

All-Solid-State Batteries with Extremely Low N/P Ratio Operating at Low Stack Pressure

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All-solid-state batteries (ASSBs) are emerging as promising candidates for next-generation energy storage systems. However, their practical implementation faces significant challenges, particularly their requirement for an impractically high stack pressure. This issue is especially critical in high-energy density systems with limited negative-to-positive electrode capacity ratios (N/P ratios), where uneven lithium (Li) stripping induces the formation of interfacial voids. This study addresses these challenges by introducing an anode with a novel structural design that operates effectively under practically viable conditions while significantly reducing the N/P ratio to less than one. The approach entails the integration of a lithiophilic magnesium (Mg) film beneath a thin layer of the silicon-graphite (SiGr) active materials. This structure facilitates the deposition of excess Li beneath the SiGr layer during overcharging, which enables stable cycling even at room temperature and at a low stack pressure of 3 MPa. By mitigating the poor contact that is characteristic of ASSBs with a low stack pressure, and simultaneously increasing the energy density by lowering the N/P ratio, the design significantly advances the key electrochemical properties of ASSBs.

1. Introduction

The rapid growth of the electric vehicle (EV) industry is driving the surging demand for next-generation energy storage solutions. Conventional lithium-ion batteries (LIBs), despite their widespread uptake, offer limited energy density and safety.^[1] This has catalyzed substantial investment from battery researchers in the development of all-solid-state batteries (ASSB), with the aim of meeting contemporary exigencies.^[2] ASSBs are expected to resolve the shortcomings of LIBs by employing non-flammable solid electrolytes (SEs) and advanced anode materials with high specific capacities.^[3] Among the various types of SEs that are being actively researched for ASSBs, sulfides stand out as the most promising ones.^[4] This distinction arises from their superior ionic conductivity at room temperature along with their exceptional mechanical properties that facilitate interparticle contact.^[5]

The type and amount of the anode active material have a significant impact on the energy density and other key performance indicators. In conventional LIBs, graphite has been favored as the anode active material due to its low cost and long cycle life.^[6] However, in ASSBs, the thick SE layer surpasses the thickness of the separator in conventional LIBs and requires the SE to be included in the electrodes to facilitate ionic conduction, which can negatively impact the energy density. Consequently, substantial enhancement of the specific capacity of each electrode is imperative to elevate the energy density. Several next-generation anode materials, such as silicon (Si)^[7] and lithium (Li) metal,^[8] have garnered discernable attention along this direction. Among the anode systems considered to date, the ultimate option would be an anode-less one from which specific active materials are absent.^[9] In an anode-less cell, Li metal is deposited directly on the anode current collector during charging, which constitutes a zero N/P ratio (the ratio of the capacity of the negative electrode to that of the positive electrode).^[10] The N/P ratio is a critical parameter in battery cell design as this value determines the energy density and reversibility in each cycle. Typically, an N/P ratio of 1.05 to 1.2 is adopted for LIBs.^[11] N/P ratios lower than these can lead to unwanted Li metal precipitation, whereas higher ratios tend

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The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aenm.202404817>

DOI: 10.1002/aenm.202404817

to sacrifice the Coulombic efficiency (CE) and the energy density. This trade-off relation applies to an anode-less configuration with an N/P ratio of zero, and therefore, a strategy is required to ensure stable operation and long-term durability while maintaining the N/P ratio as low as possible.

Another critical challenge encountered by ASSBs is their requirement for high operating temperatures and pressures for sustainable cycling. These conditions are in relation to maintaining close proximity between the solid-state constituents and securing ion conduction.^[12] This necessity becomes even more pronounced when confronted with Li dendritic growth, which is often accompanied by the formation of numerous voids at the anode interface upon Li stripping. At low N/P ratios, Li deposition becomes more inhomogeneous and challenging to manage.^[13] For this reason, practical examples with low N/P ratios, combined with room-temperature operation at low stack pressure, remain scarce.

We endeavored to devise a novel anode structure for sulfide-based ASSBs featuring significantly reduced N/P ratios for operation at room temperature and low stack pressure. The Si-graphite (SiGr) composite was chosen as the anode material due to its relatively high capacity, the lithiophilicity of Si, and based on extensive research experience.^[14] Our approach was to introduce an additional thin layer of Mg beneath a restricted amount of SiGr (MgSiGr) to facilitate high reversibility even during overcharging. The lithiophilic nature of Mg^[15] gives rise to the formation of a Li–Mg alloy, which induces uniform Li deposition beneath the SiGr layer (Figure S1, Supporting Information). The SiGr-SE interface demonstrates superior stability compared to the Li-SE interface. The latter is known to foster the unavoidable growth of dendritic Li, and this creates significant void spaces after stripping, which makes it difficult to self-heal under low stack pressure conditions.^[16] Furthermore, the theoretical calculations indicate that the overcharge-based MgSiGr anode cell delivers higher energy density than conventional SiGr (Tables S1, S2 and Figure S2, Supporting Information). Despite the added volume from in situ Li deposition during overcharge, MgSiGr offers superior volumetric energy density due to its thinner initial thickness and compact Li plating. This novel approach to designing anode systems for high-energy-density sulfide-based ASSBs, for operation under practical operating conditions and with extended lifespans, leverages the controlled overcharging of existing high-capacity materials as the key innovation.

2. Results and Discussion

Lithiophilicity refers to the ability of a material to form a stable alloy with Li, a property that is advantageous for lowering the overpotential during charging, which makes it suitable for use at the anode interface.^[17] Among the various lithiophilic metals, Mg emerged as the most appropriate candidate owing to its favorable solid-solution reaction with Li.^[18] Fabrication of the MgSiGr anode commenced with sputtering a uniform thin film of Mg onto the stainless steel (SUS) current collector. The top-view scanning electron microscopy (SEM) image (Figure S3, Supporting Information) and cross-sectional SEM image along with energy-dispersive spectroscopy (EDS) (Figure S4, Supporting Information) confirmed that the Mg coating was sufficiently uniform and thin. The limited thickness of the Mg film of ≈ 200 nm adequately

aligns with the motivation of the anode-less concept, namely to maximize the energy density of the cell.^[19] The effect of the Mg thin-film on stabilizing the cycling of Li (de) plating was demonstrated in half-cell tests (Figure S5, Supporting Information). In contrast to the rapid short-circuiting observed with the bare SUS current collector, the Mg-coated SUS sample exhibited superior cyclability, maintaining over 250 cycles of Li plating-stripping without any failure.

