ENERGY

www.advenergymat.de

Taming Metal–Solid Electrolyte Interface Instability via Metal Strain Hardening

Lihong Zhao, Wei Li, Chaoshan Wu, Qing Ai, Liqun Guo, Zhaoyang Chen, Jie Zheng, Matthew Anderson, Hua Guo, Jun Lou, Yanliang Liang, Zheng Fan, Juner Zhu, and Yan Yao*

Solid-state lithium metal batteries have emerged as a promising technology for electric vehicles due to their high specific energy and safety potential. Obtaining intimate contact between Li and electrolyte during cell fabrication, however, remains challenging. Adequate fabrication pressure is required to promote close contact, but this pressure can cause Li deformation and penetration into the electrolyte, resulting in poor battery performance. Here, a strategy for addressing this problem is presented by incorporating 3 at% Mg into Li. Unlike pure Li which obeys the Voce hardening law and allows unconstrained deformation, Li—Mg alloy follows the Swift hardening law and strengthens with strain under compression stress. Because of the constrained deformation of Li—Mg, intimate contact with solid electrolytes is possible even at high fabrication pressure (50–65 MPa), resulting in high critical current densities. These findings underscore the importance of understanding Li metal deformation properties to improve solid-state battery performance.

1. Introduction

The demand for high-energy and high-power batteries is everincreasing in consumer electronics and electric vehicles.^[1]

L. Zhao, L. Guo, Z. Chen, J. Zheng, M. Anderson, Y. Liang, Y. Yao Department of Electrical and Computer Engineering and Texas Center for Superconductivity at the University of Houston University of Houston Houston 77204, TX, USA E-mail: yyao4@uh.edu W. Li, J. Zhu Department of Mechanical and Industrial Engineering Northeastern University Boston 02115, MA, USA C. Wu, L. Guo, Z. Chen, J. Zheng Materials Science and Engineering Program University of Houston Houston 77204, TX, USA Q. Ai, H. Guo, J. Lou Department of Materials Science and Nanoengineering **Rice University** Houston 77005, TX, USA Z. Fan Department of Engineering Technology University of Houston Houston 77204, TX, USA The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aenm.202300679

DOI: 10.1002/aenm.202300679

All-solid-state lithium metal batteries are emerging as a promising alternative to conventional liquid-electrolyte batteries, with the potential for higher specific energy and improved safety.^[2,3] Sulfide-based electrolytes have garnered significant attention due to their high ionic conductivity, comparable to that of liquid electrolytes.^[4,5] Most sulfide electrolytes can be easily processed into films or pellets at room temperature, eliminating the need for energyintensive sintering procedures.^[6,7] Argyrodites, such as Li₆PS₅X (where X is halogen), have recently become popular due to their self-passivating ability at the Li-metal interface, leading to greater kinetic stability during cell operation.^[8,9]

An energy-dense anode, in addition to electrolytes with high conductivity and good processability, is a critical component of solid-state batteries. Lithium (Li) metal is regarded as the ultimate anode material because of its high specific capacity and low potential.^[10,11] Poor interfacial contact between Li metal and the electrolyte, on the other hand, remains a major obstacle to achieving high current densities in solid-state batteries.^[12] This is due to the rough surfaces of the Li metal and electrolyte, which limit the effective contact area at the interface, [13,14] leading to increased local current density and eventual cell failure.^[10] One approach for improving interfacial contact is to apply higher pressure during cell fabrication. For instance, near-zero interface resistance was reported in oxide-based solid-state batteries after isostatic press at 400 MPa.^[15,16] However, it is not possible to apply such high fabrication pressures when using sulfide electrolytes and lithium metal at the same time. Pressure-induced shorting was observed when sulfide electrolyte and Li metal were pressed at 75 MPa or lower pressures.^[17–19] This is due to a combination of electrolyte surface defects,^[18] the low yield strength of Li metal,^[20,21] and the low fracture toughness of sulfide electrolytes.^[22] Therefore, achieving intimate Li-electrolyte contact while avoiding mechanical damage to the electrolyte is a significant challenge.

Several approaches have been proposed to address the challenge of balancing the requirement for high fabrication pressure to ensure intimate interfacial contact between Li and electrolyte while preventing Li from penetration. One strategy is to use appropriate pressurization techniques, such



as short-time, high-pressure fabrication^[18] or long-time, moderate-pressure fabrication,^[19] to reduce contact resistance without short-circuiting the cell. Another option is to use mechanically robust alternative materials. For instance, an electrolyte with a smoother surface and smaller grain size reduces the possibility of Li penetration.^[14] Alternatively, soft Li metal can be replaced with rigid Li intermetallic alloys, which, at the expense of increased anode potential, also inhibit anode penetration into the electrolyte at high fabrication pressure.^[23,24]

A Li solid solution with a similar redox potential to Li metal, such as Li-Mg alloy, has also been investigated as a promising alternative anode material.^[25] In comparison to many metals with limited solubility in Li,^[7,26-28] Mg is a one-of-a-kind element with a high solubility with up to \approx 70 at% in the Li BCC phase,^[28] enabling the Li-Mg alloy to maintain phase stability despite high stripping capacity. After delithiation, Li-Mg alloy showed improved contact with oxide electrolytes.^[29-33] However, no reports of its use in sulfide-based electrolytes have been published, and further research is needed to understand the mechanical properties of Li-Mg alloy and their impact on the metalelectrolyte interface. Both Li and β -phase Li–Mg alloy have the same BCC lattice structure and similar redox potential (0 V and 1 mV vs Li⁺/Li).^[32] The low redox potential facilitates the passivation of argyrodite electrolyte (e.g., Li₆PS₅Cl) with decomposition products such as Li₂S, Li₃P, and LiCl at both metal surfaces.[34]

