

# Mechanisms of Transformation of Bulk Aluminum–Lithium Alloys to Aluminum Metal–Organic Nanowires

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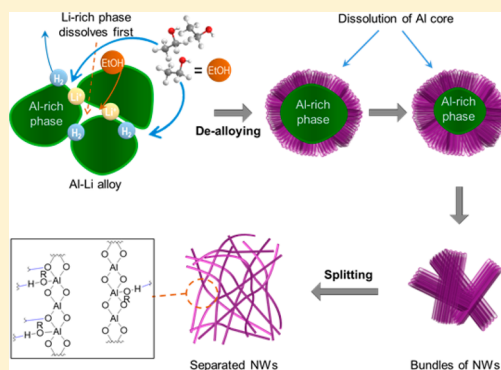
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## S Supporting Information

**ABSTRACT:** Fabrication and applications of lightweight, high load-bearing, thermally stable composite materials would benefit greatly from leveraging the high mechanical strength of ceramic nanowires (NWs) over conventional particles or micrometer-scale fibers. However, conventional synthesis routes to produce NWs are rather expensive. Recently we discovered a novel method to directly convert certain bulk bimetallic alloys to metal–organic NWs at ambient temperature and pressure. This method was demonstrated by a facile transformation of polycrystalline aluminum–lithium (AlLi) alloy particles to aluminum alkoxide NWs, which can be further transformed to mechanically robust aluminum oxide ( $\text{Al}_2\text{O}_3$ ) NWs. However, the transformation mechanisms have not been clearly understood. Here, we conducted advanced materials characterization (via electron microscopy and nuclear magnetic resonance spectroscopies) and chemo-mechanical modeling to elucidate key physical and chemical mechanisms responsible for NWs formation. We further demonstrated that the content of Li metal in the AlLi alloy could be reduced to about 4 wt % without compromising the success of the NWs synthesis. This new mechanistic understanding may open new avenues for large-scale, low-cost manufacturing of NWs and nanofibers for a broad range of composites and flexible ceramic membranes.



## INTRODUCTION

One dimensional (1D) ceramic nanowires (NWs) exhibit ultrahigh stiffness and strength.<sup>1,2</sup> When used as a reinforcement filler, 1D ceramic NWs can significantly improve the load-bearing characteristics of epoxy, metal, glass, and polymer composites.<sup>3–5</sup> However, most conventional synthesis methods of ceramic NWs have proved to be difficult and not appropriate for low-cost industrial scale production.<sup>6,7</sup> The only example of a commercially successful 1D nanomaterial is carbon nanotubes (CNTs), which is already manufactured in quantities of several thousand metric tons per year at a price of 100–10 000 USD kg<sup>−1</sup> (USD: United States dollars).<sup>8</sup> The high price of ceramic NWs is related to the use of expensive synthesis tools and precursors, corrosive and dangerous chemicals, and small throughput (mass of NWs produced in the reactors per unit reactor volume per unit time) using conventional techniques, such as various template-assisted approaches, chemical vapor deposition, and electrospinning.<sup>9–11</sup>

Recently, we discovered a novel method to directly convert certain bulk bimetallic alloys to metal–organic NWs at ambient temperature and pressure. By immersing bulk AlLi (1:1) alloy in suitable anhydrous alcohols (ethanol, iso-

propanol, or *tert*-butanol) at near room temperatures, we produced 10–100  $\mu\text{m}$  long Al alkoxide NWs which could be easily converted into ceramic oxide NWs by heating in air.<sup>12</sup> This transformation of alkoxide to ceramic oxide NWs is based on the fact that most metal–organic compounds (including alkoxides) feature strong bonds between metal and organic ligands (e.g., OR, NR<sub>2</sub>) and can be used as precursors for synthesis of various ceramic materials with controlled shape and dimensions.<sup>13,14</sup> This is because of the covalent bonding maintained in various substitution, oxidation, or hydrolysis reaction pathways accompanying metal–organic to ceramic transformations.<sup>15</sup> The simplicity of our method and the flexibility to control the NWs dimensions by the synthesis conditions and size of AlLi alloy grains are more advantageous than other reported procedures of NWs synthesis.<sup>12</sup> The demonstrated ability to fabricate thermally stable all-ceramic flexible nonwoven/paper separators based on produced  $\text{Al}_2\text{O}_3$  NWs and their outstanding performance in battery applications highlighted great potential for the new processing method for

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NWs.<sup>12</sup> However, a fundamental understanding of metal–organic NWs formation and growth mechanism is lacking.

In this work, we conducted a combined experimental and modeling study to understand the key physical and chemical mechanisms that govern the formation and growth of aluminum alkoxide NWs. In particular, solid-state nuclear magnetic resonance (NMR) spectroscopy revealed the evolution of molecular structures in the intermediate and final reaction products. These NMR results highlight the pivotal role of Al in the formation of polymeric chains from the alkoxide monomer units, leading to the production of aluminum alkoxide NWs as polymeric chain bundles. By using phase-field and finite-element simulations, we further demonstrated that the NW size (i.e., diameter) is critically controlled by strain misfit at the reaction interface between the alloy particle surface and the base of growing NWs. Based on the new mechanistic understanding, we were able to substantially reduce the Li content in the  $\text{Li}_x\text{Al}_{1-x}$  alloys used for NWs synthesis, which may lead to a marked cost reduction for large-scale fabrication of the NWs. This work advances our mechanistic understanding of large-scale, low-cost conversion of bulk alloys into metal–organic NWs.

