increases, as demonstrated in Table S6. When adopting 30 MPa pressure here, the MP degree (characterized by \( x \) value in LiAl,AlMnSi) is estimated to reach the saturation limit of 0.751 by molar ratio (calculation details could be found in Table S7).
We find there are also 19.53/α = 14.4 μm of unreacted AlFCC retained within $t_{\text{react}}$ which accounts for 5.13/50.6 = 10% volume. Just like the retained austenite phase after martensitic transformation of steels can improve the ductility of steel, we believe the retained AlFCC phase in $t_{\text{react}}$ improves its LDD. It means the measured $E[t_{\text{react}}] = 50.6$ μm layer consists of 11 vol % porosity, 10 vol % retained AlFCC, and 79 vol % LiAl, while the intact $E[t_{\text{unreact}}] = 14.4$ μm layer is 100% AlFCC consistent with the FIB-SEM serial-sectioning observation in Figure S4b and 3D reconstruction image in Figure 2c. The pure Li,Al case also has retained AlFCC inside, but that is to no avail in terms of ductility because the 27.2% porosity after shock in the form of long, deep cracks (Figure S1) would negate any beneficial effect of retained ductile FCC phase. The above proves our claim that the initial shock damage of metal foils during MP is much reduced, with the introduction of minute amount of nanoparticles that enables the refined grain size from ~50 μm of pure Al to ~10 μm of AlMnSi. On the basis of this, one could confidently foresee better LDD/SOHe behavior in Li,AlMnSi foil than in LiAl foil during subsequent electrochemical cycling.

Interestingly, after carefully examining our LiAl phase with XRD (Figure S4a) and TEM (Figure 2d), we find the lithiation product is ultrananocrystalline right after MP. On the basis of Scherrer equation: $L = K\lambda/(\text{FWHM} \times \cos \Theta)$, where the calculation parameters are listed in Table S8, we could obtain that average crystal size of LiAl in Li,AlMnSi foil is ~25 nm. Such nanograin characteristics of LiAl after chemomechanical shock (2) seem to be at the heart of the phase transformation during MP. It should profoundly affect subsequent electrochemical cycling by changing the effective Li diffusivity through the ample LiAl/LiAl GBs, as discussed previously. The formation of the nanograin LiAl in MP is the result of chemomechanical shock, akin to nanocrystallization of metals in well-known severe plastic deformation (SPD) processing like equal channel angular extrusion (ECAP). In both cases, there is injection and dissipation of large amount of mechanical energy, there is severe geometry constraint, and the transformation occurs near room temperature. The main difference is that here, in MP, the volume change and stress are generated by chemomechanical shock brought by metallurgical reaction 2. We know from EBSD that AlMnSi had 10 μm-scale grains right before MP (Figure 1d) that are already refined by the Mn or Si nanoprecipitates compared to the 50 μm-scale grains of pure Al (Figure S1) but still quite large. To understand how 25 nm scale “nano” LiAl was generated in a cubic-to-cubic phase transformation (2), we need to appreciate the constraints in this system (as illustrated in Figure 2e). The phase transformation propagates as a front from the LiBCC side to the interior. The LiAl (cubic) entails a ~100% volume expansion (Figure 2e I and II), but it cannot expand isotropically, as it is constrained on the bottom (Figure 2e I and III). It needs to expand mostly uniaxially upward, as the LiBCC phase on top has a much softer yield strength (few MPa) than the AlFCC phase (few hundred MPa) on the bottom. To do this, it needs to break up into orientational domains (e.g., grains) to fit into the designated box. It is akin to breaking up a big sugar cube to pour the sugar fragments into a tall glass (whose footprint is compatible with the bottom, harder constraint). The fact that the measured $\alpha_{\text{LiAl}} = 1.228$ but $\alpha_{\text{LiAlMnSi}} = 1.0$ means that the 1–2 wt % Mn and Si dopants significantly harden the not-yet-transformed substrate in Figure 2e as it is under in-plane tension during MP, preventing its stretching and damage.

Unlike slurry-casting electrodes, which usually have at least 30% porosity that facilitates electrolyte percolation and SOHi, it is critical for the lithiated foil to have sufficient lithium transport paths so as to afford long-range Li supply (SOHi) for...
sustainable electrochemical cycling. Post-mortem examination is carried out on the Li\textsubscript{1-x}AlMnSi anode that was electrochemically lithiated/delithiated just once. After disassembling the cell and directly drying out the electrolyte solvent on/in the anode without further washing so as to “freeze” the electrolyte salt, EDS inspection was conducted to investigate the distribution of fluorine element, the characteristic element of the electrolyte, along the depth direction. The cross-sectional SEM image of the electrode after the first cycle is shown in Figure S7a, which reveals a relatively dense feature without long and deep cracks. Combined with the EDS mapping in Figure S7b, two consecutive layers, including upper Li\textsubscript{1-x}AlMnSi (∼52 μm) layer and bottom unreacted AlMnSi (∼16 μm) layer, are evidently identified, suggesting that electrolyte does percolated deep into the 11% porosity of the reacted Li\textsubscript{1-x}AlMnSi layer. Therefore, long-range Li\textsuperscript+ transportation and the global SOHi are ensured in the ultrananocrystalline, long-crack free Li\textsubscript{1-x}AlMnSi foil. Besides, we also measured electrolyte wettability of Li\textsubscript{1-x}AlMnSi foil, which seems to be much improved right after MP, as reflected by the significantly decreased contact angle (Figure S7c,d). Such better electrolyte wettability would also facilitate uniform distribution of electrolyte and reduce the propensity for electrolyte localiztion (EL),\textsuperscript{5} which is highly damaging to the foil both in terms of SOHi and SOHe.