In this work, we report a method for suppressing metal penetration into the sulfide electrolyte at high fabrication pressures using a commercially available Li—Mg alloy (10 wt% Mg, $Li_{0.97}Mg_{0.03}$) anode. We determined the optimal pressure range for achieving optimal interfacial contact. Our results show that the different strain-hardening properties of Li—Mg alloy versus pure Li play a crucial role in preventing electrolyte penetration, which we validated using tensile and compression tests as well as finite element modeling. As a result, this method enables high-current cycling in solid-state batteries. This method strikes a balance between the need for high pressure to ensure intimate contact between Li and electrolyte and the protection of the electrolyte. Our research highlights the significance of mechanical properties of metal electrodes in solid-state battery processing.

2. Results and Discussion

2.1. Intimate Contact and Electrolyte Integrity at the Same Time

By using Li–Mg alloy instead of pure Li, we achieved intimate metal–electrolyte contact without causing metal penetration into solid electrolytes through surface defects (Figure S1, Supporting Information). To assess the simultaneous interfacial contact and the electrolyte integrity, we used electrochemical impedance spectroscopy (EIS).^[15,18] Figure 1a,b plots the evolution of impedance spectra of symmetric cells with Li and Li–Mg electrodes, and Li₆PS₅Cl (LPSCl) electrolyte with increasing fabrication pressure. Randle's circuit was used to fit the EIS spectra, as illustrated in the inset of Figure 1a and Figure S2, Supporting Information, where R_{bulk} represents the ionic resistance of the electrolyte and R_{int} represents the interface resistance.^[15,17,18,35] Figure 1f summarizes the evolution of R_{int} during the pressurization process, considering two interfaces in symmetric cells. The overall trend is that interfacial resistance decreases as the fabrication pressure increases, as previously observed in studies using garnet electrolytes^[15] and attributed to metal anode plastic deformation. In these studies, R_{int} shows an inverse correlation with external pressure less than 41 MPa.^[13] In our tests with sulfide electrolytes at low pressures (<40 MPa), R_{int} follows $P^{-1.20}$ and $P^{-0.88}$ scaling laws in symmetric cells with Li and Li–Mg, respectively (Figure 1d,e). Above 40 MPa, R_{int} rapidly decreases with $\approx P^{-3}$ scaling, suggesting a different metal deformation mechanism.^[15,20] When the pressure rises above 40 MPa the metal–electrolyte comes into close contact.

Interestingly, we discover that at moderate pressures less than 40 MPa, simply increasing fabrication time is insufficient to achieve close contact. We measured the impedance of a symmetric cell subjected to constant pressure over time. Figure S3, Supporting Information, shows the impedance evolution of a symmetric cell with a Li metal anode at 25 MPa, where there is no decrease in R_{int} over 15 h. After 16 h of stacking pressure, there was Li penetration and cell shorting, as shown by a resistor-like impedance spectrum (green dot in Figure S3, Supporting Information).^[18] During cell fabrication, the plastic deformation of Li metal may involve creep deformation,^[15] which follows a power law, and the overall deformation is influenced by the fabrication time.^[20,21] The negligible change in R_{int} at 25 MPa over time suggests that the contribution of time-dependent factors is minimal at the low-to-moderate pressure. This observation could be attributed to the small aspect ratio (thickness/diameter) of metal foil used in this work (0.007), which hinders creep deformation due to friction at the interfaces.^[21,36]

Higher fabrication pressure improves contact but also increases the risk of electrolyte penetration. Figure 1c reveals a scenario of Li penetration into the electrolyte. As pressure increases, R_{bulk} in symmetric cells decreases rapidly initially, most likely due to the smaller actual contact area caused by the intrinsic roughness of electrode surfaces. Above pressures above 45 MPa, R_{bulk} of the cells with Li-Mg anode remains constant, indicating a close contact with the solid electrolyte layer and a negligible effect on R_{SE}, as measured with a symmetric cell with blocking contact (Figure S4, Supporting Information). These results suggest that an intimate contact is achieved without electrolyte cracking or metal penetration, supporting previous research.^[37] However, at pressures above 65 MPa, Li-Mg displays a tendency to penetrate solid electrolyte, as evidenced by the gradual decrease of R_{bulk}. Nonetheless, using Li–Mg instead of Li establishes a pressure stability window of 50-65 MPa for cell fabrication, where R_{bulk} remains constant and R_{int} can be minimized.

In contrast, R_{bulk} with Li metal falls below R_{SE} at 25 MPa and continues to fall with increasing pressure, which suggests a decrease in effective electrolyte thickness and Li metal penetration into the electrolyte.^[18] This observation could be explained by the hypothesis that Li metal begins to damage electrolyte as early at 25 MPa before intimate contact could be achieved at pressure larger than 50 MPa.