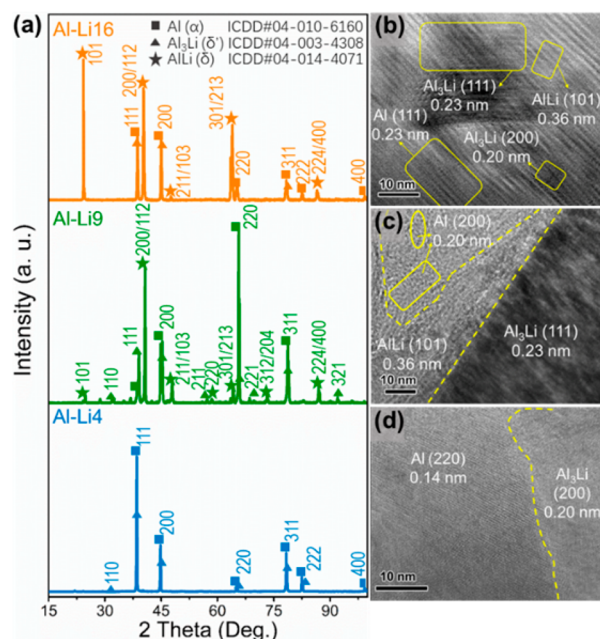
## RESULTS AND DISCUSSION

Similar to the previously described synthesis protocol,<sup>12</sup> pieces of the AlLi alloys were exposed to anhydrous ethanol, which resulted in the alloy delithiation. The Li component of the alloy reacts with alcohols, thus forming highly soluble Li alkoxides, which dissolve from the surface of AlLi alloys. Note that in spite of Al having a low oxidation potential (−1.6 V vs SHE) the reaction of pure Al with ethanol does not proceed unless a catalyst (an activator), such as iodine,<sup>16</sup> amalgam of Al,<sup>17</sup> or a mercury salt,<sup>18</sup> is used to prevent Al passivation.<sup>19,20</sup> However, upon the Li dissolution from AlLi alloy particles, the unsaturated bonds in the remaining Al were found to be sufficiently reactive to induce formation of polymeric Al ethoxide, while the continuous Li dissolution and the associated volume changes and accompanying atomic rearrangement evidently prevented passivation of the Al surface. In our previous study,<sup>12</sup>  $\beta$ -AlLi ( $\delta$  phase with Li content of  $\sim 50$  atom % or  $\sim 20$  wt %) was used. Here we systematically analyzed the alloy phases having a lower content of Li to understand the role of Li in the NWs formation. We chose AlLi alloys with 16, 9, and 4 wt % Li, which we labeled Al–Li16, Al–Li9, and Al–Li4 alloys, respectively.

The composition of the synthesized alloys was predicted in accordance with the Al–Li phase diagram,<sup>21</sup> and confirmed by X-ray diffraction (XRD) analyses. The assignment of corresponding peaks, which are respectively associated with  $\delta$  ( $\beta$ -AlLi),  $\delta'$  ( $\text{Al}_3\text{Li}$ ), and  $\alpha$  (fcc Al-rich) phases, is shown in Figure 1a.

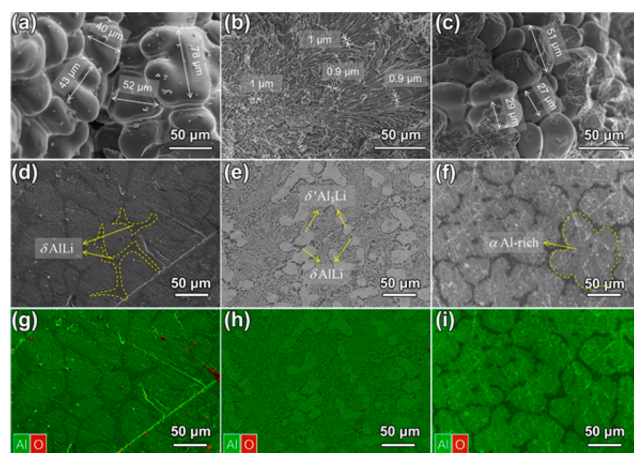
In the Al–Li16 the  $\alpha$  and  $\delta$  phases are dominant, whereas Al–Li9 can be characterized as a mixture of  $\alpha$ ,  $\delta'$ , and  $\delta$  phases (with a small fraction of the  $\delta'$ ). In the Al–Li4 alloy the  $\alpha$  phase dominates as expected due to a small Li fraction in the Al–Li4 sample. High-resolution transmission electron microscopy (TEM) studies with different magnifications have also revealed the crystallographic spacing expected for the presence of  $\alpha$ ,  $\delta'$ , and  $\delta$  phases in the corresponding Al–Li16, Al–Li9, and Al–Li4 alloys (Figures 1b–d and S10).

It was previously proposed that the alloy grain size could critically control the maximum length of the NWs.<sup>12</sup> Here we conducted careful analysis of the grain size of each studied



**Figure 1.** Crystallographic characterization of Al–Li alloy produced with different Li content (16, 9, and 4 wt %): (a) XRD; (b–d) selected TEM micrographs of the Al–Li16, Al–Li9, and Al–Li4 samples.

alloy sample. The scanning electron microscopy (SEM) analyses of both the top surface (Figure 2a–c) and the



**Figure 2.** Morphology of Al–Li alloy produced with different Li content: (a–c) SEM image of grains of Al–Li16, Al–Li9, and Al–Li4 alloy; (d–f) SEM image of cross section of Al–Li16, Al–Li9, and Al–Li4 alloy and (g–i) EDS Al and O mapping of the regions shown above.

