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# Anode-Less All-Solid-State Batteries Operating at Room Temperature and Low Pressure

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Anode-less all-solid-state batteries (ASSBs) are being targeted for next-generation electric mobility owing to their superior energy density and safety as well as the affordability of their materials. However, because of the anode-less configuration, it is nontrivial to simultaneously operate the cell at room temperature and low pressure as a result of the sluggish reaction kinetics of lithium (de)plating and the formation of interfacial voids. This study overcomes these intrinsic challenges of anode-less ASSBs by introducing a dual thin film consisting of a magnesium upper layer with a  $Ti_3C_2T_x$  MXene buffer layer underneath. The Mg layer enables reversible Li plating and stripping at room temperature by reacting with Li via a (de)alloying reaction with a low reaction barrier. The MXene buffer layer maintains the electrolyte-electrode interface by inhibiting the formation of voids even at low pressure of 2 MPa owing to the high ductility of MXene. This study highlights the importance of a combined chemical and mechanical approach when designing anode-less electrodes for practical adaptation for anode-less ASSBs.

## 1. Introduction

The increasing demand for reliable secondary batteries driven by the emergence of electric vehicles (EVs) and aircraft such as unmanned aerial vehicles has inspired the battery community to invest their resources in all-solid-state batteries (ASSBs) owing to the intrinsic superiority of these batteries in terms of their

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safety and energy density.<sup>[1]</sup> ASSBs represent a new generation of secondary batteries in which the liquid electrolytes in conventional lithium-ion batteries (LIBs) are replaced predominantly with ceramic solid electrolytes (SEs).<sup>[2]</sup> Among the various types of ASSBs, those that are sulfide-based are considered the most promising for commercialization due to the high ionic conductivity and advantageous mechanical properties of these sulfides.<sup>[3]</sup> Especially, researchers have demonstrated highly competitive battery performance with the argyrodite-type  $Li_6PS_5X$  (X = Cl or Br) electrolytes by utilizing their high ionic conductivity at room temperature and simple synthesis based on readily available raw materials.<sup>[4]</sup> Nonetheless, most ASSBs demonstrated thus far require high operating

temperatures and/or pressures to compensate for the relatively low ionic conductivity of SEs compared to their liquid electrolyte counterparts. Apart from this, the aforementioned operating conditions have been necessary to maintain close solid-to-solid contact during repeated charging and discharging cycles,<sup>[5]</sup> thereby posing a significant barrier in the way of making a real practical impact. Recent efforts have been devoted to lowering the operating pressure by developing a novel cathode binder that can effectively sustain physical inter-particle contacts under low pressures. For example, Kwon et al.<sup>[6]</sup> reported a three-dimensional cathode binder constructed via the in situ vulcanization of a butadiene rubber and achieved a high specific capacity of 150 mAh g<sup>-1</sup> even without external pressure. Gregory et al.<sup>[7]</sup> demonstrated a highly elastic binder, which conducts Li ions, and is composed of CO<sub>2</sub>-derived block polycarbonate ethers. This binder enabled stable cell cycling at a stack pressure of 1 MPa. Although these studies successfully realized reliable, low pressure operation, the use of lithium titanate (LTO) as the anode active material limits practical implementation due the high redox potential of LTO that restricts the energy density of a cell. Considering this progress toward milder operating conditions, research with the aim of developing high-energy density anode materials that are compatible with room temperature and low pressure is worthy of pursuing.