Cross-sectional SEM imaging is used to evaluate the quality of the metal–electrolyte interface and confirm the impedance results discussed earlier. We used an air-free vessel developed by our group to protect the air-sensitive samples. Figure 1g–j shows www.advancedsciencenews.com

CIENCE NEWS



Figure 1. Evolution of symmetric cell impedance and morphology with fabrication pressure. Impedance spectra of a) Li|LPSCI|Li cell and b) Li-Mg|LPSCI|Li-Mg cell at different pressures. The inset shows Randle's circuit of symmetric cell. c) Bulk resistance of symmetric cell at different pressures. The intrinsic electrolyte resistance is measured by carbon|LPSCI|carbon symmetric cell. d-f) Interface resistance of a symmetric cell at different pressures. Logarithmic plot of interface resistance versus fabrication pressure in symmetric cells. Circles highlight to the pressures used to fabricate samples in (g-j). g,h) Li-electrolyte interface shows poor contact at 25 and 50 MPa. i,j) Li-Mg-electrolyte interface shows poor interfacial contact at 25 MPa and good contact without electrolyte penetration at moderately high fabrication pressure (50 MPa). Blue and red in the color bar represent favorable and unfavorable interfaces with respect to different fabrication pressures.

the cross-section of metal-sulfide interfaces prepared at two different fabrication pressures (25 and 50 MPa), corresponding to pressures in Figure 1c,f labeled with circles. These images are representative of the quality of contact (blue: good contact; red: poor contact) and the integrity of electrolyte (blue: no Li penetration; red: Li penetration); we color-coded such properties on the fabrication pressure scale. Figure 1g,h shows that when Li is used, intimate contact and damage-free electrolyte cannot be obtained at any pressure value. In contrast, Li—Mg has a pressure stability window (50–65 MPa) at which simultaneous intimate contact and damage-free electrolyte are possible. This is significant because forming such a contact is required for subsequent cycles of uniform Li plating–stripping.^[38] We attribute the enhanced high-pressure stability of Li–Mg to its different mechanical properties, as shown below.

2.2. Voce and Swift Hardening Laws

Li and Li—Mg exhibit distinct levels of electrolyte penetration during cell fabrication due to their different hardening laws. To understand the deformation and hardening of these two electrodes, tensile tests on dog-bone–shaped samples were performed (**Figure 2**a). Both metals deform elastically at first, as shown by a rapid increase in engineering stress within 1% engineering strain (Figure 2c and Figure S5a,b, Supporting

www.advenergymat.de





Figure 2. Tensile tests of Li and Li–Mg. Dog-bone samples of a) Li and b) Li–Mg before and after the tensile test. c) Engineering stress–strain curve of Li and Li–Mg in tensile test at 1.3×10^{-3} s⁻¹ strain rate. d) Corresponding true stress-plastic strain curve of Li and Li–Mg, calculated based on data in (c) before necking. Experimental data of Li and Li–Mg are fitted with the Voce and Swift hardening laws, respectively.

Information). As strain exceeds the yield point, both metals deform plastically. Based on five samples, the yield strengths ($\sigma_{\text{yield, 0.2\%}}$) of Li and Li—Mg are 0.55 ± 0.03 and 0.8 ± 0.04 MPa, respectively (Figure S5c, Supporting Information). The yield strength of Li is comparable to previous tensile test results.^[20,21,39] Li—Mg shows a 45% increase in yield strength compared to Li due to solid-solution hardening. Because of the low yield strength (<1 MPa), metal anodes can deform plastically during fabrication.

The engineering stress–strain curves of Li and Li—Mg are presented in Figure 2c, with labeled necking and fracture points. In the true stress–true strain curves (Figure 2d), only the stress– strain profile before necking is plotted to ensure that the sample is under a uniaxial tensile state. Li shows elongation without significant hardening after yielding, as evidenced by the increased sample length in Figure 2a and the plastic flow region in Figure 2d and Figure S5a, Supporting Information, where the strain of Li increases without a corresponding increase in stress. On the other hand, Li—Mg exhibits strain hardening, where the true stress increases continuously with plastic strain before necking occurs when tested at the same strain rate.

The difference in the stress–strain curves of Li and Li–Mg can be depicted with different hardening laws.^[40] The Voce hardening law^[41] (Equation (1)) is used to fit the experimental stress– strain curve of Li metal before the necking and predict the mechanical properties at higher strains, where σ is the true stress, ε is the plastic strain, k_0 , Q are constants in the hardening equation, and β is the strain-hardening exponent in the Voce equation.^[40,42] The fitted parameters are listed in Table S1, Supporting Information.

$$\sigma = k_0 + Q \left(1 - \exp\left(-\beta \times \epsilon \right) \right) \tag{1}$$

In contrast, the stress–strain response of Li–Mg follows Swift hardening law^[43] (Equation (2)) which implies a continuous

hardening process, where *A* is the strength coefficient, ε_0 is the equivalent pre-strain, and *n* is the strain-hardening exponent in the Swift equation.^[42]

$$\sigma = A \left(\varepsilon + \varepsilon_0 \right)^n \tag{2}$$

The low yield strength and good ductility of Li metal can be attributed to its low melting point ($T_{\rm m}$ = 453.5 K). Li undergoes simultaneous recovery and recrystallization when deformed at room temperature (298 K, 0.66 Tm). It is unlikely for dislocations to accumulate and entangle, thus allowing unconstrained metal deformation.^[20,21,44-46] In contrast, the introduction of solute atoms (Mg) increases localized stress to initiate dislocation motion and suppresses recovery and recrystallization.^[47] Consequently, the deformation of Li-Mg is constrained, especially at large strains. This explains the differences in the yield strength and hardening behavior between Li and Li-Mg observed in tensile tests. Further increasing the Mg content is expected to increase the yield strength and enhance strain hardening but may decrease its processability as a metal anode. A high yield strength of 77 MPa has been reported for composition Li_{0.34}Mg_{0.66} near its two-phase region,^[48] which supports our finding.