Subsequently, the SiGr anode active material (Figures S6 and S7, Supporting Information) was positioned onto the Mg film to fabricate the MgSiGr anode. Cross-sectional SEM-EDS images of the pristine MgSiGr electrode (Figure S8, Supporting Information) confirmed that the SiGr powder was thoroughly mixed and also that the $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) (Figures S9 and S10, Supporting Information) SE was present on the thin Mg film.

The energy density of a cell increases as the N/P ratio decreases, thereby underscoring the importance of lowering the N/P ratio. This ratio typically refers to the ratio of the capacity of the negative electrode to that of the positive electrode in a full-cell. However, in this study, a modified N/P ratio was defined specifically for half-cells (Equation 1) to explicitly characterize the overcharging phenomenon. In this context, the half-cell N/P ratio represents the proportion of capacity delivered by the SiGr active material compared to the total capacity, which includes the contribution from overcharging.

$$\text{Modified N/P ratio} = \frac{\text{Capacity delivered by the SiGr}}{\text{Total capacity}} \quad (1)$$

First, we evaluated the maximum available capacity of our SiGr active material by subjecting it to (dis)charge without overcharging in the voltage range 0.01–1.5 V. A corresponding assessment was conducted on a SiGr|LPSCl|Li all-solid-state half-cell. Generally, evaluations of the anode active material in half-cells adopt a charge voltage cutoff of 0.01 V, as Li precipitation can occur below this threshold. In our subsequent overcharge experiments, we deliberately bypassed utilizing this cutoff by allowing Li deposition (overcharge) to continue. Therefore, we referred to the capacity delivered until 0.01 V as the charge capacity of SiGr. The maximum available capacity of the SiGr anode material, measured at a current density of 0.1 C (0.05 mA cm⁻²), was determined to be 825 mAh g⁻¹, whereas the capacity measured at a higher current density of 1 mA cm⁻² was only 277 mAh g⁻¹ (Figure S11, Supporting Information) because the utilization of the SiGr at this current density was limited. This suggests that the actual capacity contributed by the SiGr at practical current densities is significantly lower than its maximum available capacity. Therefore, it is noted that, for the evaluation of the overcharge, the modified N/P ratio depends largely on the current density.

During plating-stripping tests in half-cells, the SiGr active material was charged until the voltage reached 0 V, after which excess Li metal was plated. To enable us to focus solely on the stability of the Li metal plating process, the stripping cutoff voltage was set to 0.1 V. For the plain SiGr anode, Li precipitation occurred after charging to 0.22 mAh cm⁻². This initial capacity contributed by SiGr corresponds to the numerator in the modified N/P ratio, and a steep voltage slope was maintained until the onset of Li plating. However, in the case of the MgSiGr anode, a relatively gradual slope was observed near the onset point, whereupon the

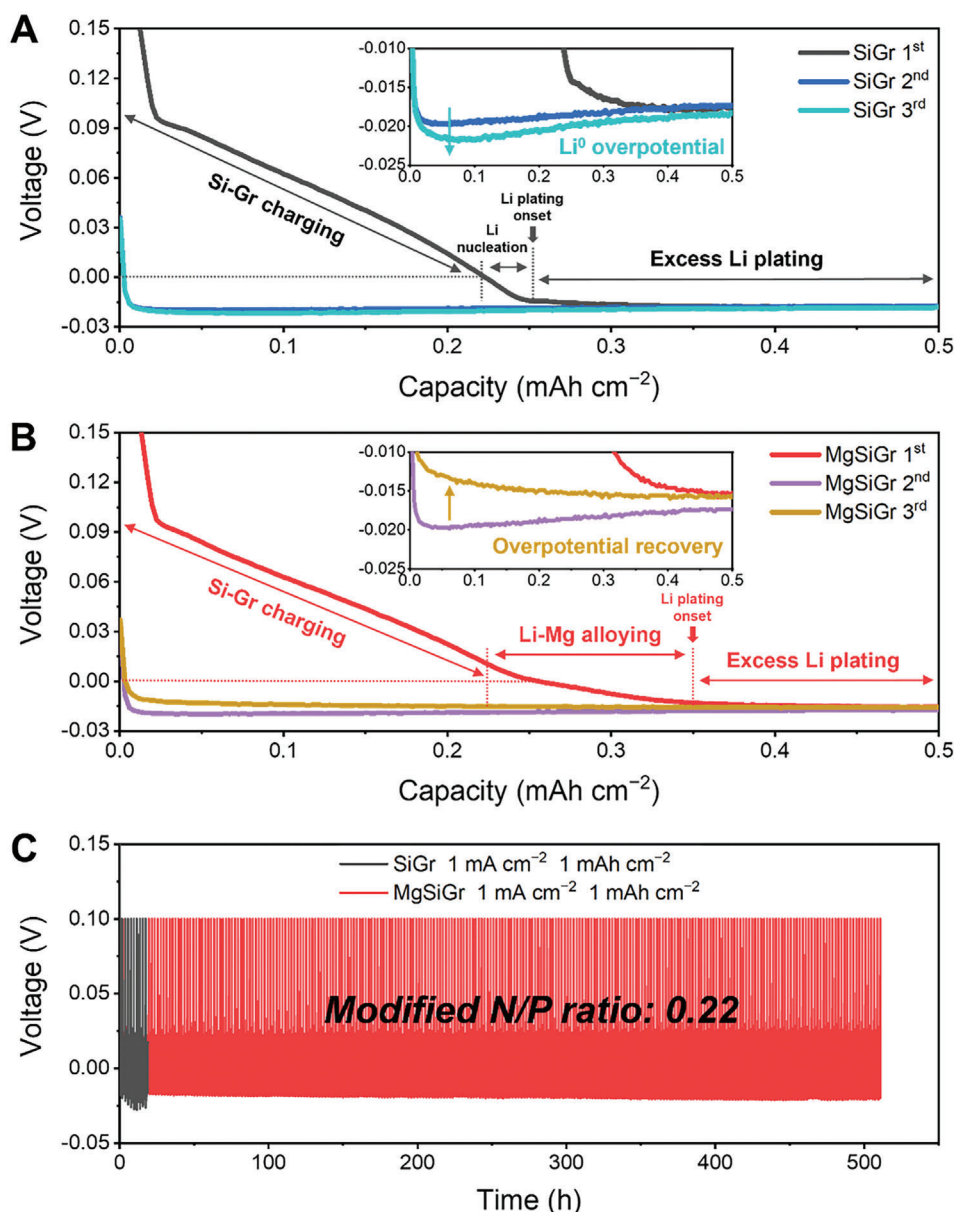


Figure 1. Voltage profiles of the all-solid-state half-cells with overcharging: A) SiGr and B) MgSiGr anode at a current density of 1 mA cm⁻² and capacity of 1 mAh cm⁻². C) Voltage versus time profiles (modified N/P ratio = 0.22).