Generally speaking, liquid electrolyte percolation in the anode is bound to affect SOHe, since the liquid electrolyte or SEI is electronically insulating, as it penetrates into the pores including short or long GB gaps and cracks and forms insulating SEI layers, hindering e\textsuperscript– (metallic) to hop across. It might not be a problem for fine grains or very thin SEI because insulation of one of them has little impact on the global e\textsuperscript– conductivity when the rest of grains still maintain electronic contact and because electrons may tunnel through thin SEIs of 1–3 nm thickness. However, wider fissures (width on the order of tens of nm) would be impossible for electron to tunnel through. Therefore, we quantitatively monitor the evolution of electron conduction (SOHe) of Li\textsubscript{1-x}Al and Li\textsubscript{1-x}AlMnSi foils during cycling with a three-electrode pouch cell prototype (experimental details in Figure S8). The in-plane SOHe test results at different cycles are shown in Figure 3a, where both Li\textsubscript{1-x}Al and Li\textsubscript{1-x}AlMnSi anodes are starting with initially small resistance <1 Ω. However, the resistance of Li\textsubscript{1-x}Al foil increases dramatically with electrochemical cycling and reaches up to 2785 Ω after only 6 cycles, which indicates that the in-plane electron hopping is starting to encounter great resistance. In contrast, Li\textsubscript{1-x}AlMnSi anode shows only slight increase and remains at between 100 and 200 Ω in the first 20 cycles (Figure S8), revealing stability in SOHe of Li\textsubscript{1-x}AlMnSi even if nanocracks may be generated (as we will show later) to imbibe liquid electrolyte, forming patches of SEI, which, however, seem to be thin (and narrow) enough that electron can tunnel through GBs.

From the investigation above, with the same LiInv (Figure S9a), enhanced electrochemical cycling stability is expected for Li\textsubscript{1-x}AlMnSi. To verify this, we have assembled LiFePO\textsubscript{4}||Li\textsubscript{1-x}AlMnSi and LiFePO\textsubscript{4}||Li\textsubscript{1-x}Al full cells. The initial charge/discharge curves of the two kinds of cells are shown in Figure S10a, from which we discovered that they showed almost the same charge capacities but different discharge capacities, where the LFP||Li\textsubscript{1-x}Al shows 2.2 mAh cm\textsuperscript–2 first-cycle discharge capacity (ICE = 77.8%), and the LFP||Li\textsubscript{1-x}AlMnSi full cell shows 2.35 mAh cm\textsuperscript–2 first-cycle discharge capacity (ICE = 87.7%). Such discrepancy in first-cycle capacity can be induced.

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**Figure 4.** Post-mortem examination of metal foil anodes after 20 cycles. (a) Top surface SEM image of the Li\textsubscript{1-x}Al foil. (b) Cross-sectional image of the Li\textsubscript{1-x}Al foil. (c) Top surface image of the Li\textsubscript{1-x}AlMnSi foil. (d) Cross-sectional image of the Li\textsubscript{1-x}AlMnSi foil.
by parasitic reactions with electrolyte, or by some kind of impedance, or both,\textsuperscript{25,26} and Figure S10 discussed this discrepancy in detail from the perspective of cracking.

In long cycling, which is most critical for rechargeable batteries, the LFP||Li\textsubscript{x}AlMnSi full-cell can maintain 90\% retention after 70 cycles (Figure 3b). In contrast, the Li\textsubscript{x}Al anode starts to decay from the 10th cycle and reaches 80\% capacity even before the 30th cycle. The voltage profiles of LFP||Li\textsubscript{x}AlMnSi full cells in Figure 3c exhibit stable working voltage platform between 2.3 and 4.0 V, while the Li\textsubscript{x}Al shows a severe polarization, resulting in an evident reduction of discharge voltage platform to around 2.7 V at around the 30th cycle (Figure S9b). The same trend is also reflected in the CE as shown in Figure 3d, where Li\textsubscript{x}AlMnSi comes with an extremely high CE, exceeding 99.9\% for more than 60 cycles, but CE of the Li\textsubscript{x}Al is always lower than 99.5\% and plunges dramatically at around 20 cycles. Such a big difference in CE performance was discussed in detail with the aid of EIS measurements in Figure S11. Notably, the Li\textsubscript{x}AlMnSi-based lithiated foil enhanced the cycle life of full cells by three time compared to Li\textsubscript{x}Al anode and was well adapted to various current densities (Figure S12).