2.3. Constrained Metal Deformation for Li-Mg Alloy

Metal electrodes in solid-state batteries undergo compressive strain during fabrication. Thin metal samples hardly neck or break when compressed, as they do in tensile tests. Instead, factors such as friction at the sample surface and barreling influence compression behavior.^[21] To mimic the fabrication process, high stresses (25 and 50 MPa) were applied to Li and Li–Mg metal films for 2 min. The changes in area and thickness under compression were used to assess the deformation behavior. **Figure 3**a,b shows the optical images, area increase, and

thickness change of Li and Li—Mg disks after compression. The area of Li disks increased by 10% and 20% after compression at 25 and 50 MPa, respectively, whereas, the area of Li—Mg disks increased by 1.5% and 4.0%.

Li and Li—Mg behave differently under compressive stress against a solid electrolyte. The deformation of Li is governed by Voce hardening law,^[40] allowing for unconstrained plastic flow into cracks and surface defects in the sulfide electrolyte, resulting in the formation of a Li-in-electrolyte microstructure that serves as a precursor for further crack propagation.^[22,49] Conversely, the Swift hardening law governs the deformation of Li—Mg, which hinders further deformation and limits the development of a metal-in-electrolyte structure.

Figure 3c,d models the behavior of Li and Li-Mg under pressure using the finite element analysis (FEA) based on their respective hardening laws and parameters obtained from the tensile tests in Table S1, Supporting Information. The model considers a 1 µm elliptical hole on the electrolyte surface, as shown in Figure S1, Supporting Information, and depicts metal deformation into electrolyte surface defects. We used two common assumptions in metal deformation modeling: 1) the compressive behavior and tensile behavior of Li metal are symmetric (no Bauchinger effect) and 2) the hardening law predicts the hardening curve after the necking point.^[50] When external stress is applied, Li metal deforms into the hole and completely fills it, as seen in Figure 3c. The stress at the tip of Li remains 0 MPa, indicating no excess stress is imposed. This results in the formation of a Li-in-electrolyte structure that decreases the effective electrolyte thickness and acts as a precursor for current accumulation and stress inhomogeneity during the plating process.^[20,49] Under the same pressure, however, Li—Mg only experiences minor deformation and does not intrude into the defect, as shown in Figure 3d, due to its strain hardening behavior in accordance with the Swift hardening law.

In practice, much higher pressures than those modeled are needed to initiate Li deformation and achieve intimate contact with the electrolyte. Excess pressure may be required due to friction between the current collector, metal anode, and solid electrolyte (Figure 3e).^[21] This friction force prevents metal deformation, particularly in thin metal electrodes with low aspect ratios.^[36] Consequently, the majority of applied pressure is converted to hydrostatic stress at the metal-electrolyte interface, which has no effect on metal deformation. Moreover, lithium metal exhibits higher yield strength at μ m-scale than in bulk samples.^[39] Higher pressure is required for lithium to flow into µm-sized pores. Fabrication pressures ranging from 25 to 100 MPa have been shown in studies to be required to generate sufficient deviatoric stresses (stress tensors that lead to deformation) to enhance interfacial contact in sulfide-based solid-state batteries with various cell geometries.[18,51,52]

2.4. Cycling Performance

Plating on a non-ideal interface can lead to cell failure. **Figure** 4 shows the cross-sectional images of Li and Li–Mg anodes, fabricated at 25 and 50 MPa, respectively, after plating 3 mAh cm^{-2} . At the poor-contact interface (25 MPa fabricated) in both Li and Li–Mg cases (Figure 4a,c), Li experiences inhomogeneous



Figure 3. Deformation of Li and Li–Mg under compressive stress. a) Optical image of Li and Li–Mg disks after 50 MPa compression for 2 min. The scale bar is 1 cm. b) Area and thickness change of Li and Li–Mg disks compressed at different pressures. Finite element analysis of c) Li intrusion and d) suppressed Li–Mg intrusion into a 1 μ m surface defect. e) Schematic of a compressed metal anode attached to a solid electrolyte. Hydrostatic force dominates at the metal–electrolyte interface.



Figure 4. Cross-sectional images of the interface after plating 3 mAh cm⁻² for samples fabricated at 25 and 50 MPa. 3 mAh cm⁻² was plated at 1 MPa stack pressure and 0.5 mA cm⁻² at room temperature on a) Li fabricated at 25 MPa. b) Li fabricated at 50 MPa. c) Li–Mg fabricated at 25 MPa. d) Li–Mg fabricated at 50 MPa. The scale bar is 10 μ m.

nucleation and growth, resulting in the formation of Li globules. Consequently, the electrolyte cracks and promotes Li filament growth. When fabricated at 50 MPa with Li metal, electrolyte penetration still occurs in a similar case. However, no electrolyte crack or Li filament is observed after Li plating when an intimate interfacial contact is established (Figure 4d) using Li—Mg fabricated at 50 MPa.