Li–Mg alloying reaction took place. This suggests that the underlying Mg effectively participates in the initial Li nucleation. These observations were corroborated by the cyclic voltammetry (CV) profiles (Figure S12, Supporting Information), in which the sharp current dip of the plain SiGr anode near 0 V indicates sudden Li deposition, whereas the current response of the MgSiGr anode changes less abruptly near 0 V owing to the Li nucleation of Mg.

Additionally, in repeated cycles, in the case of the SiGr anode, excess Li plating led to an increase in the Li nucleation overpotential (inset in Figure 1A). This is attributed to the lack of stable Li nucleation seeds and non-uniform deposition of Li within and on the SiGr composite anode. Conversely, for the MgSiGr

anode, subsequent excess Li deposition tended to result in overpotential recovery (inset in Figure 1B). This phenomenon is typically observed when Li metal repeatedly nucleates on a lithiophilic substrate,^[20] and indicates that the MgSiGr can induce stable Li plating from the bottom layer of the electrode during overcharging. Indeed, the MgSiGr anode demonstrated a far longer cycle life in excess of 500 h, in contrast with the plain SiGr anode, which failed by short-circuiting even before 20 h of operation (Figure 1C).

The morphology of the Li precipitation on the (Mg)SiGr anodes during overcharging was visualized with the aid of cross-sectional SEM-EDS. When the plain SiGr anode was charged to a capacity of 3.5 mAh cm⁻², with a modified N/P ratio of

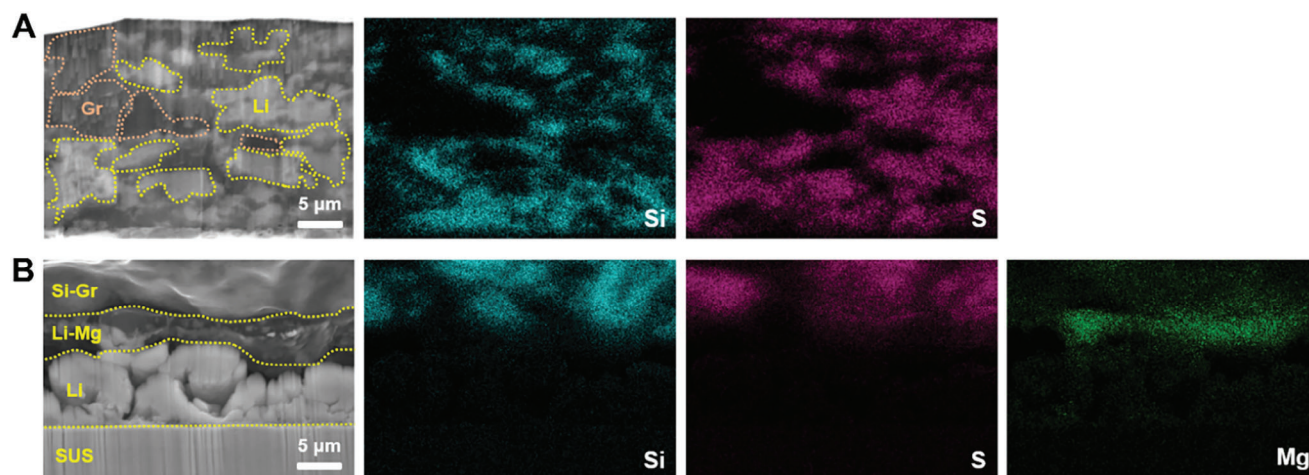


Figure 2. Cross-sectional SEM-EDS images of the (Mg)SiGr anode after overcharging. Morphologies after overcharging the A) SiGr and B) MgSiGr anodes (modified N/P ratio = 0.06). In the case of simple SiGr, Li precipitates between the active materials. However, with the underlying Mg layer, the Li is neatly stacked beneath the SiGr active material.

0.06, Li deposition inside the composite anode was irregular and sparse (**Figure 2A**). Overcharging resulted in the accumulation of precipitated Li on the active particles, leading to pronounced Li dendritic growth. In contrast, in the case of the MgSiGr anode, the lithiophilic Mg coating below the SiGr induced stable Li deposition via the formation of a Li–Mg alloy, the stability of which was reflected in a clearly distinguishable intermediate layer (**Figure 2B**). Furthermore, the deposition of Li beneath this layer not only decreases the contact area between Li and the SE to reduce the formation of the solid-electrolyte interphase (SEI) for improved reversibility, but also contributes to enhancing the stability of the anode-SE interface. This interfacial stability is crucial for reliable operation at low stack pressure, as is discussed later.

Additional cycling tests were conducted to further evaluate the overcharging behavior of the (Mg)SiGr anodes. These tests were carried out in a half-cell at a current density of 1 mA cm^{-2} , with a capacity of 3.5 mAh cm^{-2} . Under these operating conditions, the modified N/P ratio was measured to be 0.06. This extremely low N/P ratio aligns with anode-less behavior, where almost all of the capacity is allocated to Li deposition. Consistent with the above results obtained with the modified N/P ratio of 0.22 (**Figure 1A,B**), the voltage profile of MgSiGr stabilized near 0 V compared to that of its SiGr counterpart (**Figure 3A**). It is worth noting that the MgSiGr demonstrated a higher initial Coulombic efficiency (ICE) of 90.3% compared to 85.2% of SiGr, a result that was attributed to the stability of the underlying Li deposition. For the two different N/P ratios of 0.22 and 0.06, depending on the areal capacity (**Figure 3B**), the MgSiGr exhibited superior CEs and cycle lives to those of the plain SiGr. Additionally, the voltage-time profiles further corroborated that the MgSiGr anodes exhibited lower overpotentials during extended cycling (**Figure S13**, Supporting Information), whereas the plain SiGr anodes experienced a sharp rise in overpotential and a short cycle life of fewer than 15 cycles. Cross-sectional imaging conducted after the 51st overcharge demonstrated that the Mg layer remained anchored beneath the SiGr layer during cycling (**Figure S14**, Supporting Information). These findings highlight the pivotal role of bottom-

Li-inducing seeds in enhancing both the lifetime and reversibility during overcharging cycles.