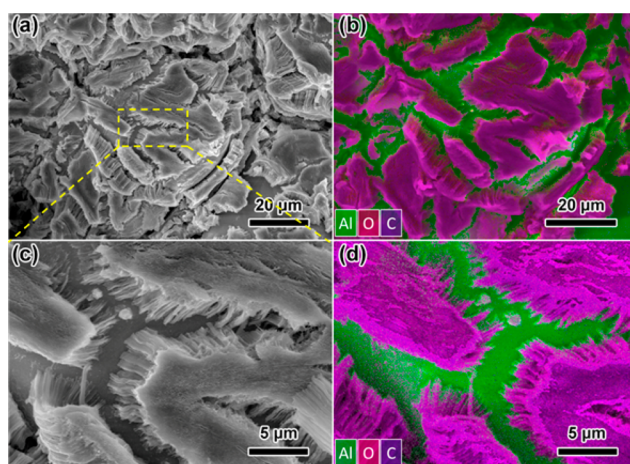
polished cross sections (Figure 2d–f) of the produced alloy samples revealed the presence of well-defined grains with grain boundaries clearly visible in all three cases. Because back-scattered electrons (which are sensitive to the atomic number of the elements, 3 for Li, 8 for O, and 13 for Al) contribute to the SEM images, the darker area in the cross-sectional images correspond to Li-rich regions (e.g.,  $\text{Li}_2\text{O}$  formed upon surface oxidation of AlLi or other grains or  $\delta'$   $\text{Al}_3\text{Li}$  vs  $\delta$  AlLi or  $\delta'$   $\text{Al}_3\text{Li}$  vs  $\alpha$  Al-rich, depending on the sample composition). Chemical mapping of Al conducted using energy dispersive X-ray spectroscopy (EDS) provides complementary information

about the Al-rich regions in the samples (compare Figure 2d–f with g–i). Interestingly, both Al–Li16 and Al–Li4 alloys exhibited large (40–100  $\mu\text{m}$  in diameter) ellipsoidal-shaped grains of presumably  $\delta$  AlLi (darker, Figure 2d) and  $\alpha$  Al-rich (lighter, Figure 2f) compositions, respectively. The depth-dependent X-ray photoelectron spectrometry (XPS) spectra of the as-synthesized Al–Li alloy samples demonstrated higher Li content on the grain surfaces and thus confirmed the presence of Li-rich phases (such as  $\delta$  AlLi or  $\delta'$  Al<sub>3</sub>Li) (Figure S9) at grain boundary regions (Figure 2). With etching time increasing, Al-rich phases become exposed to beam gradually (Figure S9).

Such a microstructure may result from homogeneous nucleation and growth of crystallographic grains from the melt upon cooling. At the same time, the Al–Li9 alloy showed a mixture of smaller (20–50  $\mu\text{m}$ ) ellipsoidal grains and regions of elongated (0.9–1  $\mu\text{m}$  in width and up to 100  $\mu\text{m}$  in length) grains, likely formed upon spinodal decomposition<sup>22</sup> and the formation of crystalline  $\delta'$  Al<sub>3</sub>Li precipitates (lighter regions in Figure 2e and h) in a more disordered (as in Figure 1c)  $\delta$  AlLi alloy matrix (darker regions in Figure 2e and h), as previously demonstrated in Al–Li alloys of similar compositions.<sup>22,23</sup> By comparing the SEM samples (transferred from a sealed container to the SEM chamber within seconds, Figure 2) with the Al–Li alloy samples intentionally exposed to air overnight (Figure S11) we conclude that the SEM images of both the top surface and the polished cross sections of the produced alloy samples (Figure 2) are representative and reliable.

Exposure of all these alloy samples to ethanol resulted in their eventual conversion to Al ethoxide metal–organic NWs. However, a significant difference was noticed in the reaction rates, which monotonically decreased with the reduction in the Li content. While large (3–5 mm+) pieces of Al–Li16 samples completely converted to the NWs bundles in 24 h, the reaction of similar sized Al–Li9 slows down to 6–7 days and in the case of Al–Li4 alloy to nearly 15 days at room temperature. When Li fraction in the alloy decreased to 2 wt % or below, delithiation ceased completely and no NWs could be detected within 2 weeks. According to the Al–Li phase diagram<sup>21</sup> the maximum solubility of Li in  $\alpha$  (fcc Al-rich) phase is approximately 4 wt %. This means that upon rapid cooling of an Al–Li melt, a pure  $\alpha$  (fcc Al-rich) solid phase likely forms with no Li-rich phases (such as  $\delta$  AlLi or  $\delta'$  Al<sub>3</sub>Li) remaining in the grain boundary regions if the amount of Li is significantly below 4 wt %. The absence of such Li-rich phases in the grain boundary is likely responsible for the extremely low reactivity of the alloys.