Such dramatic improvements in electrochemical performance compel us to look further into microstructural disparities after electrochemical cycling. Although large volume change happens locally for the Li\textsubscript{x}AlMnSi anode due to the nature of the alloying reaction 1, we find that the apparent volume expansion seems to be mitigated, as amply revealed in Figure S13. Then post-mortem examination is carried out on metal foils upon further cycling. We found that the Li\textsubscript{x}Al anode has been torn apart into small pieces after just 10 cycles, and the broken structure contrasts sharply with the intact Li\textsubscript{x}AlMnSi anode (Figure S14). After 20 cycles, an isolated piece of the broken Li\textsubscript{x}Al anode was examined by SEM, which presented a rugged cracked surface with electrolyte localization\textsuperscript{5} phenomenon (unreacted area marked with red dot line in Figure 4a), where the marked area is deprived of liquid electrolyte and does not contribute capacity. As the electrolyte localizes, it concentrates drastic phase transformation there, deteriorating the structural integrity even further of the already mechanically poor Li\textsubscript{x}Al foil (Figure S1c). Thus, the cross-sectional image of Li\textsubscript{x}Al after 20 cycles (Figure 4b) reveals a 10 μm wide crack that cuts through the whole foil. Once coarse grains were fully packed with insulating liquid electrolyte or thick SEI layers, electron tunneling and interfacial Li\textsuperscript{+} transportation are no longer feasible, degrading the local SOHe and global SOHi. Eventually, this grain cluster becomes electrochemically inactive, which is reflected by the increase in interfacial resistance (Figure S15a) and well consistent with the as-mentioned SOHe measurement in Figure 3a. In striking contrast, after 20 deep charge/discharge cycles, Li\textsubscript{x}AlMnSi anode still exhibits compact structure without conspicuous cracks or electrolyte localization area (Figure 4c,d), demonstrating clearly enhanced LDD. Note that there is also increase in the interfacial resistance with prolonged cycling, but the increment is much gradual than the Li\textsubscript{x}Al anode (Figure S15).

We speculate that such improvement intrinsically originated from the dense GB network in the ultrananocrystalline Li\textsubscript{x}AlMnSi that provides sufficient sliding system for stress relief to ensure a relatively mechanically intact structure with more stable SEI and less void/gas pores that prevent the rendezvous of e\textsuperscript{-} (metallic) and Li\textsuperscript{+} (electrolyte). Here, instead of sustaining a single chemomechanical shock (2) in a matter of tens of seconds in MP, the foil sustains up to hundreds of electrochemomechanical shocks brought by (1), each thousands of seconds in duration, and the Li\textsubscript{x}AlMnSi anode, with its myriad of ultrananocrystalline GBs and phase boundaries (PB), behaves quite admirably.

To demonstrate potentially wide applications of Li\textsubscript{x}AlMnSi foil anode, we paired it against the higher-voltage 4 V class...
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.9b03626.

Experimental details, schematic diagram, XRD patterns, optical photographs, top-view SEM images, cross-sectional image, EBSD image, TEM images, BSE images, SOHe test results, Li inventory, voltage curves, charge/discharge curves, EIS pattern, Coulombic efficiencies, rate performances, interfacial resistance, batteries performance, thickness measurements, lateral area expansion, prelithiation degree, mole ratio calculation, calculation parameters, parameters of pouch cell (PDF).

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### Notes
The authors declare no competing financial interest.

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Supporting Information

Nanocrystalline Li-Al-Mn-Si foil as reversible Li host: electronic percolation and electrochemical cycling stability

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This PDF file includes:

Figures S1 to S18, Tables S1 to S10
Experimental Details

Materials. Pure Al and AlMnSi foils (40μm thick); Li\textsubscript{x}Al and Li\textsubscript{x}AlMnSi were manufactured by mechanical prelithiation, Li (50μm) and Al/AlMnSi (40μm) foil were stacked together and got lithiated by rolling machine at different pressure. Commercial one-side coated LiFePO\textsubscript{4} (2.65 mAh cm\textsuperscript{-2}), commercial LiNi\textsubscript{0.5}Co\textsubscript{0.2}Mn\textsubscript{0.3}O\textsubscript{2}(NCM) (2.4 mAh cm\textsuperscript{-2}), with 12mm diameter were used in full cells. Li\textsubscript{x}Al electrodes were managed to punched out from the broken structure with great care due to the fragile structure of 65μm-thick Li\textsubscript{x}Al anode. LiCoO\textsubscript{2} cathodes with 4.0 mAh cm\textsuperscript{-2} rated capacity was employed in the pouch cells. 40μL of 1M lithium hexafluorophosphate (LiPF\textsubscript{6}) in a 1:1 vol/vol mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 10 wt.% fluorinated ethylene carbonate (FEC) and 1 wt.% vinylene carbonate (VC) was used as electrolyte. The Li\textsubscript{x}AlMnSi/Li\textsubscript{x}S batteries worked in 40μL 1 M LiTFSI in a solution of 1,3-Dioxolane (DOL) and 1,2-Dimethoxyethane (DME) (volume ratio: 1:1) with/without 2 wt% LiNO\textsubscript{3} as additive respectively.