Variation of the N/P ratio of the half-cells in additional plating-stripping tests at different SiGr loadings (**Figure S15**, Supporting Information) revealed that the MgSiGr anodes outperformed their SiGr counterparts across all N/P ratios. Notably, the MgSiGr anodes performed more stably even at lower N/P ratios, a finding we attributed to the 0.1 V stripping voltage cutoff. After the initial charge, only Li metal undergoes repeated plating and stripping during cycling, thus the presence of less SiGr atop the deposited Li facilitates Li stripping from the bottom upward. Conversely, for the plain SiGr anodes, no discernible trend was observed because dendritic Li growth within or atop the composite anode resulted in consistent and rapid degradation, regardless of the N/P ratio.

The impact of the Mg layer at the bottom on the internal cell resistance was investigated through electrochemical impedance spectroscopy (EIS) analysis (**Figure 3C,D**). The x-intercept of the plot represents the bulk electrolyte resistance (R_b), whereas the semi-circle corresponds to the charge transfer resistance (R_{CT}) (**Figure S16**, Supporting Information).^[21] The shape of the plot (**Figure S17**, Supporting Information) offers valuable insights into the internal cell resistance and Li filament growth within the SE.^[22] In the case of the cell that experienced a soft short circuit, the additional parallel resistance associated with this short circuit (r_{ss}) is taken into account due to the substantial electronic conduction through it, which reduces R_b and R_{CT} accordingly.^[23] For the plain SiGr (**Figure 3C**), R_b suddenly decreased from 23.6 to 15.7Ω after 7 cycles, which indicated the onset of the short circuit. This was accompanied by the appearance of an extra semi-circle in the high-frequency region, which corresponded to the SEI resistance (R_{SEI}), and resulted from uncontrollable side reactions between the overcharged Li metal and the SE. In contrast, the MgSiGr anode (**Figure 3D**) consistently maintained R_b without the appearance of new semi-circles over 50 cycles. This result is attributed to the confinement of Li plating beneath the Li–Mg layer, which effectively suppresses direct contact between the plated Li and the SE.

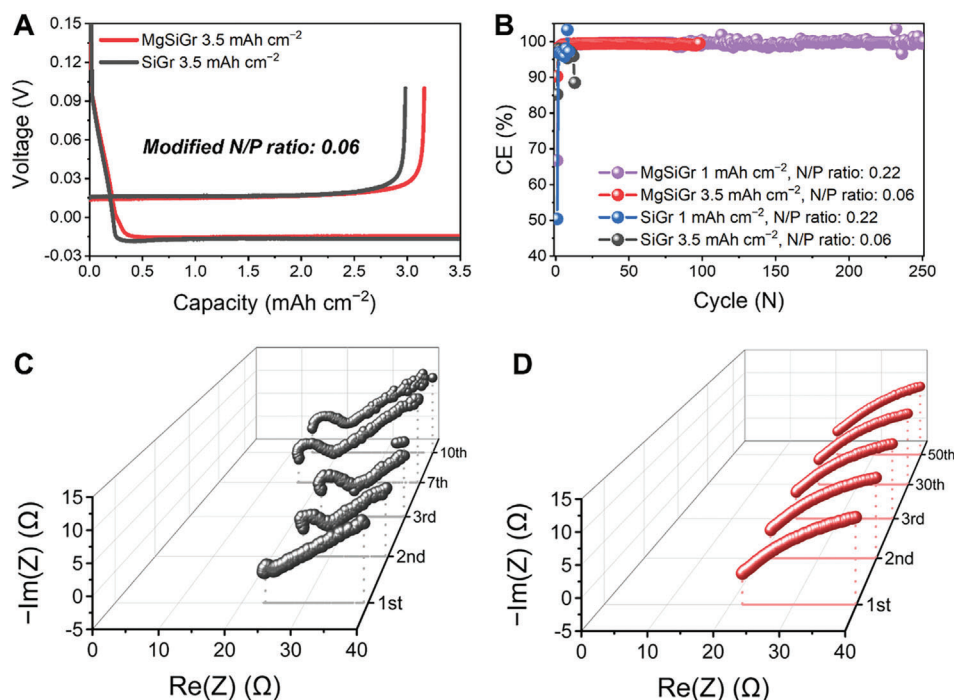


Figure 3. A) Voltage profiles of the first cycle in the Li plating-stripping test in the half-cell, at a current density of 1 mA cm^{-2} and capacity of 3.5 mAh cm^{-2} (modified N/P ratio = 0.06 at the given current density). B) CEs at a current density of 1 mA cm^{-2} and different capacities. EIS Nyquist plots after cycling with the C) SiGr and D) MgSiGr anodes at a current density of 1 mA cm^{-2} and a capacity of 1 mAh cm^{-2} (modified N/P ratio = 0.22).

Additional in situ EIS measurements were conducted at intervals of 0.1 mAh cm^{-2} during the first charge to capture the overcharging dynamics of the (Mg)SiGr anodes (Figure S18, Supporting Information). In the case of the plain SiGr, R_b declined during the early charging stage of SiGr lithiation (Figure S19A, Supporting Information), in reflection of the growth of Li filaments through the SE even prior to overcharging. This suggests the vulnerability of SiGr composite anodes to internal short-circuiting at the given current density of 1 mA cm^{-2} . On the other hand, for the MgSiGr anode, R_b decreased to below its initial value during overcharge (Figure S19B, Supporting Information), indicating that the Mg film enhances the tolerance against a short circuit, particularly during the early pre-charge stage with SiGr.

Subsequently, additional half-cell tests were conducted on (Mg)SiGr anodes with a stripping cutoff voltage as high as 1.5 V (Figure S20, Supporting Information) to include the lithiation of SiGr active materials during each charge. The voltage profiles in the first cycles closely resembled those with the 0.1 V cutoff evaluations. However, the introduction of the Mg film significantly improved the cyclability even with the heightened voltage cutoff, whereas the plain SiGr anode was short-circuited after only two cycles.

We expanded the electrochemical evaluation to full-cells by pairing the anodes with LiNbO_3 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811) (Figure S21, Supporting Information) cathodes at an extremely low N/P ratio of 0.15. Using a current density of 0.1C for the initial formation, MgSiGr exhibited an initial reversible capacity of 185 mAh g^{-1} , surpassing that of SiGr (176 mAh g^{-1}), along with a higher ICE (Figure 4A): 92.4% versus 87.7%. MgSiGr demonstrated stable operation up to the 75th cy-

cle with capacity retention of 83.7% (Figure 4B), contrary to SiGr, which experienced a short circuit after just 16 cycles (Figure 4C). MgSiGr achieved an impressive average CE of 99.2% for the 75 cycles (Figure 4D).