**Multistage Reactions.** During stage I of the dealloying reaction (1–5 min), the alcohol molecules preferentially react with the Li-rich grain boundaries, forming short ( $\sim 1$   $\mu\text{m}$ ) NWs which separate grains from each other (Figures S1 and S2). During the next 15 min, ethanol initiates reactions with Al-rich phases and the length of the NWs increases (to  $\sim 5$ –10  $\mu\text{m}$ ), as seen in SEM micrographs and corresponding EDS mappings (Figure 3). The bundles (purple color in EDS maps) are homogeneously formed around the Al-rich core. The cracks on the surface seen in Figure 3a, b are likely caused by the “mud cracks” phenomenon when ethanol evaporates from the top alkoxide layer inducing its shrinkage. When the related strain becomes too large to be elastically accommodated by very weakly bonded nanowires, crack form in the dried-up surface to relieve strain. The drying process also causes slight

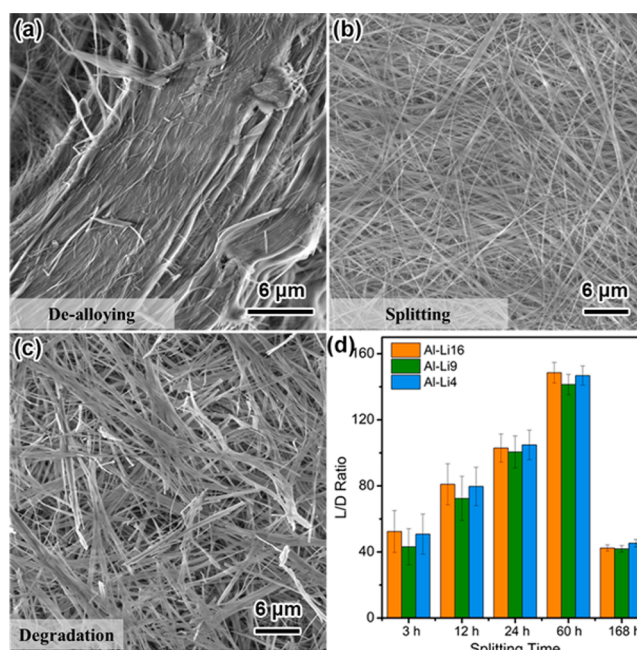


**Figure 3.** Evolution of the NWs growth. (a) low and (c) high magnification SEM images of grains of Al–Li16 alloy treated with ethanol for 10–20 min; (b) and (d) corresponding EDS Al, O, and C mappings of the regions shown beside.

detachment of the NWs bundles from the surface of the grain. However, we believe that in the solution the bundles homogeneously cover the grains.

The formation of a visible protective layer on top of NWs bundles is indicative of the inward growth of the NWs from the surface to the core of the grain. No other species apart from the NWs bundles are seen, which is characteristic of the unique conversion of Al–Li alloy to the NWs.

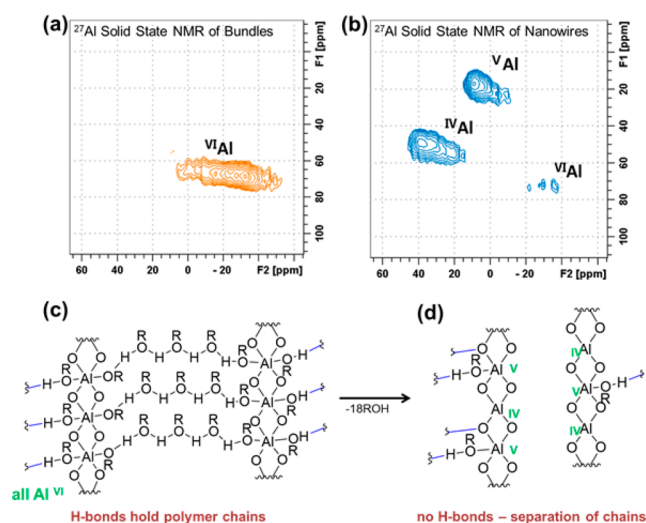
After the treatment in ethanol at 25  $^{\circ}\text{C}$  and drying, no separated NWs could be detected even after the completion of the dealloying reaction. The produced ethoxide structures remain in the form of large bundles (Figure 4a), where individual NWs branches are distributed. Simple sonication



**Figure 4.** Morphology of (a) NWs bundles; (b) separated NWs after 60 h treatment of the bundles in ethanol; (c) degraded NWs formed after treatment in ethanol for 168 h; (d) length/diameter (L/D) ratio of the NWs versus reaction time of NWs bundles with ethanol.

cannot exfoliate bundles into individual NWs. However, a large number of individual NWs together with a few much smaller diameter bundles (50–200 nm) can be prepared upon subsequent treatment of the decanted bundles in fresh ethanol (preferably at a slightly elevated temperature of 60 °C for faster separation). The separated NWs formed upon the subsequent interaction of larger bundles with ethanol (stage II of splitting) are shown in Figure 4b. Note that the starting bundles should be washed by fresh ethanol to completely remove Li ethoxide prior to this stage. Interestingly, overexposure of the samples to ethanol (in our example beyond 60 h of reaction with ethanol at 60 °C) induces degradation of the separated NWs, which break into shorter pieces and start refusing together (stage III of degradation, Figure 4c). The EDS line scans across the NWs are shown in Figure S12. From the SEM micrographs, we estimated the average aspect ratio of the NW bundles as a function of the treatment time in ethanol (Figure 4d). The error bars in Figure 4d show standard deviations observed in our measurements. Independent of the original alloys, the “optimal” time for the splitting of NW bundles in ethanol was ~60 h (~3 days).