The solid solution alloy Li—Mg anode has excellent interfacial contact with electrolyte, leading to exceptional cycling performance at high current densities. To avoid cell short-circuiting caused by electrolyte penetration, symmetric cells were built at the maximum pressure allowed by R_{bulk} (25 MPa for Li and 50 MPa for Li—Mg). **Figure 5**a,b shows the results of critical current density (CCD) tests in symmetric cells at various stack pressures at 60 °C. Despite the fact that CCD is greatly influenced by cell configuration (i.e., electrolyte thickness, conductivity, microstructure, metal thickness, and stack pressure),^[14,19] a comparison under the same experimental conditions highlights the cell stability at high current densities.

To avoid inaccurate measurements, impedance tests were performed after each current density to inspect for short-circuits. The CCD is defined in this work as the maximum current density before R_{bulk} decreases. Figure 5c,d shows typical sets of EIS spectra as current density increases. The EIS spectrum measured immediately after CCD is labeled in hollow stars. All EIS spectra measured above CCD show a decrease in R_{bulk} (smaller semicircle intercept on the real axis), indicating metal growth in the solid electrolyte. Figure S6a, Supporting Information, summarizes the relationship between CCD and stack pressure at 60 °C. For Li metal, the maximum CCD was 1.3 mA cm⁻² at 7 MPa, and higher and lower stack pressures resulted in lower CCD. Because of its improved initial contact and interfacial morphology after stripping, Li–Mg had a higher CCD value, reaching 4.0 mA cm⁻² at 15 MPa.^[32,33] This is because of its higher yield strength and strain hardening behavior, which prevents the metal from penetrating the electrolyte under high stack pressure. An insufficient stack pressure causes contact loss between the electrolyte and stripped metal anode, whereas an excessive stack pressure increases the chance of electrolyte penetration by metal, as illustrated in Figure S6b.^[10,12,17,53,54]

Cycling stability at room temperature is commonly constrained by the Li transport in metal anodes. In the roomtemperature CCD test, Li–Mg short-circuited at 0.7 mA cm⁻², slightly outperforming the Li metal anode which shorted at 0.5 mA cm⁻², as depicted in Figure S7, Supporting Information. Notably, we observed a significant increase in overpotential with increasing areal capacity prior to short-circuiting, as indicated by the slope in the voltage profile. This observation can be attributed to the sluggish Li transport in the metal anode at room temperature, which fails to deliver sufficient Li flux at high current densities and large areal capacities, leading to void formation and subsequent cell failure.^{53]} This limitation remains a significant factor in all-solid-state metal batteries, despite the utilization of sulfide electrolytes with high room-temperature conductivity.

Cycling within the limits of Li transport can result in improved stability, as demonstrated by the room-temperature performance of full cells presented in Figure S8, Supporting Information. Both full cells, with Li and Li—Mg anodes, displayed identical voltage profiles at a low current density (0.1 C, 0.14 mA cm⁻²). However, when the current density was increased to 0.47 mA cm⁻² (C/3), the Li anode rapidly failed during the fourth cycle. In contrast, the cell with the Li—Mg anode exhibited excellent stability, surpassing 100 cycles. In addition to the initial contact

www.advancedsciencenews.com

IENCE NEWS



Figure 5. Critical current density (CCD) tests of symmetric cells with a) Li metal and b) Li–Mg electrode at different stacking pressures at 60 °C. Li anode achieved the highest CCD at 7 MPa and Li–Mg achieved at 14 MPa. Impedance spectra of c) Li and d) Li–Mg after each current density, under the cycling conditions where the highest CCD is achieved. The spectra with hollow star symbols are measured right after the CCD.

improvement, the faster effective Li transport in Li–Mg compared to Li also contributes to enhanced cycling stability.^[32,33]

3. Conclusion

In this work, we present a method for enabling intimate contact between metal anode and solid electrolyte during cell fabrication through altering the strain-hardening behavior of Li by incorporating 3 at% Mg. The Li—Mg anode is capable of withstanding high fabrication pressures (50–65 MPa) without electrolyte penetration. In contrast, pure Li anodes struggle to maintain contact without risking electrolyte intrusion. Unlike pure Li which obeys Voce hardening law and allows unconstrained deformation, Li—Mg follows the Swift hardening law and strengthens with strain under compression stress. Furthermore, finite element analysis reveals that, in contrast to pure Li, Li—Mg does not penetrate the defects on solid electrolyte surface. Symmetric cells with Li—Mg electrodes exhibit a critical current that is 200% higher than Li metal electrodes. Understanding Li metal deformation properties is critical for improving solid-state battery performance.

4. Experimental Section

Materials: Li metal foil (750 µm thick) was purchased from Alfa Aesar. Li—Mg foil (10 wt% Mg, 90 wt% Li alloy, Li_{0.97}Mg_{0.03}, 90 µm thick) and LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂ (NMC, d50 = 3–4 µm) was purchased from MSE Supplies. Li₆PS₅Cl solid electrolyte (LPSCl, d50 = 3–4 µm) was purchased from NEI Corporation. Vapor-grown carbon fiber (VGCF, PR-19-XT-HHT) was purchased from Applied Sciences.