In additional assessments of the rate capability of full-cells with the MgSiGr anode, galvanostatic tests were conducted at various charging densities with a fixed discharging rate of 0.1C (Figure 4E,F). The MgSiGr cell delivered specific discharge capacities of 181.2, 166.5, 160.1, and 156.1 mAh g^{-1} at 0.1C, 0.3C, 0.5C, and 1C, respectively. This series of electrochemical results demonstrate highly reliable performance for a decent number of cycles, even at high current densities and is attributable to the Mg layer that facilitates reversible overcharging.

X-ray microscopy (XRM) combined with micro-computed tomography (μ -CT) was utilized to analyze the anode interfaces after Li plating and stripping.^[24] Following the first overcharge-discharge cycle during half-cell operation with a modified N/P ratio of 0.22, the interface between the anode and SE was visualized for analysis. In the plain SiGr anode, cracks were initiated at the interface due to the stress resulting from the unstable deposition of excess Li, which caused the propagation of these cracks through the SE (Figure 5A). An internal pore mapping image revealed substantial contact loss along the interface (Figure 5B), and the x - y 2D image captured at the anode-SE interface revealed irregular morphologies (Figure 5C). In contrast, the significantly smoother interface of the MgSiGr anode is attributed to the stable deposition of Li beneath the Li-Mg alloy layer, which prevented crack formation (Figure 5D). Furthermore, the interface porosity was much lower compared to that of SiGr (Figure 5E), with the 2D interface having a uniform, flat appearance (Figure 5F).

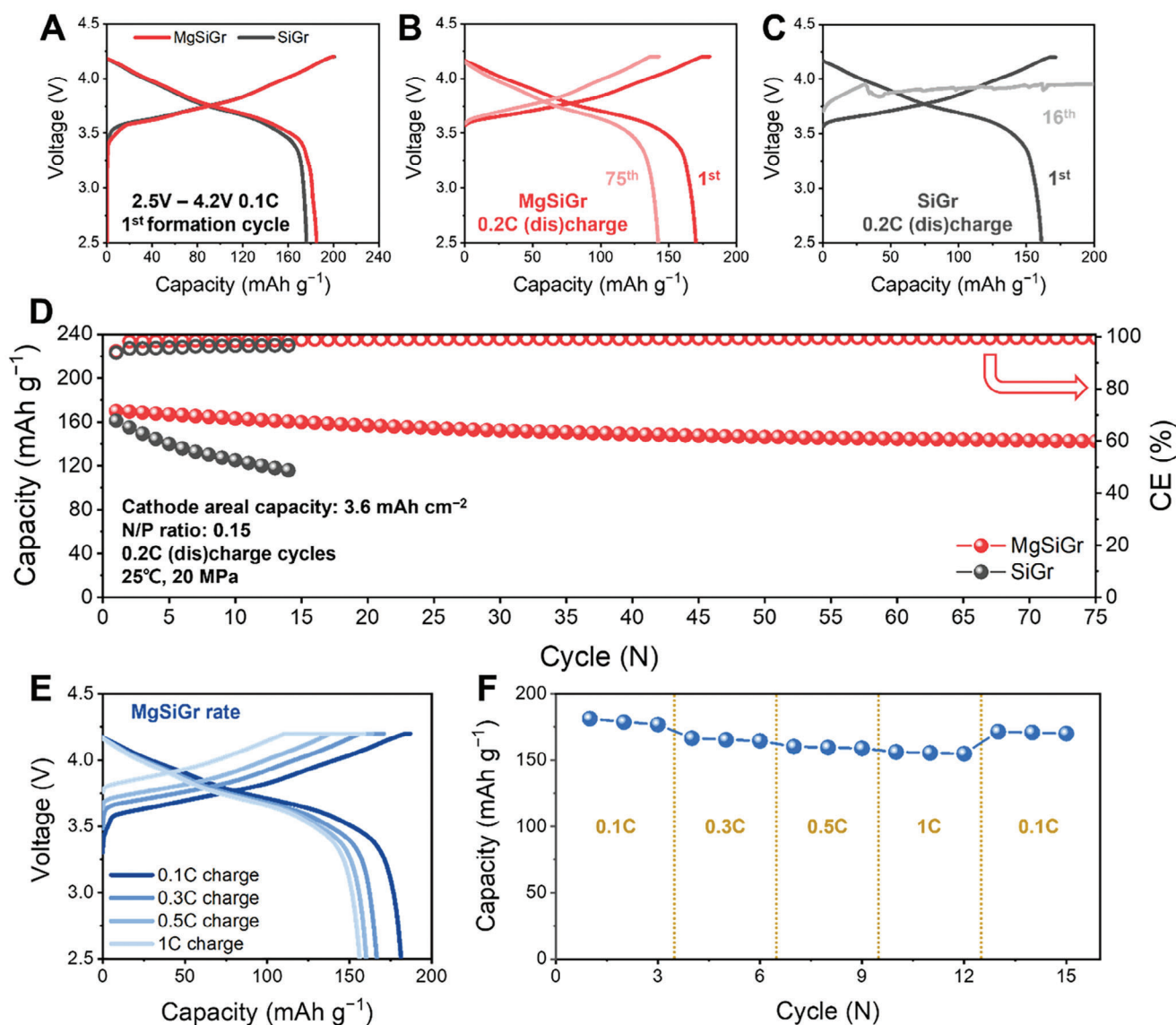


Figure 4. Full-cell evaluations of the (Mg)SiGr anodes in pairing with a LiNbO_3 -coated NCM811 cathode (N/P ratio = 0.15). A) The first formation voltage profiles of the (Mg)SiGr anodes at a current density of 0.1C ($1\text{C} = 3.6\text{ mA cm}^{-2}$). Voltage profiles of the B) MgSiGr and C) SiGr anodes during cycling at 0.2C. D) Cycling performance of the corresponding 0.2C (dis)charge evaluation. E, F) The rate capability of the MgSiGr anode at various charging rates and a fixed discharging rate of 0.1C. E) Voltage profiles and F) discharging capacities.

The x - z cross-sectional 2D images also confirmed the difference in crack propagation between the two samples (Figure S22, Supporting Information). Notably, the smooth contact between the MgSiGr anode and SE, facilitated by the Li deposition at the bottom, aligns with one of the critical goals of this study, namely to enable operation under low stack pressure conditions.