**NMR and TGA Studies.** We used  $^{27}\text{Al}$  magic-angle spinning (MAS) solid-state NMR and  $^1\text{H}/^{13}\text{C}$  solution NMR spectroscopy to gain insights into the chemical transformations as bundles gradually transformed to separated NWs and finally to degraded NWs. These NMR studies were particularly useful for understanding how aluminum ethoxide polymer networks form and evolve. The  $^{27}\text{Al}$  MAS solid-state NMR revealed that, in the bundles, the Al atoms are largely present in the six-coordinated state ( $\text{Al}^{\text{VI}}$ ) with a very characteristic isotropic chemical shift at  $-40$  to  $0$  ppm (Figure 5a).<sup>24</sup> The formation



**Figure 5.**  $^{27}\text{Al}$  MAS NMR of the NWs bundles (a) and separated NWs (b). Proposed chemical structures of the NWs bundles (c) and separated NWs (d), according to the NMR and TGA observations. The degradation pathways of six-coordinated Al atoms with tightly packed ethoxide groups leads to the less hindered four- and five-coordinated Al atoms.

of the six-coordinated Al atoms has been commonly observed in many polymerized metal alkoxides,<sup>25,26</sup> where strong bridging bonds between Al and oxygen donors (e.g., ROH, RO, O) are formed and serve as stable building blocks for polymer chains.<sup>27</sup>

The TGA revealed significantly higher weight losses of bundles upon their conversion to  $\text{Al}_2\text{O}_3$  as compared to the weight losses of separated NWs (Figure S3). Specifically, we estimate that the molar ratio of EtOH to Al atoms changes from nearly 6.2 to 1 in the case of bundles to 0.4 to 1 in the case of separated NWs, respectively (see description to Figure S3; note that the ratio of EtO to Al is 3 to 1 in case of monomeric  $\text{Al}(\text{EtO})_3$ ). The intermediate sample between the NWs and bundles (3h splitting in ethanol at 60 °C) showed intermediate content of the carbon-based groups, as expected for the gradual transformation of bundles to NWs.

The  $^{13}\text{C}$  NMR spectrum of the bundles is characterized by multiple resonances (Figure S4). Such complexity of the  $^{13}\text{C}$  NMR of the bundles indicates a hindered environment around the Al atoms. Similar to the steric hindrance in polyethylene glycol,<sup>28</sup> the hindered Et groups in bundles, although being chemically equivalent, are not equivalent in NMR due to the limited degree of freedom. The precise assignment of all the peaks in  $^{13}\text{C}$  NMR is challenging and beyond the scope of this work. Analogous to the  $^{13}\text{C}$  NMR spectrum, multiple complex resonances are seen in  $^1\text{H}$  NMR (Figure S5). Based on the analysis of integral intensity of OH groups in the  $^1\text{H}$  NMR and TGA, we conclude the presence of a large amount of ethanol which is in accordance with the TGA of the bundles.

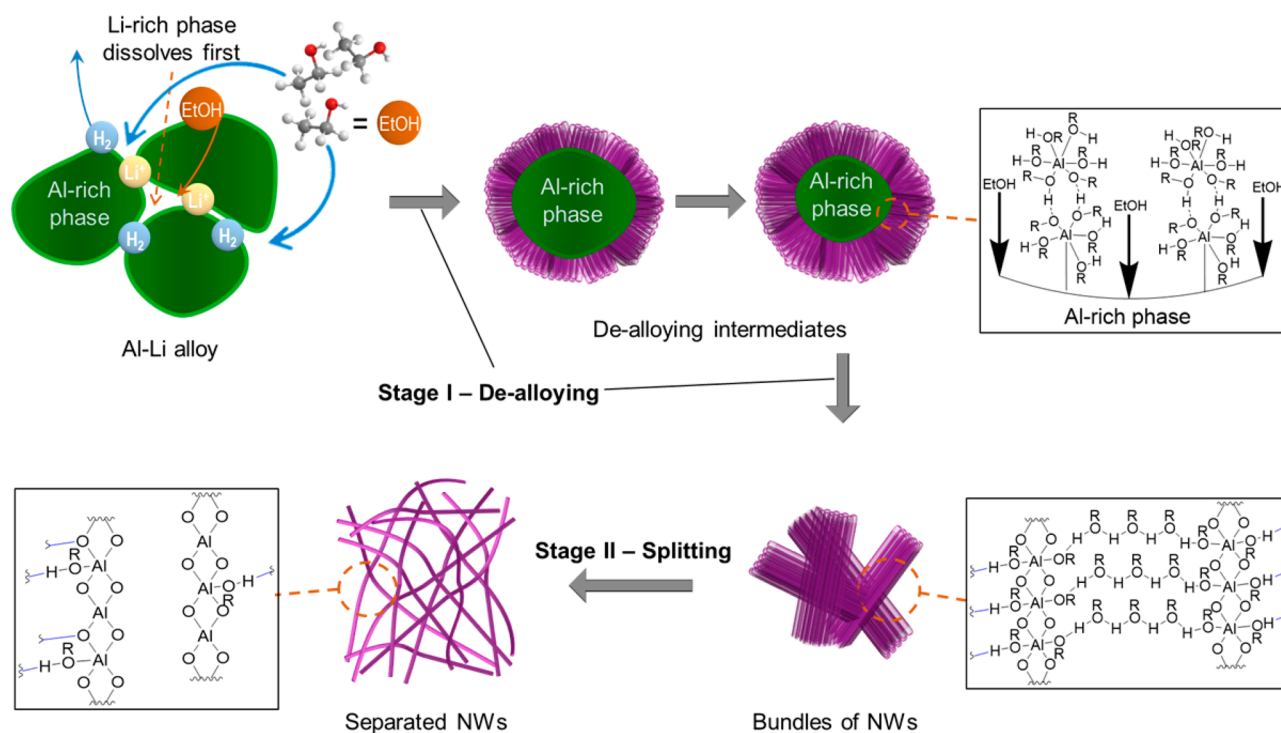
Based on the TGA and NMR results we can assume that the main building block of NWs involve O atoms ( $\mu\text{-O}$ ) and ROH groups which are linked to  $\text{Al}^{\text{VI}}$  (Figure 5c). Per our calculations of EtOH ratio per 1 mol of Al, we expect that 4 to 5 EtOH molecules can participate in the H-bonding between the polymer chains per 1 Al atom (Figure 5c). The Al atoms in the mostly individualized Al alkoxide NWs (60 h splitting, Figure 4b) exhibit mainly coordination numbers of four and five ( $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{V}}$ ), while the presence of  $\text{Al}^{\text{VI}}$  is almost negligible. Since  $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{V}}$  are formed from  $\text{Al}^{\text{VI}}$  and the content of ethanol significantly reduces, we propose that interlinks are lost between the polymer chains (Figure 5c,d). The presence of  $\text{Al}^{\text{V}}$  suggests that H-bonding is still present since one of the oxygen containing groups does not form a bridge and can still participate in the intermolecular H-bonds, linking chains into NWs (no H-bonds between the chains would result in pure  $\text{Al}^{\text{IV}}$ ).