Solid-State Battery Fabrication: To prepare a solid-state battery, 127 mg of solid electrolyte was first pressed in a Φ 12.7 mm (1.267 cm²) polyether ether ketone die at 150 MPa. The titanium plunger used for pressing was wet-polished with 3000 grit sandpaper until a mirror surface finishing (root-mean-square [RMS] roughness <0.1 μ m). The surface profile of the electrolyte pellet in Figure S1, Supporting Information, shows a relatively smooth surface with an overall RMS roughness at (0.3 \pm 0.1) μ m; however, surface bumps or cracks approximately at micrometer scale still exist. The as-pressed pellet was of 500 μ m thickness. For symmetric cells, the pellet

ENERGY MATERIALS www.advenergymat.de

was further densified at 375 MPa. Li metal foil was rolled to 90 µm (4.8 mg cm⁻²). Li and Li—Mg electrodes with the same thickness were cut out into Φ 12.7 mm disks and pressed on both sides of the solid electrolyte pellet, as shown in Figure S9, Supporting Information. The metal anode was confined within the die to ensure that its actual contact area does not exceed the electrolyte area during compression. This ensures that the decrease in $R_{\rm bulk}$ below $R_{\rm SE}$ can only be due to a decrease in effective thickness, caused by the penetration of Li into the electrolyte. For full cell fabrication, NMC, LPSCI, and VGCF (70:27:3 by mass) were first mixed in an agate mortar, then densified with electrolyte at 375 MPa. Li or Li—Mg disk was pressed onto the counter side at 50 MPa. The composite cathode loading was 10 mg cm⁻² (7 mg cm⁻² active material loading, 1.4 mAh cm⁻² theoretical capacity).

Impedance Monitoring during Pressurized Fabrication: Symmetric cells with two Li or Li—Mg electrodes were pressed by a hydraulic press (Carver) and monitored by a force sensor (Autoda). Potentiostatic EIS was scanned from 1 MHz to 1 Hz at a 7 mV amplitude with a Biologic SP300 potentio-stat. The duration of the EIS test at each pressure was less than 1 mint o minimize the possible chronical effect. The spectrum was analyzed with Randle's circuit depicted in Figure 1a inset^[15] with ZView software. Q_{int} was a constant-phase element that represents interfacial capacitance. The sistance of the electrolyte pellet was measured with carbon|LPSCI|carbon setup.^[37]

Electrochemical Testing: The assembled cell was pressurized at 25 and 50 MPa for 2 min, respectively, for Li and Li—Mg electrodes before electrochemical testing to minimize the interface resistance without introducing a short circuit. Then, different stack pressures were applied by a torque wrench calibrated by a force sensor. Unless specified, all cycling tests were carried out at 60 °C. In CCD tests, an EIS measurement was carried out after each cycle to determine whether the cell was subject to short circuit.

Mechanical Test: Tensile testing was performed in an Ar-filled glovebox. Li and Li—Mg foils were tailored into dog bone shape with 4.4 mm gage width and 6.6 mm overall width. Both samples were pulled at a strain rate of $1.3 \times 10^{-3} \, \mathrm{s}^{-1}$. True stress (σ_{true}) and true strain (ε_{true}) were calculated from the measured engineering stress (σ_{eng}) and strain (ε_{eng}) based on the correlation $\sigma_{true} = \sigma_{eng} (1 + \varepsilon_{eng})$ and $\varepsilon_{true} = \ln(1 + \varepsilon_{eng})$,^[20] assuming volume remains constant before necking occurs in tensile tests. For the compression test, Li and Li—Mg disks of the same size were sandwiched between two polyester films. After applying pressure for 2 min, the area expansion was calculated based on image analysis (Fiji) with the aid of a Φ 12.7 mm Cu disk as a reference. The thickness change was calculated by dividing the total volume by area.

Finite Element Analysis: The stress-strain curve before necking was fitted with Voce hardening law (Li) and Swift hardening law (Li–Mg) to simulate its mechanical response at large strains.^[40] FEA was carried out by Abaqus. A 1 μ m diameter defect was introduced on electrolyte surface, and the deformation of Li and Li–Mg was simulated based on the von Mises criterion at a fixed external stress.

Morphological Analysis: The surface roughness of the electrolyte pellet was measured in silicone oil with a Bruker DektakXT profilometer. The cell was cut with a razor blade for cross-section analysis, then cryo-polished with Ar⁺ beam at -30 °C (JEOL, IB-10520CCP). An air-free vessel was used to transfer samples between the glovebox and characterization tools. SEM imaging was carried out in a Helios SEM/FIB.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Vehicle Technologies Program under Contact DE-EE0008864. W.L. and J.Z. gratefully acknowledge the support of the present work through the NASA-19-TTT-0103 project (Award No. 80NSSC21M0114). They are also supported by the Northeastern University and College of Engineering startup funds. This work was conducted in part using resources of the Shared Equipment Authority at Rice University.

Conflict of Interest

Y.Y. has equity interest in LiBeyond, LLC and Solid Design Instruments, LLC. The University of Houston reviewed and approved their relationship in compliance with its conflict-of-interest policy. The remaining authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

metal anodes, solid solution, solid-state batteries, strain hardening

Received: March 5, 2023 Revised: June 17, 2023 Published online:

- P. Albertus, S. Babinec, S. Litzelman, A. Newman, Nat. Energy 2018, 3, 16.
- [2] S. Randau, D. A. Weber, O. Kötz, R. Koerver, P. Braun, A. Weber, E. Ivers-Tiffée, T. Adermann, J. Kulisch, W. G. Zeier, F. H. Richter, J. Janek, *Nat. Energy* **2020**, *5*, 259.
- [3] D. Cao, Y. Zhao, X. Sun, A. Natan, Y. Wang, P. Xiang, W. Wang, H. Zhu, ACS Energy Lett. 2020, 5, 3468.
- [4] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno, *Nat. Energy* **2016**, *1*, 16030.
- [5] C. Wu, J. Lou, J. Zhang, Z. Chen, A. Kakar, B. Emley, Q. Ai, H. Guo, Y. Liang, J. Lou, Y. Yao, Z. Fan, *Nano Energy* **2021**, *87*, 106081.
- [6] B. Emley, Y. Liang, R. Chen, C. Wu, M. Pan, Z. Fan, Y. Yao, *Mater. Today Phys.* 2021, 18, 100397.
- [7] Y.-G. Lee, S. Fujiki, C. Jung, N. Suzuki, N. Yashiro, R. Omoda, D.-S. Ko, T. Shiratsuchi, T. Sugimoto, S. Ryu, J. H. Ku, T. Watanabe, Y. Park, Y. Aihara, D. Im, I. T. Han, *Nat. Energy* **2020**, *5*, 299.
- [8] S. Wenzel, S. J. Sedlmaier, C. Dietrich, W. G. Zeier, J. Janek, Solid State Ionics 2018, 318, 102.
- [9] L. Zhou, N. Minafra, W. G. Zeier, L. F. Nazar, Acc. Chem. Res. 2021, 54, 2717.
- [10] T. Krauskopf, F. H. Richter, W. G. Zeier, J. Janek, Chem. Rev. 2020, 120, 7745.
- [11] P. Albertus, V. Anandan, C. Ban, N. Balsara, I. Belharouak, J. Buettner-Garrett, Z. Chen, C. Daniel, M. Doeff, N. J. Dudney, B. Dunn, S. J. Harris, S. Herle, E. Herbert, S. Kalnaus, J. A. Libera, D. Lu, S. Martin, B. D. McCloskey, M. T. McDowell, Y. S. Meng, J. Nanda, J. Sakamoto, E. C. Self, S. Tepavcevic, E. Wachsman, C. Wang, A. S. Westover, J. Xiao, T. Yersak, ACS Energy Lett. 2021, 6, 1399.
- [12] J. Kasemchainan, S. Zekoll, D. S. Jolly, Z. Ning, G. O. Hartley, J. Marrow, P. G. Bruce, *Nat. Mater.* **2019**, *18*, 1105.
- [13] X. Zhang, Q. J. Wang, K. L. Harrison, S. A. Roberts, S. J. Harris, Cell Rep. 2020, 1, 100012.
- [14] D. K. Singh, A. Henss, B. Mogwitz, A. Gautam, J. Horn, T. Krauskopf, S. Burkhardt, J. Sann, F. H. Richter, J. Janek, *Cell Rep.* 2022, 3, 101043.

www.advenergymat.de

www.advancedsciencenews.com

SCIENCE NEWS

- [15] T. Krauskopf, H. Hartmann, W. G. Zeier, J. Janek, ACS Appl. Mater. Interfaces 2019, 11, 14463.
- [16] Q. Tu, L. Barroso-Luque, T. Shi, G. Ceder, Cell Rep. 2020, 1, 100106.
- [17] J. Doux, H. Nguyen, D. H. S. Tan, A. Banerjee, X. Wang, E. A. Wu, C. Jo, H. Yang, Y. S. Meng, *Adv. Energy Mater.* **2020**, *10*, 1903253.
- [18] C. Hänsel, D. Kundu, Adv. Mater. Interfaces 2021, 8, 2100206.
- [19] S.-Y. Ham, H. Yang, O. Nunez-cuacuas, D. H. S. Tan, Y.-T. Chen, G. Deysher, A. Cronk, P. Ridley, J.-M. Doux, E. A. Wu, J. Jang, Y. S. Meng, *Energy Storage Mater.* **2023**, *55*, 455.
- [20] W. S. LePage, Y. Chen, E. Kazyak, K.-H. Chen, A. J. Sanchez, A. Poli, E. M. Arruda, M. D. Thouless, N. P. Dasgupta, J. Electrochem. Soc. 2019, 166, A89.
- [21] A. Masias, N. Felten, R. Garcia-Mendez, J. Wolfenstine, J. Sakamoto, J. Mater. Sci. 2019, 54, 2585.
- [22] F. P. McGrogan, T. Swamy, S. R. Bishop, E. Eggleton, L. Porz, X. Chen, Y. Chiang, K. J. V. Vliet, *Adv. Energy Mater.* **2017**, *7*, 1602011.
- [23] S. Luo, Z. Wang, X. Li, X. Liu, H. Wang, W. Ma, L. Zhang, L. Zhu, X. Zhang, Nat. Commun. 2021, 12, 6968.
- [24] Y. Huang, B. Shao, F. Han, J. Mater. Chem. A 2022, 10, 12350.
- [25] M. Z. Butt, P. Feltham, J. Mater. Sci. 1993, 28, 2557.
- [26] S. Jin, Y. Ye, Y. Niu, Y. Xu, H. Jin, J. Wang, Z. Sun, A. Cao, X. Wu, Y. Luo, H. Ji, L.-J. Wan, J. Am. Chem. Soc. 2020, 142, 8818.
- [27] Z. Zeng, S. Wang, J. Cheng, G. Hou, D. Li, G. Han, L. Ci, ACS Sustainable Chem. Eng. 2021, 9, 4282.
- [28] K. Yan, Z. Lu, H.-W. Lee, F. Xiong, P.-C. Hsu, Y. Li, J. Zhao, S. Chu, Y. Cui, Nat. Energy 2016, 1, 16010.
- [29] Z. Shi, M. Liu, D. Naik, J. L. Gole, J. Power Sources 2001, 92, 70.
- [30] L. Kong, L. Wang, Z. Ni, S. Liu, G. Li, X. Gao, Adv. Funct. Mater. 2019, 29, 1808756.
- [31] C. Yang, H. Xie, W. Ping, K. Fu, B. Liu, J. Rao, J. Dai, C. Wang, G. Pastel, L. Hu, *Adv. Mater.* **2019**, *31*, 1804815.
- [32] T. Krauskopf, B. Mogwitz, C. Rosenbach, W. G. Zeier, J. Janek, Adv. Energy Mater. 2019, 9, 1902568.
- [33] M. Siniscalchi, J. Liu, J. S. Gibson, S. J. Turrell, J. Aspinall, R. S. Weatherup, M. Pasta, S. C. Speller, C. R. M. Grovenor, ACS Energy Lett. 2022, 7, 3593.
- [34] T. K. Schwietert, V. A. Arszelewska, C. Wang, C. Yu, A. Vasileiadis, N. J. J. de Klerk, J. Hageman, T. Hupfer, I. Kerkamm, Y. Xu, E. van der Maas, E. M. Kelder, S. Ganapathy, M. Wagemaker, *Nat. Mater.* 2020, 19, 428.