The full-cell assessment was subsequently conducted at low stack pressure (3 MPa) to verify the operational feasibility of the MgSiGr anode. Precise control of the stack pressure was ensured by positioning a spring with a specific spring constant atop the cell (Figure S23, Supporting Information). For comparison, in addition to plain SiGr, a thin Li metal anode with a thickness identical to that of the MgSiGr anode (10 μm) was employed to directly evaluate the impact of the Li plating position (top vs bottom:

top for Li and SiGr, bottom for MgSiGr). An abnormal capacity increase and considerable noise were evident from the voltage profiles of the plain SiGr anode within 15 cycles, indicating the onset of soft short circuits (Figure 6A).^[25] At the 21st cycle, this anode also entered the infinite-charging phase as a result of persistent short circuits (Figure S24, Supporting Information). Similarly, the Li metal anode exhibited early short-circuiting behavior at the 15th cycle due to the growth of Li dendrites (Figure 6B). Contrary to this, the MgSiGr anode displayed stable voltage profiles for both the 1st and 15th cycles (Figure 6C). This anode also maintained 64.7% of the original capacity after 75 cycles under the challenging conditions of low stack pressure, room temperature, and a low N/P ratio of 0.66 (Figure 6D). Additionally, the (Mg)SiGr full-cells were evaluated in the pouch-cell format with

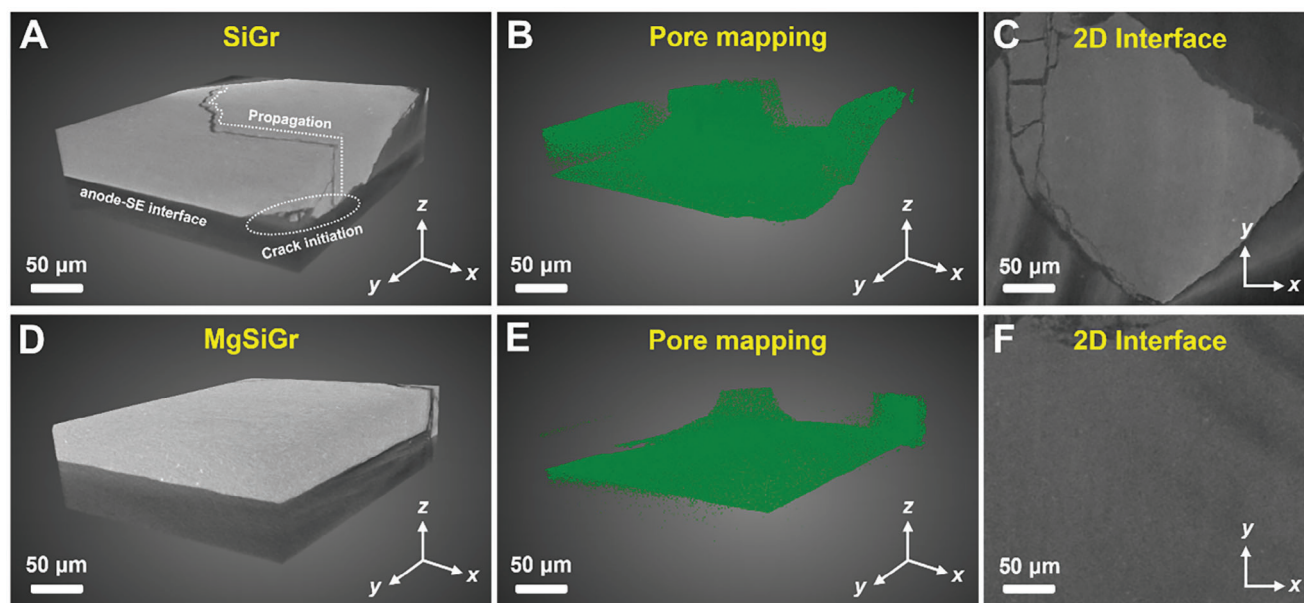


Figure 5. X-ray microscopy (XRM) with micro-computed tomography (μ -CT) results of the anode-SE interfaces after the first overcharge–discharge cycle. A–C) XRM images of the SiGr anode: A) 3D image at the anode-SE interface, B) pore mapping of the corresponding 3D image, and C) x-y 2D image at the anode-SE interface. D–F) XRM images of the MgSiGr anode: D) 3D image at the anode-SE interface, E) pore mapping of the corresponding 3D image, and F) x-y 2D image at the anode-SE interface.

a size of $20 \times 20 \text{ mm}^2$ and an N/P ratio of 0.6. Under a stack pressure of 3 MPa, the MgSiGr cells exhibited well-defined charge and discharge profiles. In contrast, the SiGr cells experienced short-circuiting during the first formation cycle at 0.1C, showing infinite charging behavior (Figure S25, Supporting Information). For the MgSiGr cell, the transition from the SiGr charging stage to the Li plating stage (overcharging) proceeded smoothly and was attributed to the lithophilicity of Mg. When cycled at 0.5C, the MgSiGr pouch-cell sustained short-circuit-free cycling for 75 cycles to demonstrate decent cyclability at room temperature and low stack pressure of 3 MPa (Figure 6E).

Figure 7 schematically summarizes the effect of the anode choice on the reversibility of combined Li intercalation and plating cycles. The aforementioned findings coherently inform that the MgSiGr-based anode achieves superior reversibility in both pellet-cells and pouch-cells under low stack pressure by taking advantage of the lithophilic Mg layer at the bottom, which directs Li plating toward the current collector. As counter-examples, the bare SiGr and Li metal anodes adversely experience indiscriminate Li dendritic growth because of the absence of lithophilic seeds. Thus, the interfacial stability, the most critical factor for the cyclability of ASSBs operating at low stack pressure, highly depends on the lithiation kinetics of the anode, which, in turn, is largely determined by its lithophilicity and geometrical features such as the pore volume.

Low N/P ratio conditions enhance battery energy density but compromise long-term durability due to volume changes during overcharging, especially under low stack pressure. Potential improvements may involve the implementation of advanced elastic binders to maintain intimate inter-particle contact, thereby preserving both proper Li insertion and plating dynamics through prolonged cycling.

3. Conclusion

The Li storage mechanism in the anode plays a decisive role in achieving high-energy-density ASSBs, which inevitably contain an SE layer of a certain thickness. From the perspective of energy density, Li metal deposition is the most suitable mechanism to resolve this dilemma. However, during actual cell operation, warranting repeated uniform Li (de) plating during cycling remains a formidable challenge, particularly under operating conditions that are practically viable in terms of the temperature and stack pressure, considering that the interface of the SE-electrode is prone to Li dendritic growth and subsequent degradation. To overcome this hurdle, we adopted the established chemistry of SiGr for the initial charging process for stable early Li storage, followed by Li plating for overcharging to maximize the Li storage capability. Moreover, a lithophilic metal, Mg, was inserted at the base of the composite anode to uniformly direct the deposition of overcharged Li to the bottom of the anode and thus enhance its long-term reliability. This anode design allows successful operation at remarkably low N/P ratios at room temperature and at low stack pressure. Overall, this study offers a useful design strategy and operational mechanism for overchargeable anodes in ASSBs with high energy density and sustainable operation.