Electrochemical Measurements. Cells were assembled in the CR2025-type coin cells, and the electrochemical performance of cells are carried out by Neware test system (CT-4008, Newark). The Al||Li half-cell was delithiated to 2.3V at a current of 0.3mA cm\textsuperscript{-2}. The LFP||Li\textsubscript{x}AlMnSi/Li\textsubscript{x}Al full cells were examined between 2.0V to 4.0V. The electrochemical test on NCM||Li\textsubscript{x}AlMnSi full cells were carried out between 2.5~4.2V. The Li\textsubscript{x}AlMnSi/Li||S batteries were test from 1.5 to 2.5V. The electrochemical impedance spectroscopy (EIS) were conducted by Chi660E Electrochemical workstation at a frequency between 0.01–100 KHz (CHI660E, Shanghai Chen Hua Instrument Co., Ltd.).

SOHe test. We quantitatively estimate the ability of electron conduction (SOHe) of the different lithiated foils (Li\textsubscript{x}Al/Li\textsubscript{x}AlMnSi) at different electrochemical cycling stages. In order to ensure a totally free-standing anode, three electrode-tabs were assembled to test its SOHe with pouch cells instead of coin cells, aiming at eliminating the role of steel housing in current collector. Given the fragile structure of 65μm-thick Li\textsubscript{x}Al foil, here we fabricated two equal 70μm-thick Li\textsubscript{x}Al and Li\textsubscript{x}AlMnSi foils from initial 50μm-thick Al and AlMnSi foil, they can slightly keep an intact structure as the free-standing anodes. The test mode is shown in Figure S8, where two wires were led form the diagonal of anode (Li\textsubscript{x}Al/Li\textsubscript{x}AlMnSi) to test the in-plane SOHe.

Characterization. The morphologies and structures of Li\textsubscript{x}AlMnSi alloy were determined by a field emission scanning electron microscopy (SEM, FEI, QUANTA 250FEG) under an accelerate voltage of 10 kV. XRD measurements were carried out on a Bruker D8-Advance powder X-ray diffractometer operating at 40 kV and 30 mA, using Cu K\textsubscript{α} radiation (λ = 0.15405 nm). The signal was collected for diffraction angles (2θ) from 10° and 80° at a scan rate of 3° min\textsuperscript{-1}. The transmission electron microscope (TEM, FEI Talos F200) was performed to determine the grain size on both pristine Al foil and S-Al foil. The electron back-scattered diffraction (EBSD) of
Al/AlMnSi foil were carried out on OXFORD EBSD. The serial-sectioning FIB-SEM were performed by GATAN 3view 2XP instrument. The XPS measurements were carried out on the X-ray photoelectron spectroscopy under Ar-gas protection (XPS, Thermo Scientific Escalab 250Xi).

Figure S1. (a) Schematic diagram of roll-to-roll mechanical lithiation process. (b) XRD pattern of the prelithiated pure Al foil. (c) Optical photograph of the as-obtained Li$_x$Al foil. (d) Top view SEM image of Li$_x$Al foil. (e) Cross-sectional image of Li$_x$Al foil. (f) EBSD image of grain size of pure Al foil.
Figure S2. TEM image of pure Al foil.

Figure S3. XRD pattern of the AlMnSi foil and EDS mapping of Mn and Si elements.
Figure S4. (a) XRD pattern of the prelithiated AlMnSi foil. (b) BSE image of the cross-sectional image of Li$_x$AlMnSi foil. (c) Optical photograph of the as-obtained Li$_x$AlMnSi foil. (d) Surface morphology of Li$_x$AlMnSi foil in large field.

Figure S5. (a) and (b) BSE images of Li$_x$AlMnSi layer, and the nano scaled “free volume” is marked by yellow circles.
**Figure S6** SEM image of reacted layer thickness measurement of Li$_x$AlMnSi foil.

**Figure S7.** (a) Cross-sectional SEM image of nanocrystalline Li$_x$AlMnSi after charge/discharge once. (b) Cross-sectional fluorine elements distribution of Li$_x$AlMnSi after charge/discharge once. Wetting angle of (c) AlMnSi and (d) Li$_x$AlMnSi foil.
**Figure S8.** (a) SOHe test results of Li\textsubscript{x}AlMnSi anode in the first 20 cycles. (b) and (c) Test mode of the three-electrode pouch cell prototype.

As illustrated in Figure S8 b and c, electrodes a (Li\textsubscript{x}Al/Li\textsubscript{x}AlMnSi anode) and b (cathode) are used for routine charging/discharging, and after every two cycles, we apply a slight voltage bias across electrode a (Li\textsubscript{x}Al/Li\textsubscript{x}AlMnSi anode) and c (Li\textsubscript{x}Al/Li\textsubscript{x}AlMnSi anode), and calculate the resistance across the anode foil by reading the current from the multimeter (Ohm’s Law).