The  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra of the separated NWs support our assumption that the result of the disproportionation is a less hindered environment for Al atoms (Figures S6 and S7).

According to the above analysis of NMR and TGA results, the formation of individual NWs from bundles can be related to their shrinkage accompanied by the disproportionation of octahedral Al alkoxides to the simpler tetrahedral and 5-vertex polyhedra Al atoms.<sup>24,29,30</sup> The majority of H-bonded ethanol molecules are lost during the disproportionation reactions. Figure 5c,d shows the schematic illustration of changes of chemical composition in the corresponding NWs structures. Here we use just two representative polymer chains (perfectly straight for simplicity) in bundles and separated NWs to explain how the coordination number of Al as well as the functional moieties change during stage II of splitting. The key process involves the desaturation of 6-coordinated Al to a lower coordination number Al atom, loss of ethanol associates and H-bonding.

Additionally, we utilized the  $^{27}\text{Al}$  MAS NMR to track changes in the coordination number of Al that take place during overexposure of NWs in ethanol at 60 °C (Figure 3d).

**Scheme 1. Schematic Representation and Molecular Mechanism of the Formation of Polymer Ethoxide NWs as a Result of Exposure of the Al–Li Alloys to Anhydrous Ethanol<sup>a</sup>**



<sup>a</sup>For simplicity, individual NWs are represented by single chains.

The results indicate that degraded NWs exhibit only Al<sup>VI</sup> (Figure S8), whereas Al<sup>V</sup> is absent. This observation suggests that the presence of Al<sup>V</sup> is critical for maintaining bridges between individual chains, so as to keep structural integrity and adequate mechanical properties of the NWs.

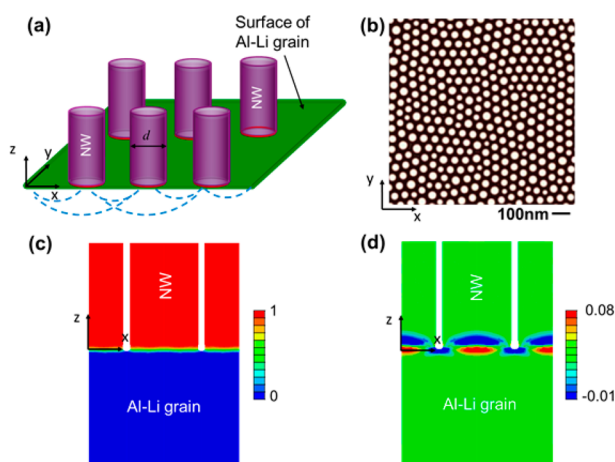
**Molecular Mechanisms of NW Formation.** Scheme 1 shows an expanded molecular model depicting the critical stages of NW formation upon exposure of AlLi alloys to anhydrous ethanol based on the SEM, EDS, NMR, and TGA studies discussed above. During stage I of dealloying, exposure of the pellet results in the diffusion of ethanol molecules into Li-rich grain boundaries. Fresh Al is activated to react with ethanol whereas the continuous supply of Al atoms from the bulk grain toward the surface results in the formation of bundles consisting of interconnected long polymer chains. The formation of polymer chains is highly dependent on the ability of the oxygen-donor atoms to form stable bonds with Al.<sup>30</sup> Initially, the fresh Al at the surface of the alloy reacts with ethanol to form the mononuclear complex of Al with EtOH groups, the immediate association of which with subsequent Al monomer occurs through the formation of H-bonds. The latter disproportionate with the formation of bridging O atoms, whereas the remaining EtOH groups remain linked with Al. More of the surface Al atoms react with the ethanol supplying more Al<sup>VI</sup>, whereas EtOH groups serve as a source of H-bonds to the side polymer chains. The presence of multiple H-bonds between the polymer chain results in strong interlinkages between the polymer chains. During stage II of splitting, reactions at elevated temperatures (60 °C) break Al–O bonds at the octahedral vertices with the release of ethanol molecules and split of bundles into much thinner separated NWs.