To increase the energy density of ASSBs, researchers have been exploring various electrode designs, particularly on the anode side.<sup>[8]</sup> In this line, the anode-less concept, from the viewpoint of the cell configuration, offers the possibility of achieving energy density close to the theoretical maximum. Lowering the cost of materials and simplifying the manufacturing scheme are other fortuitous advantages of the anode-less configuration.<sup>[9]</sup> However, anode-less ASSBs experience a rapid decline in capacity over time due to the absence of an active material that stores Li ions stably during charging and discharging. Researchers attempting to address this challenge had partial success by covering the current collector with a thin protective layer.<sup>[10]</sup> Yet, the realization of a room temperature, low pressure anode-less ASSB remains nontrivial. For example, Lee et al.<sup>[11]</sup> reported anode-less type ASSB cells with a silver-carbon composite layer in contact with a sulfide SE laver. These cells exhibited unparalleled energy density and cyclability by taking advantage of silver seeds to nucleate metallic Li in a spatially uniform manner. However, a relatively high temperature of 60 °C was required for sustainable operation due to sluggish Li ion diffusion in the composite layer. Anode-less cells that incorporate silver fluoride as a Li metal seed and that are capable of operating at room temperature were also introduced.<sup>[12]</sup> Unfortunately, the necessity for high operating pressure (i.e., 20 MPa) stands in the way of immediate commercialization.

In the current work, we developed an anode-less protective layer that enables sulfide-based ASSBs to simultaneously operate at room temperature and low pressure (2 MPa). The protective layer consists of a thin magnesium film that promotes the reversibility of Li (de)plating with a substantial capacity at room temperature. Furthermore, an additional Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene buffer layer was employed beneath the Mg film to introduce the required ductility for low pressure operation. The proposed anode-less ASSBs with the protective layer constitute a remarkable progress in that they satisfy the critical operating requirements of room temperature and low pressure for the first time as anode-less ASSBs, a major step toward their widespread commercial adoption. Taking a broader perspective, this investigation highlights the synergistic effect of chemical (lithiophilic metallic seeding) and mechanical (high ductility) strategies in advancing anode-less ASSBs to practically viable energy storage options.

#### 2. Results and Discussion

Aiming to realize anode-less ASSBs that can operate at room temperature, we deposited a lithiophilic thin film onto the anode current collector and evaluated it as an anode-less protective layer. The thin lithiophilic film was incorporated to foster an alloying reaction between the metallic thin film and Li ions and thereby induce uniform Li plating and stripping through the anode-less electrode over cycling. Importantly, the limited thickness of the metallic film does not sacrifice the energy density of the corresponding cell much, thus preserving the main merit of the anodeless concept.<sup>[13]</sup> The (de)alloying reaction was expected to largely resolve the inferior reversibility of Li (de)plating, the major disadvantage of anode-less systems based on the absence of an active material with well-defined storage sites or space. The (de)alloying reaction was therefore envisaged to greatly limit the capacity decay over cycling.

Four metals, namely Mg, Ag, Au, and Zn, were chosen for this investigation in consideration of their lithiophilic properties

characterized by the high solubility of Li in these metals and the low overpotential during lithiation.<sup>[14]</sup> To evaluate their performance as an anode-less electrode, anode-less|SE|Li all-solid-state half-cells were tested using an argyrodite type Li<sub>6</sub>PS<sub>5</sub>Cl (LPSCl) SE and a thin metallic film with a thickness of 200 nm at room temperature at a high stack pressure of 10 MPa. Each Li plating process was allowed to progress for 3 h at a current density of 1 mA cm<sup>-2</sup>. The plating period of 3 h commenced once the voltage of the cell reached 0 V. The 1st voltage profiles of the cells with the four films indicate that Li plating and stripping in the first cycle was kinetically facile, as represented by their low overpotentials (Figure 1A). The initial coulombic efficiencies (ICEs) were 96.8%, 96.2%, 96.7%, and 92.7% for Mg, Ag, Zn, and Au, respectively (inset in Figure 1B). Along with its highest ICE, Mg demonstrated the longest cycle life, surpassing 1100 h, whereas the cells with the other metals failed earlier: 270 h with Ag, 50 h with Zn, and 210 h with Au (Figure 1C). The longer cycle life of Mg and Ag compared to that of Zn and Au can be explained by their distinct reaction mechanisms; whereas Mg and Ag undergo a kinetically favorable solid-solution reaction with Li, Zn, and Au engage in an intermetallic reaction with Li.<sup>[15]</sup> The discrete phase boundary formed during the intermetallic reaction is well known to be responsible for the relatively sluggish kinetics when Li ions proceed through the given metallic medium, most notably compared to its solid-solution counterpart, in which the reaction proceeds without forming clear phase boundaries.<sup>[16]</sup> Moreover, the superior performance of Mg over Ag can be attributed to the higher diffusion coefficient of Li in Mg compared to Ag.[8c,17] The higher diffusion coefficient enhances the uniformness of Li deposits in the early cycles by facilitating more homogeneous nucleation during Li deposition and mitigating the formation of voids during Li stripping. In the same context, the uniformness of Li deposits in the early cycles greatly affects that of Li deposits in the subsequent cycles and thus the cyclicality in the entire period.<sup>[18]</sup>