**Figure S9.** (a) Li inventory of the Li\textsubscript{x}AlMnSi and Li\textsubscript{x}Al foil. (b) Voltage curves of LFP||Li\textsubscript{x}Al full cell during cycling.
**Figure S10.** (a) The initial charge/discharge curves of the LFP||Li$_x$AlMnSi/Li$_x$Al cells. (b) EIS pattern of LFP||Li$_x$AlMnSi/Li$_x$Al full cells at the end of the 1$^{st}$ discharge. (c) Charge/discharge capacity of the LFP||Li$_x$AlMnSi/Li$_x$Al cells in the initial cycles. (d) EIS pattern of LFP||Li$_x$AlMnSi/Li$_x$Al full cells at the end of charge/discharge state during 2~3 cycles.

We believe such discrepancy in first-cycle capacity can be induced by parasitic reactions with electrolyte, or by some kind of impedance, or both. From the perspective of cracking, more fracture opening is apparently observed in Li$_x$Al (Figure S1d), which further caused serious parasitic reactions and subsequent capacity degradation during the initial cycle, and therefore bigger capacity loss is expected. One might argue that there is excess active lithium (1.8 ×) in the anode at the beginning; however, the problem is whether this LiInv could be “mined” under the condition of fixed cut-off voltage and constant current. To comprehensively understand the underlying kinetic limitations, we examined the impedance through the in-situ EIS test of two kinds of full cells in Figure S10 (b and d). The LFP||Li$_x$Al full cell exhibits almost four times larger resistance than that of LFP||Li$_x$AlMnSi cell at the end of first discharge, indicating the bigger delithiation hindrance and subsequently making it more difficult to pump out lithium from Li$_x$Al anode, even if there is abundant LiInv. Therefore, we could conclude that for the two cells using the same LFP cathodes with excess active lithium (1.8 ×), the different capacities during the initial several cycles before LiInv is depleted are mainly originated from the kinetic factors when applying a fixed cut-off voltage and
constant current. Note that the disparate resistance is due to the initial cracked LiₙAl foil (Figure S1c) exposing more free-surface than the intact LiₙAlMnSi foil (Figure 2a) for electrolyte corrosion, significant amount of SEI was formed on the free surface, leading to greater resistance and thus variation in ICE. As a matter of fact, the influence of kinetic factors is also reflected from the capacity and CE of the following several cycles. From Figure S10c, both the charge and discharge capacities of LFP||LiₙAlMnSi cell are superior to that of LFP||LiₙAl cell even though two of them have excess LiInv at that time, which however is well consistent with the impedance results in Figure S10d.

**Figure S11.** (a) Coloumbic efficiency of LFP||LiₙAlMnSi full-cells in the initial cycles. (b) EIS pattern of LFP||LiₙAlMnSi full-cell at the 2nd cycle. (c) EIS pattern of LFP||LiₙAlMnSi full-cell at the end of initial three discharge state. (d) The cross-sectional SEM image of LiₙAlMnSi anode after the initial cycle.

Moreover, we found that the Coloumbic efficiencies of all four LiₙAlMnSi samples raised to >100% in the second cycle, as shown in Figure S11a and Table S9. While this behavior would be uncommon for graphite anode (typically first cycle CE ~ 90%, raising to CE >99.5% in 5 or so cycles) which does not come with its own LiInv. We think for LiₙAlMnSi anode, which starts with its own LiInv before cycling, this is possible, in a 1st cycle deposit-then-strip / 2nd cycle deposit-then-strip / … scenario.
Basically, the question is why within fixed full-cell voltage cutoffs \([V_{\text{upper}}, V_{\text{lower}}]\), one can get more Lithium out of the anode than one can put into that anode, in a particular cycle. Note that one will not be violating mass conservation here, because even with the dissipation of cyclable LiInv to non-cyclable Li in SEI, due to the excess inventory \((1.8 \times)\) in \(\text{Li}_x\text{AlMnSi}\), one can still pump more Li out of the \(\text{Li}_x\text{AlMnSi}\) than one puts in, in the 2nd cycle.

Note that in the 1st cycle before the 2nd cycle, one actually did put more Li into the anode, that one pumped out (CE ~ 87%) – granted, some of those lost are converted into SEI – but it is possible that some of those lost (~13%) are just temporarily unusable because of kinetic limitations\(^1-2\), in the stripping leg of the 1st cycle. In the depositing part of the 2nd cycle, with the GB sliding that subsequently induces extra free-volume to allow faster Li atom (neutral) GB diffusion, as indicated by the impedance comparison between the cycles in Figure S11b, it is becoming easier and easier to “mine” the Lithium inventory embedded in \(\text{Li}_x\text{AlMnSi}\). Such kinetic facilitation should help to make the 2nd cycle extraction, 3rd cycle extraction, … easier, and so in the stripping part of the 2nd cycle, 3rd cycle …, they can contribute again, to push the CE of the second/third… cycles slightly above 100%. It’s like a business that lost quite a bit of money in the first year, but some of those losses turned out to be exaggerated and are actually investments, that they contribute to a small profit in year 2. Besides, from the low-frequency Warburg resistance shown in Figure S11c, which symbolizes long-range Li diffusion inside the anode’s active material, it is clear that impedance in charge and discharge at the same \(V\) are different, for the same cycle, suggesting improved kinetics during discharge, which we speculate is also partly responsible for the additional lithium capacity in the discharging process that makes the discharge/charge ratio (CE) over 100%. The impact of impedance on the apparent capacity and Coulombic efficiency measured at finite rate are elucidated in our previous work\(^3,4\).