In spite of very low solubility of Al ethoxide in ethanol,<sup>31</sup> it is also possible that a portion of Al atoms are escaping the

polymerization sites in the form of soluble (e.g., Al(OEt)<sub>4</sub><sup>−</sup> or Al(OEt)<sub>6</sub><sup>−</sup>) anions because according to our estimations the yield of the alkoxide NWs in the reaction between the Al–Li16 alloy and ethanol is 60–70 wt %. Such losses, however, could possibly be reduced by fine-tuning the reaction/polymerization conditions.

The final length of the NWs is controlled by the number of Al atoms in the Al–Li alloy grain and thus the grain diameter, while the diameter of the NWs is controlled by the chemomechanical effects, which are studied by computational modeling described below.

**Chemomechanical Modeling of NW Formation.** To understand the chemomechanical effects on the transformation of AlLi alloys to NWs, we developed computational models to study the formation of NW arrays as well as the associated stress generation in NWs. Figure 6a shows a schematic illustration of the chemomechanical effects that arise during NW formation from the surface of individual grains. At a typical instance of the formation process, AlLi alloy grains are considered as a large substrate covered with an array of vertically aligned NWs. The interface reactions and resulting interface stresses dictate the mean diameter *d* of the NWs. Specifically, upon conversion of the alloy into ethoxide, there is a significant volume expansion and the associated mismatch strains between the NW and substrate. Such mismatch strains and resultant interface stresses elastically strain the substrate. More importantly, the elastic strain/stress fields generated from different NWs interact with each other within the substrate. As a result, the specific elastic energy in the substrate (measured in terms of per unit interface area) depends on the NW diameter and thus the spacing between adjacent NWs. On the other hand, the specific surface energy of NWs (per unit interface area) also depends on the diameter of NWs. The



**Figure 6.** Computational modeling of formation of a NW array from an AlLi alloy grain. (a) Schematic illustration of the physical factors controlling NW formation. The green plane indicates the interface between the NW and the AlLi alloy substrate and the blue dashed lines indicate the elastic interactions among NWs through the alloy substrate. (b) Phase-field simulation snapshot showing the formation of a NW array with the characteristic NW diameter  $d$  on the surface of the AlLi alloy substrate (corresponding to the  $x$ – $y$  plane in (a)). The normalized concentration field  $C(x, y, t)$  (varying between 0 and 1) is defined on the surface, such that a fully formed NW phase corresponds to  $C = 1$  (colored in white) and the phase between NWs corresponds to  $C = 0$  (in black). Chemo-mechanical finite element simulation snapshots show the distribution of (c) the normalized concentration field  $C(x, y, t)$  and (d) the associated stress component of  $\sigma_{xx}$  normalized by Young's modulus.

energy minimization requirement on the system dictates the mean diameter of NWs formed through balances between the specific strain energy (which decreases with decreasing NW diameter) and the specific surface energy of NWs (which increases with decreasing NW diameter). Considering the above energy competition, a scaling analysis can be performed to derive the characteristic NW diameter  $d$  as

$$d \sim E\gamma_s/\phi^2$$

where  $E$  is the effective elastic modulus of the substrate and NWs,  $\gamma_s$  is the surface energy of NWs, and  $\phi$  is the reaction-induced interface stress. This scaling relation highlights the key physical effects and parameters that control the NW diameter, and it will be used to guide our numerical simulations.

Figure 6b–d shows the computational modeling results at the NW array and individual NW levels, respectively. As shown in Figure 6b, a simplified two-dimensional (2D) phase-field model is developed to simulate the formation of a NW array on the surface of the alloy substrate. Here a normalized concentration field  $C(x, y, t)$  (varying between 0 and 1) is defined on the substrate surface as a function of time  $t$ . The distributed concentration field  $C(x, y, t)$  generates the interface stress, which is modeled separately by a chemo-mechanical finite element model as shown in Figure 6c,d. In the 2D phase-field model, the interface stress is considered to produce elastic stress and strain fields in the substrate, which can be solved using the elastic solution in a half-space due to a tangential point force acting on the surface by Cerruti, in conjunction with a linear superposition scheme that gives the resultant elastic field due to the distributed interface/surface stress on the surface.<sup>32,33</sup> Meanwhile, the gradient of the nonuniform concentration field represents the effective surface energy of

NWs. The phase-field simulation dynamically evolves the concentration field  $C(x, y, t)$  to minimize the sum of strain energy and surface energy. The final equilibrium state of  $C(x, y, t)$  from the phase-field simulation determines the characteristic diameter of the NWs. The details of the phase field model and parameters are described in the Supporting Information. As shown in Figure 6b, the average diameter of the simulated NWs is around 45 nm, consistent with experimental results.

At the individual NW level and for a given NW diameter, the interface stress induced by the transformation reaction is studied using a chemo-mechanical finite element model (see Experimental Section), as shown in Figure 6c,d. Here we simulate the concurrent processes of reaction associated with the addition of ethanol as well as the resultant stress generation near the reaction front. Figure 6c shows the simulation snapshot of the concentration field near the reaction front and Figure 6d shows the resulting stress field. Here the sharp reaction front naturally enforced the anisotropic volume expansion associated with ethanol insertion along the longitudinal direction of NWs,<sup>34</sup> so as to reduce the strain mismatch across the reaction interface; in addition, the weak bonding between neighboring NWs through ROH groups are neglected, such that the side faces of NWs are assumed to be traction free to a first approximation. The simulated nonuniform stress distribution near the reaction front in Figure 6d represents the effective interface stress  $\phi$  in the phase-field model that controls the selection of the NW diameter as shown in Figure 6b. Hence, these computational modeling results support the earlier analysis of chemomechanical effects on the interface reactions and resulting interface stresses that dictate the mean diameter of the NWs formed.