4. Experimental Section

Electrode Preparation: The Mg layer for the MgSiGr anode was formed by depositing a 200 nm-thick layer of elemental Mg onto a SUS current collector (SUS316L-H foil, Wellcos) via metal sputtering. The SiGr composite powder was prepared by dry-mixing Si nanoparticles (NanoAmor, D50 = 40 nm) with artificial graphite in a 1:6 weight ratio, followed by blending with LPSCl (NEI Corporation) (7:3 weight ratio) using an agate

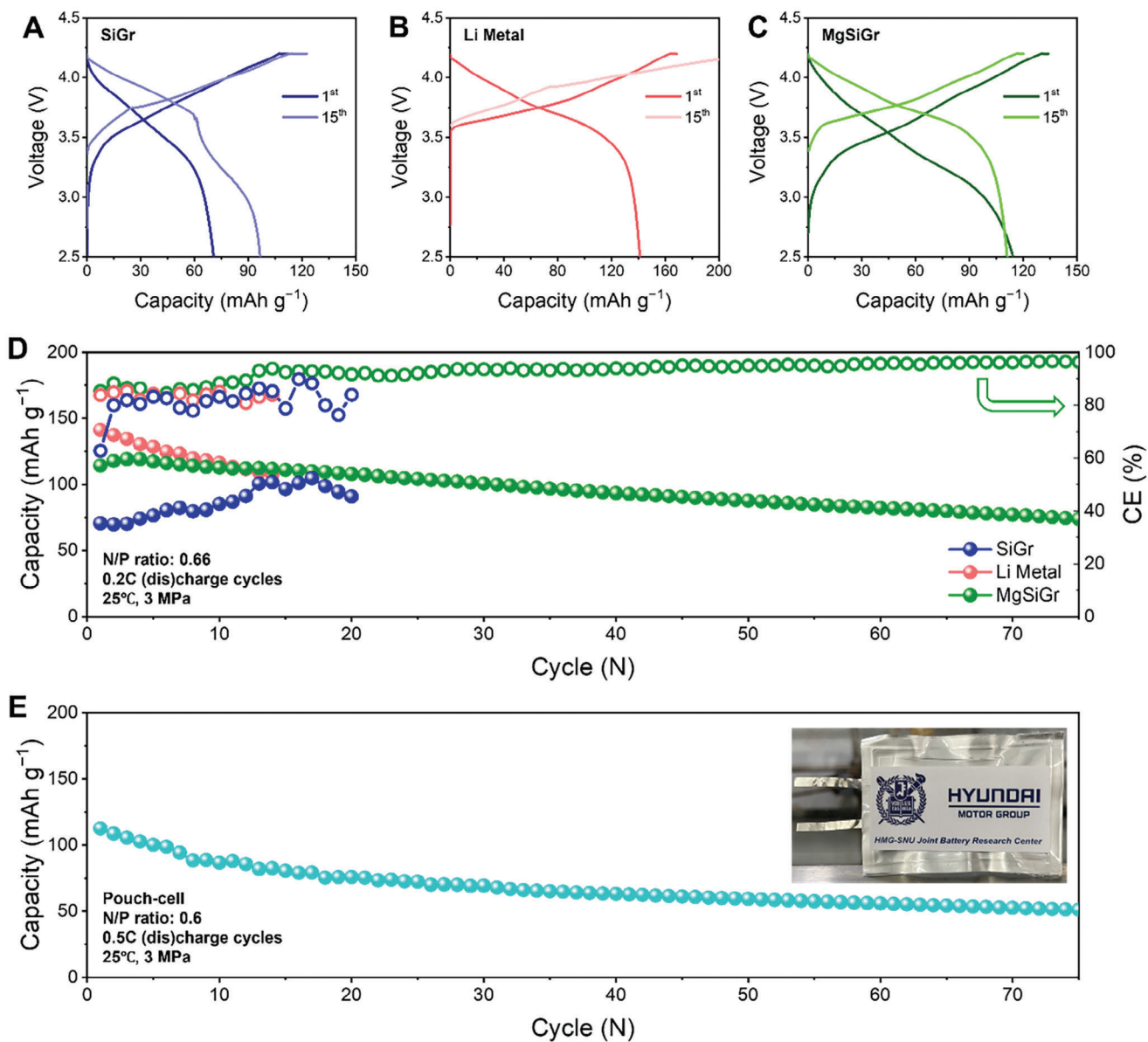


Figure 6. Full-cell evaluation under practical conditions at room temperature (25 °C) and low stack pressure (3 MPa). Voltage profiles of the A) SiGr, B) Li metal (10 μm -thick), and C) MgSiGr anodes at 0.2C for both charge and discharge (N/P ratio = 0.66). D) Cycling performance at 0.2C for both charge and discharge. E) Pouch-cell performance of the MgSiGr full-cell (N/P ratio = 0.6).

mortar and pestle. The MgSiGr anode was assembled by loading the SiGr composite powder onto the Mg-coated SUS current collector. The plain SiGr anode was prepared through the same procedure but using an uncoated SUS current collector. The mass loading of the SiGr was 0.8 mg cm⁻². The composite cathode, which contained LiNbO₃-coated NCM811 (supplied from Wellcos), LPSCI, and vapor-grown carbon fiber (VGCF) in a 68:30:2 weight ratio, was prepared using the dry-mixing method. The cell preparation was completed by pelletizing the corresponding powders at 380 MPa during cell assembly. Cathode loading was set at 20 mg cm⁻² for high-stack pressure evaluations and 6 mg cm⁻² for low-stack pressure tests.

Cell Assembly: All solid state half-cells were assembled by pelletizing LPSCI (150 mg) into a SE layer with a diameter of 13 mm, followed by cold pressing at 150 MPa. The (Mg)SiGr anode was placed under the SE

layer and pressed at 380 MPa, following which Li foil was placed on top. The full-cells were assembled similarly by placing a composite cathode and a (Mg)SiGr anode on either side of the SE pellet, with subsequent compression at 380 MPa. For the Li metal anode full-cell, the composite cathode was placed beneath the SE pellet, compressed at 380 MPa, and Li foil (10 μm thick) was positioned on the opposite side. The stack pressure was set at either 20 or 3 MPa using a spring with a specific spring constant for precise pressure control. All procedures were performed in an Ar-filled glove box.