In addition, for \(\text{Li}_x\text{AlMnSi}\), based on SEM examination in (Figure S11d), where negligible fracture opening is observed, we reasonably assume that the cracking has not caused serious parasitic reactions and subsequent capacity degradation during initial cycles. Besides, EIS measurement (Figure S11b) that reveals a decrement in delithiation hindrance with prolonged cycles also indicates no severe SEI generation, which otherwise would bring about significant impedance. Considering that the overall capacity fade can be induced either reversibly by kinetic limitations or irreversibly by parasitic reactions due to the cracking, we think both the improved kinetics and insignificant capacity loss from cracking support the CE constantly above 100% in the initial several cycles in Figure S11a.
Figure S12. Rate performance of LFP||Li$_x$AlMnSi full cells (current density ranges from 0.5mA cm$^{-2}$ to 7.5mA cm$^{-2}$) (a), and at a higher current density of 1C (2.5mA cm$^{-2}$) (b).

In terms of rate performance, the LFP||Li$_x$AlMnSi full cells are also well accommodated to current from 0.2C to 3C (current density ranges from 0.5mA cm$^{-2}$ to 7.5mA cm$^{-2}$) without short circuiting (Figure S12a), and meanwhile, it succeeds in keeping a stable performance for 60 cycles at a higher current density of 2.5mA cm$^{-2}$ (1C) (Figure S12b).

Figure S13. Cross-sectional SEM images of Li$_x$Al and Li$_x$AlMnSi foils before and after the electrochemical lithiation.
As revealed in Figure S13, large volume change still happens even for the Li$_x$AlMnSi anode, which intrinsically is originated from the nature of alloying anodes. However, although we acknowledge that the absolute volume expansion would not be restrained, in this study we find the apparent volume expansion seems to be mitigated. From the thickness comparison between the Li$_x$AlMnSi and Li$_x$Al, before the electrochemical lithiation process, Li$_x$AlMnSi (Figure S13a) and Li$_x$Al (Figure S13 b) anodes show 65 μm thick and 66-67μm thick respectively from the original 40μm thick after MP. Note that besides the average thickness that Li$_x$Al demonstrates 1-2μm thicker than Li$_x$AlMnSi, some variation in their surface roughness is also observed. By measuring the thickness of 30 different points on the two anodes with micrometer, surface roughness of Li$_x$Al is determined to be 2.0 μm (Table S1), while that of Li$_x$AlMnSi is 1.4μm (Table S2), which means apparent volume expansion is smaller and more uniform in AlMnSi during mechanical prelithiation. Further cross-sectional SEM analysis in Figure S13b reveals that the multiple damages, including cracks and pores, is attributed to the bigger apparent volume change of Li$_x$Al. In contrast, Li$_x$AlMnSi in Figure S13a exhibits a much more compact structure, which on the other hand implies smaller grain size and denser GB network that are induced by Zener pinning of metal alloy through adding impurity elements indeed alleviate the damage caused by the large volume change so as to reduce the apparent volume expansion.

Figure S13c and S13d respectively demonstrate the cross-sectional SEM images after electrochemically lithiating 2mAh cm$^{-2}$ lithium into the above-obtained Li$_x$Al and Li$_x$AlMnSi. The thickness of Li$_x$AlMnSi anode grew to 74μm, and the Li$_x$Al anode swelled to 77μm, corresponding to 13.8% and 14.9% expansion rate, respectively. Although Li$_x$AlMnSi and Li$_x$Al foils have similar volume change ratio, they demonstrate totally different morphologies. As can be seen in Figure S13, evident cracks of Li$_x$Al anode penetrate the thickness direction (Figure S13d), and the electrode is damaged after lithiation, making the structure porous and fragile, which justifies well its larger apparent volume change. In a sharp contrast, the Li$_x$AlMnSi anode keeps tight structure without any cracks before (Figure S13a) and after electrochemical lithiation (Figure S13c) despite the same absolute volume change. That is to say, compared to Li$_x$Al, the Li$_x$AlMnSi anode have mitigated the fatal cracking consequences of volume expansion. We think it is attributed to the sufficient GB sliding system, by which the Li$_x$AlMnSi anode could easily release the residual stress during the lithiation and then avoid the growth of cracks, thus further alleviate concomitant side-effects caused by volume expansion.
**Figure S14.** Optical photos of pre-cyclic Li$_x$AlMnSi (a and b) and Li$_x$Al (d and e), and Li$_x$AlMnSi (c) and Li$_x$Al(f) after 10 cycles in full-cells.