## CONCLUSIONS

We demonstrated the transformation mechanism of bulk Al–Li alloy to metal–organic Al alkoxide NWs. This transformation has several stages. During stage I (dealloying), the ethanol solvent molecules first etch through the Li-rich grain boundaries in the AlLi alloy forming soluble Li ethoxides. Consequently, the ethanol reacts with the surface of each grain, forming Al ethoxides in the shape of the NWs, whose growth is directed toward the center of each grain. Therefore, the length of the NWs is proportional to the length of the AlLi alloy grains. The dealloying stage is seen throughout the AlLi alloy with as little as 4 wt % Li in the alloy. The NWs initially form tightly linked bundles, which could be transformed into individually separated NWs by simply heating them in ethanol (stage II, the splitting process). This process changes the coordination number of Al atoms from VI to V and IV, triggers the release of ethanol molecules and leads to the eventual disappearance of H-bonds that hold Al ethoxide chains. The computational modeling at the interface between NWs and the alloy substrate reveals the influence of stresses in controlling the diameter of NWs.

## EXPERIMENTAL SECTION

**Materials.** Lithium foil (battery grade, 0.75 mm, Sigma-Aldrich), aluminum pellets (3–12 mm, 99.99% trace metals basis, Sigma-Aldrich), and ethyl alcohol (pure, 200 proof, anhydrous,  $\geq 99.5\%$ , Sigma-Aldrich).

**Synthesis of Al–Li Alloy.** Three different Al–Li alloys were synthesized following our previous strategy.<sup>12</sup> In particular, Al and Li were rapidly heated to 750 °C ( $\sim 895$  °C/min) in a graphite crucible with an induction heater. The heating was stopped once temperature

reached 750 °C, and the samples were allowed to cool in Ar (cooling rate of ~150 °C/min).

**Synthesis of Al Alkoxide Bundles.** An alloy pellet was placed in 30 mL of anhydrous ethanol for different time (ca. 24 h for Al–Li16, ca. 150 h for Al–Li9, and ca. 340 h for Al–Li4) without stirring/agitation. After initial reaction, the pellet transformed into soluble Li alkoxides and white Al alkoxide precipitate. Then, the delithiated sample was washed with an extra 20 mL of anhydrous solvent at least three times to remove soluble Li alkoxides. Subsequently, white Al alkoxide bundles were immersed into 15 mL of anhydrous ethyl alcohol.

**Synthesis of Al Alkoxide NWs.** Al alkoxide NWs were prepared by heating Al alkoxide bundles immersed in dry ethanol up to 60 °C. After 60 h, the bundles were completely converted into the nanowires under argon protection.

**Characterization.** Scanning electron microscopy (SEM) images were obtained using a Hitachi SU8230 SEM instrument equipped with an Oxford Instruments Aztec Energy EDX system. Transmission electron microscopy (TEM) images were recorded on a JEOL TEM 4000EX instrument (JEOL, Japan) operating at 300 kV. Powder X-ray measurements were performed by using a PANalytical Empyrean XRD system with Cu K $\alpha$  radiation to identify the crystalline phase of the composite. Thermogravimetric analysis (TGA) was conducted on a TGA Q600 analyzer (TA Instruments) under air atmosphere at a heating rate of 5 °C·min<sup>-1</sup>. Solid-state 2D 3QMAS <sup>27</sup>Al NMR was recorded at 25 °C with spinning 12 kHz on a 400 MHz Bruker Avance III spectrometer. <sup>1</sup>H and <sup>13</sup>C spectra were acquired on a Bruker 700 spectrometer in CDCl<sub>3</sub>. The depth-dependent chemical composition was characterized via X-ray photoelectron spectrometry (XPS, Kratos Analytical Ltd.), and the etching was conducted with 90 s at 3000 eV.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b06261.

SEM images of grains of Al–Li16 alloy treated with ethanol for 1–5 min; SEM image of Al–Li16 alloy treated with ethanol for 10 min; TGA of the splitting process; 700 MHz <sup>13</sup>C NMR of the bundles in CDCl<sub>3</sub>; 400 MHz <sup>1</sup>H NMR of the bundles in CDCl<sub>3</sub>; 700 MHz <sup>13</sup>C NMR of the NWs in CDCl<sub>3</sub>; 700 MHz <sup>1</sup>H NMR of the NWs in CDCl<sub>3</sub>; <sup>27</sup>Al MAS NMR of the degraded NWs; comprehensive description of the modeling method; distribution of Li and Al in different Li content alloys: the depth-dependent XPS analysis of Al–Li16, Al–Li9, and Al–Li4 samples; TEM micrographs of Al–Li alloy produced with different Li content; TEM images of Al–Li16, Al–Li9, and Al–Li4 alloy samples; morphology of Al–Li16 alloy exposed to air overnight; line-scan EDS analysis across representative Al ethoxide NWs (PDF)

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### Notes

The authors declare no competing financial interest.

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