- [35] D. K. Singh, T. Fuchs, C. Krempaszky, P. Schweitzer, C. Lerch, F. H. Richter, J. Janek, *Matter* 2023, 6, 1.
- [36] C. G. Haslam, J. B. Wolfenstine, J. Sakamoto, J. Power Sources 2022, 520, 230831.
- [37] J.-M. Doux, Y. Yang, D. H. S. Tan, H. Nguyen, E. A. Wu, X. Wang, A. Banerjee, Y. S. Meng, J. Mater. Chem. 2020, 8, 5049.
- [38] Z. Ning, D. S. Jolly, G. Li, R. D. Meyere, S. D. Pu, Y. Chen, J. Kasemchainan, J. Ihli, C. Gong, B. Liu, D. L. R. Melvin, A. Bonnin, O. Magdysyuk, P. Adamson, G. O. Hartley, C. W. Monroe, T. J. Marrow, P. G. Bruce, *Nat. Mater.* 2021, 20, 1121.
- [39] C. D. Fincher, D. Ojeda, Y. Zhang, G. M. Pharr, M. Pharr, Acta Mater. 2020, 186, 215.
- [40] J. Zhu, T. Wierzbicki, W. Li, J. Power Sources 2018, 378, 153.
- [41] E. Voce, J. Inst. Met. 1948, 74, 537.
- [42] W. M. Sing, K. P. Rao, J. Mater. Process. Technol. 1997, 63, 105.
- [43] H. W. Swift, J. Mech. Phys. Solids 1952, 1, 1.
- [44] W. Pichl, M. Krystian, Phys. Status Solidi 1997, 160, 373.
- [45] S. Tariq, K. Ammigan, P. Rurh, R. Schultz, P. Liu, J. Shang, Proceedings of the 2003 Particle Accelerator Conference, IEEE, Piscataway, NJ 2003, pp. 1452–1454.
- [46] D. Hull, H. M. Rosenberg, Philos. Mag. 1959, 4, 303.
- [47] K. Edalati, D. Akama, A. Nishio, S. Lee, Y. Yonenaga, J. M. Cubero-Sesin, Z. Horita, Acta Mater. 2014, 69, 68.
- [48] J. H. Jackson, P. D. Frost, A. C. Loonam, L. W. Eastwood, C. H. Lorig, JOM 1949, 1, 149.
- [49] L. Porz, T. Swamy, B. W. Sheldon, D. Rettenwander, T. Frömling, H. L. Thaman, S. Berendts, R. Uecker, W. C. Carter, Y. Chiang, *Adv. Energy Mater.* 2017, *7*, 1701003.
- [50] T. Sedlatschek, J. Lian, W. Li, M. Jiang, T. Wierzbicki, M. Z. Bazant, J. Zhu, Acta. Mater. 2021, 208, 116730.
- [51] J. Doux, H. Nguyen, D. H. S. Tan, A. Banerjee, X. Wang, E. A. Wu, C. Jo, H. Yang, Y. S. Meng, *Adv. Energy Mater.* **2020**, *10*, 1903253.
- [52] J. A. Lewis, C. Lee, Y. Liu, S. Y. Han, D. Prakash, E. J. Klein, H.-W. Lee, M. T. McDowell, ACS Appl. Mater. Interfaces 2022, 14, 4051.
- [53] D. S. Jolly, Z. Ning, G. O. Hartley, B. Liu, D. L. R. Melvin, P. Adamson, J. Marrow, P. G. Bruce, ACS Appl. Mater. Interfaces 2021, 13, 22708.
- [54] J. A. Lewis, F. J. Q. Cortes, Y. Liu, J. C. Miers, A. Verma, B. S. Vishnugopi, J. Tippens, D. Prakash, T. S. Marchese, S. Y. Han, C. Lee, P. P. Shetty, H.-W. Lee, P. Shevchenko, F. D. Carlo, C. Saldana, P. P. Mukherjee, M. T. McDowell, *Nat. Mater.* **2021**, *20*, 503.