**Figure S15.** Interfacial resistance of LFP∥Li$_x$Al(a) and LFP∥Li$_x$AlMnSi (b) in the first 25 cycles.
In addition, the rate performance of Li$_{x}$AlMnSi||S batteries is shown in Figure S16 (b), where the current density increased stepwise from 0.24 to 2.4 mA cm$^{-2}$. From Figure S16 (b), no significant capacity degradation occurs as current intensifies, indicating a decent rate performance of Li$_{x}$AlMnSi||S batteries. However, it is worth mentioning that Li$_{x}$AlMnSi is still chemically unstable against Li$_2$S$_n$, as indicated in Figure S17 (a), where the same ether-based electrolyte except for no LiNO$_3$ as additive was used in Li$_{x}$AlMnSi-S batteries. In contrast with Figure 6c (CE~99%), CE (CE=109%) in Figure S17 (a) deteriorates significantly when electrolyte consists of no LiNO$_3$, which is generally believed to form passivation layer so as to prevent the corrosion of Li$_2$S$_n$ in Li-S batteries. Such speculation also gets verified by postmortem XPS examination in Figure S17 (c and d) and sulfur-containing species, including Li-S-O, Li-S composites, were detected on the cycled Li$_{x}$AlMnSi electrode surface. Therefore, it is reasonable to infer that Li$_{x}$AlMnSi anodes are still chemically reactive with Li$_2$S$_n$. Note that Li$_{x}$AlMnSi anodes are relatively more stable with Li$_2$S$_n$ than Li metal anodes, where CE=125% (Figure S17 (b)) is observed.

Figure S16. (a) Rate performance of NMC523||Li$_{x}$AlMnSi full cells and (b) Li$_{x}$AlMnSi||S batteries.
Figure S17. Li$_x$AlMnSi||S (a) and Li||S (b) batteries performance in the ether-based electrolyte consisting of 1 M LiTFSI in a solution of 1,3-Dioxolane (DOL) and 1,2-Dimethoxyethane (DME) (volume ratio: 1:1) without LiNO$_3$ additive. (c and d) XPS spectra of S2p and O1s after cycling of the Li$_x$AlMnSi||S battery.

Figure S18. (a) Voltage curves of LCO || Li$_x$AlMnSi pouch cell of the first cycle, inset picture is the photograph of the pouch cell. (b) Discharge capacity of the LCO || Li$_x$AlMnSi pouch cell in the initial 5 cycles.
Table S1. Thickness (μm) measurement result of the Li$_x$Al sample.

<table>
<thead>
<tr>
<th>Thickness (μm) of the foil</th>
<th>Average thickness</th>
<th>Standard Deviation</th>
<th>Total thickness</th>
</tr>
</thead>
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<tr>
<td>68.0 67.0 70.0 64.0 64.0</td>
<td>66.5μm</td>
<td>2.0μm</td>
<td>66.5 ± 2.0μm</td>
</tr>
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<td>67.0 70.0 63.0 67.0 68.0</td>
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<td></td>
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<tr>
<td>68.0 65.0 64.0 64.0 67.0</td>
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<td></td>
<td></td>
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<tr>
<td>70.0 64.0 68.0 65.0 66.0</td>
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<tr>
<td>68.0 65.0 67.0 63.0 68.0</td>
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<td></td>
</tr>
</tbody>
</table>

Table S2. Thickness (μm) measurement result of the Li$_x$AlMnSi sample.

<table>
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<th>Thickness (μm) of the foil</th>
<th>Average thickness</th>
<th>Standard Deviation</th>
<th>Total thickness</th>
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<td>64.9μm</td>
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<td>64.9 ± 1.4μm</td>
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<td></td>
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<td>64.0 65.0 65.0 64.0 65.0</td>
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<tr>
<td>69.0 63.0 64.0 66.0 67.0</td>
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<td></td>
</tr>
<tr>
<td>65.0 64.0 65.0 66.0 64.0</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>65.0 66.0 66.0 65.0 67.0</td>
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Table S3. Measured actual apparent thickness of all the samples.

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>Al</th>
<th>AlMnSi</th>
<th>Li$_x$Al</th>
<th>Li$_x$AlMnSi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total thickness ($t_{total}$)</td>
<td>40</td>
<td>40</td>
<td>66.5</td>
<td>65.0</td>
</tr>
<tr>
<td>Reacted layer ($t_{react}$)</td>
<td>--</td>
<td>--</td>
<td>66.5</td>
<td>50.6</td>
</tr>
<tr>
<td>Unreacted layer ($t_{unrea}$)</td>
<td>--</td>
<td>--</td>
<td>0</td>
<td>14.4</td>
</tr>
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Table S4. Thickness (μm) measurement result of the reacted layer of Li$_x$AlMnSi sample.