Preparation of Pouch-Cell: The composite cathode for pouch-cell evaluations was prepared by dispersing LiNbO₃-coated NCM811, LPSCI, VGCF, and NdBR binder in butyl butyrate in a weight ratio of 70:26:1.5:2.5. The slurry was cast onto Al foil using the doctor blade method, then dried at 100 °C for 15 h. The MgSiGr anode was prepared similarly, by mixing

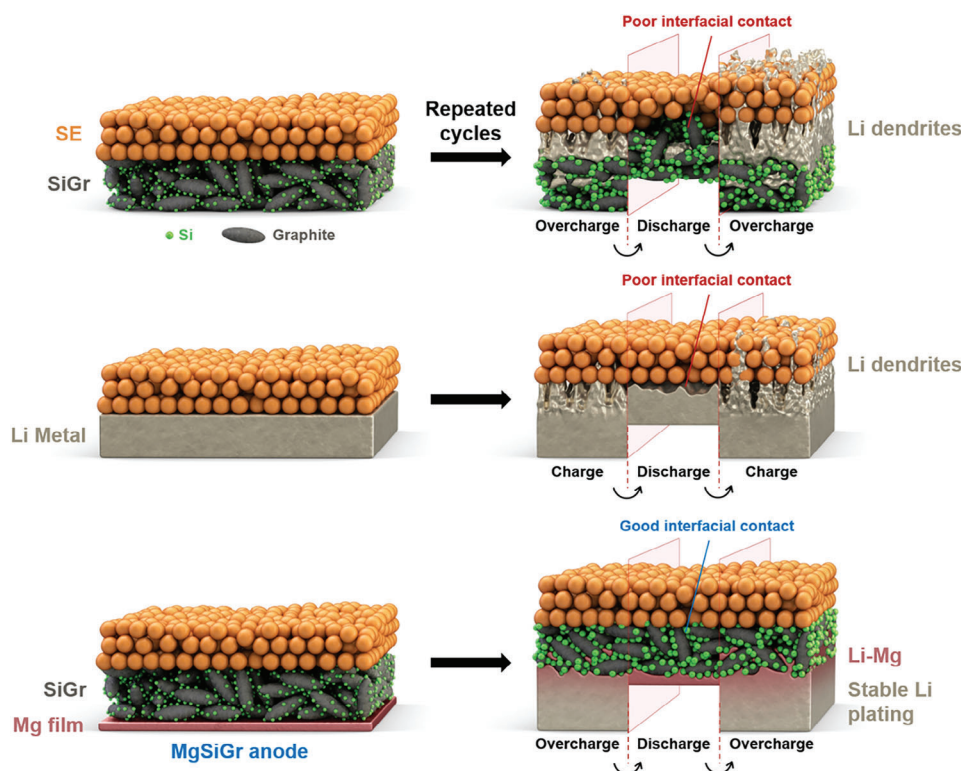


Figure 7. Comparative illustration of charging processes in SiGr, Li metal, and MgSiGr anodes.

SiGr and LPSCI in a 1:1 weight ratio with NdBR binder (3 wt.%). The mixture was coated onto Mg-coated SUS film and dried at 100 °C for 15 h to form a 10 μm -thick MgSiGr layer. The mass loading of the SiGr was 0.8 mg cm^{-2} . SE sheets containing LPSCI were also prepared using the same doctor blade method. LPSCI and the NdBR binder were dispersed in butyl butyrate, followed by casting onto a polyethylene terephthalate (PET) release film, to form a 100 μm -thick SE sheet on the PET film. A 20 $\times$ 20 mm^2 pouch-cell was assembled by removing the PET film and stacking the electrodes and SE sheet in a laminate bag. After vacuum sealing, the bag was pressurized at 450 MPa and 75 °C for 15 min using a warm isostatic press (WIP, ISA-W50-6000, Ilshin Autoclave). The fabricated pouch-cell was positioned between insulating polyether ether ketone (PEEK) substrates and pressurized at 3 MPa for electrochemical cycling. This stack pressure was applied by tightening bolts and nuts at the four substrate corners with a torque of 3.5 Nm.

Characterization Method: Top and cross-sectional images of the electrodes were acquired using field emission-scanning electron microscopy (FE-SEM, JSM-7800F Prime, JEOL, Japan) and focused ion beam (FIB, Helios 650, FEI, USA), respectively. The crystal structure of the SiGr was analyzed via X-ray diffraction (XRD, New D8 Advanced, Bruker, USA). 3D imaging and pore assessment of the anode-SE interfaces were conducted using high-resolution X-ray microscopy (XRM) with micro-computed tomography ($\mu\text{-CT}$, Xradia 620 Versa, Carl Zeiss, USA) at the National Center for Inter-university Research Facilities (NCIRF), Seoul National University. The interfaces were exposed to X-rays for 4 h, and the diffractometer was operated at 80 kV, 125 μA , and 10 W. The raw XRM data were processed with Dragonfly software (ORS) for 3D image construction.

Electrochemical Characterization: All of the electrochemical evaluations were conducted at room temperature (25 °C). The areal capacity of the half-cell was galvanostatically determined by time-cutoff discharge within a 0–0.1 V or 0–1.5 V (vs Li/Li⁺) range using a battery cycler (WBCS 3000, WonATech, South Korea). Full-cell evaluations were conducted within the 2.5–4.2 V range in constant current (CC) and constant

voltage (CV) modes for charging, and CC mode for discharging. Rate capability tests involved a discharge current density of 0.1C, with charge currents of 0.1C, 0.3C, 0.5C, and 1C. Cyclic voltammetry was performed in a 0–1.5 V (vs Li/Li⁺) range at 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was carried out within a frequency range of 1 MHz to 0.01 Hz using a potentiostat (VSP, Biologic, France), with Nyquist plots deconvoluted using EC-Lab software.

Supporting Information

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

Acknowledgements

J.O. and D.K. contributed equally to this work. J.W.C. acknowledges the National Research Foundation of Korea (NRF) (Grant No. NRF-2022M3J1A1054151), the Korea Institute of Machinery and Materials (KIMM) (Grant No. NK243H), and the Swiss National Science Foundation (SNF) (Grant No. Sinergia CRSII5_202296). J.W.C. also acknowledges support from the Institute of Engineering Research (IOER), the Research Institute of Advanced Materials (RIAM), and the Institute for Battery Research Innovation (IBRI) at Seoul National University. This work was also supported by Hyundai Motor Company.

Conflict of Interest

The 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

all-solid-state battery, lithiophilicity, low stack pressure, n/p ratio, over-charging

Received: October 16, 2024

Revised: November 23, 2024

Published online: December 15, 2024

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