<table>
<thead>
<tr>
<th>Thickness (μm) of the reacted layer</th>
<th>Average thickness</th>
<th>Standard Deviation</th>
<th>Reacted layer thickness $t_{react}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.5 51.0 50.0 50.0 52.0</td>
<td>50.6μm</td>
<td>1.43μm</td>
<td>50.6 ± 1.43μm</td>
</tr>
<tr>
<td>50.0 49.0 51.5 51.5 53.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52.0 50.0 49.0 49.0 50.0</td>
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<td>50.0 52.0 52.0 53.0 50.0</td>
<td></td>
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</table>
Table S5. Lateral areal expansion of the two samples after MP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li$_x$AlMnSi</th>
<th>Li$_x$Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Size (before MP)</strong></td>
<td>4 cm × 3 cm</td>
<td>4 cm × 3 cm</td>
</tr>
<tr>
<td><strong>Size (after MP)</strong></td>
<td>4 cm × 3 cm</td>
<td>4.4 cm × 3.35 cm</td>
</tr>
<tr>
<td><strong>Lateral areal expansion</strong></td>
<td>0%</td>
<td>22.8%</td>
</tr>
<tr>
<td><strong>$\alpha$</strong></td>
<td>1</td>
<td>1.228</td>
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</table>

Table S6. Prelithiation degree at different mechanical pressure.

<table>
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<tr>
<th>Mechanical Pressure</th>
<th>10MPa</th>
<th>15MPa</th>
<th>20MPa</th>
<th>30MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li inventory (mAh cm$^{-2}$)</td>
<td>1.2</td>
<td>2.7</td>
<td>3.1</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table S7. Mole ratio calculation of the Al and Li inside the Li$_x$AlMnSi layer.

<table>
<thead>
<tr>
<th>Component</th>
<th>Li</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Area (cm$^2$)</strong></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Thickness (cm)</strong></td>
<td>0.0025</td>
<td>0.00256</td>
</tr>
<tr>
<td><strong>Density (g/cm$^3$)</strong></td>
<td>0.534</td>
<td>2.699</td>
</tr>
<tr>
<td><strong>Mass (mg)</strong></td>
<td>1.335</td>
<td>6.909</td>
</tr>
<tr>
<td><strong>Mole (mmol)</strong></td>
<td>0.1923</td>
<td>0.2560</td>
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Table S8. Calculation parameters of the grain size.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>K</th>
<th>$\lambda$ (Å)</th>
<th>FWHM (°)</th>
<th>2θ (°)</th>
<th>L (nm)</th>
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<tbody>
<tr>
<td><strong>Values</strong></td>
<td>0.94</td>
<td>1.54178</td>
<td>0.35</td>
<td>40.10</td>
<td>25</td>
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</table>
**Table S9.** Coloumbic efficiency of four LFP|| Li\textsubscript{x}AlMnSi full-cells in the initial cycles.

<table>
<thead>
<tr>
<th>CE(%)</th>
<th>1\textsuperscript{st}</th>
<th>2\textsuperscript{nd}</th>
<th>3\textsuperscript{rd}</th>
<th>4\textsuperscript{th}</th>
<th>5\textsuperscript{th}</th>
<th>6\textsuperscript{th}</th>
<th>7\textsuperscript{th}</th>
<th>8\textsuperscript{th}</th>
<th>9\textsuperscript{th}</th>
<th>10\textsuperscript{th}</th>
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<tr>
<td>1#</td>
<td>85.8</td>
<td>101.15</td>
<td>100.64</td>
<td>100.5</td>
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<td>100.34</td>
<td>100.29</td>
<td>99.76</td>
<td>100.66</td>
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<td>2#</td>
<td>87.71</td>
<td>100.93</td>
<td>100.53</td>
<td>100.31</td>
<td>100.16</td>
<td>100.24</td>
<td>100.11</td>
<td>100.15</td>
<td>100.12</td>
<td>100.05</td>
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<tr>
<td>3#</td>
<td>87.10</td>
<td>100.60</td>
<td>100.35</td>
<td>100.08</td>
<td>100.12</td>
<td>100.03</td>
<td>99.97</td>
<td>99.99</td>
<td>99.88</td>
<td>99.97</td>
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<tr>
<td>4#</td>
<td>86.10</td>
<td>100.40</td>
<td>100.12</td>
<td>99.93</td>
<td>99.85</td>
<td>99.81</td>
<td>99.80</td>
<td>99.91</td>
<td>99.85</td>
<td>99.91</td>
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**Table S10.** Parameters of the LCO || Li\textsubscript{x}AlMnSi pouch cell.

<table>
<thead>
<tr>
<th>Components</th>
<th>Thickness(μm)</th>
<th>Mass(mg)</th>
<th>Volume(μL)</th>
<th>Capacity(mAh)</th>
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<tbody>
<tr>
<td>LiCoO\textsubscript{2}</td>
<td>290</td>
<td>630</td>
<td>--</td>
<td>72.7</td>
</tr>
<tr>
<td>Li\textsubscript{x}AlMnSi</td>
<td>140</td>
<td>272</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Separator</td>
<td>15</td>
<td>32.5</td>
<td>--</td>
<td>--</td>
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<tr>
<td>Electrolyte</td>
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<td>288</td>
<td>240</td>
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REFERENCES