Next, we focused on the effect of the thickness of the Mg thin film. To this end, additional half-cell plating-stripping tests were conducted by varying the thickness of the Mg film as a parameter. As the thickness of Mg decreased, the ICE increased (**Figure 2**A), but the lifetime shortened (Figure 2B). Specifically, the ICE values of the Mg thin films with thicknesses of 50 nm, 200 nm, and 500 nm were 98.5%, 96.8%, and 88.2%, respectively, and their cycle life before short-circuiting was 140, 1100, and 1450 h. The observed trend can be attributed to the fact that a thicker Mg thin film provides a greater amount of lithiophilic Mg. The greater amount of Mg can offer a larger number of nucleation sites towards more uniform Li deposition for the given areal capacity, enhancing the cyclability.

However, as the thickness of the Mg thin film increases, the volume expansion of Mg that accompanies the alloying reaction with Li becomes more severe, leading to mechanical destruction of the film and destabilization of the SEI layer, explaining the inferior reversibility of Li plating and stripping. Based on the evaluation of a capacity of 3 mAh cm<sup>-2</sup>, the Mg film with the thickness of 200 nm exhibited the most balanced and reliable efficiency and lifespan characteristics, and led us to proceed with this sample in subsequent analyses. This anode-less electrode was then paired with a LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811) cathode for evaluation in an all-solid-state full-cell setting. Even with a high areal capacity of 6.2 mAh cm<sup>-2</sup> (loading of active material = 32.5 mg cm<sup>-2</sup>),

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**Figure 1.** Half-cell plating stripping evaluation of a representative lithiophilic metal thin film at room temperature (25 °C) and high stack pressure (10 MPa). A) First cycle voltage profile of the half-cell plating stripping test, with a current density of 1 mA cm<sup>-2</sup> and capacity of 3 mAh cm<sup>-2</sup>. B) Coulombic efficiency and C) time versus voltage profile of the corresponding test.

a first specific capacity of 190 mAh g<sup>-1</sup> with an ICE of 89.6% was achieved at a stack pressure of 20 MPa (Figure 2C). Unlike a control full-cell with a bare current collector (SUS), a short slopping region was observed in higher magnification in reflection of the alloying reaction of Mg (Figure S1, Supporting Information). This slopping region also shows lower overpotential during the initial charge as a result of facilitated nucleation. This cell also cycled quite decently such that 82.4% of the original capacity was preserved after 30 cycles with an average CE of 98.9% (Figure 2D). These initial results demonstrated the feasibility of operating an all-solid-state full-cell incorporating the Mg thin film at room temperature with commercially viable cell specifications.

The aforementioned results portrayed the picture that the inevitable problem of Li dendrite growth in the case of an anodeless system (**Figure 3**A) can be effectively addressed by depositing a lithiophilic Mg thin film on the current collector (Figure 3B). The electrodes with the Mg thin film demonstrated high reversibility and a competitive lifespan at room temperature, albeit requiring high-pressure conditions of 10–20 MPa. The subsequent challenge would therefore be to lower the stack pressure to increase the practical viability of the anode-less ASSBs. Toward this end, a single bare Mg thin film was considered to be inadequate because it was unlikely to remain in contact with the SE-electrode during cycling because of the significant volume changes the film undergoes during the (de)alloying reaction with Li. Attempting to solve this problem, we proposed the insertion of an additional soft and ductile layer underneath the Mg film to release the stress caused by the volume change of the film (Figure 3C). The absorption of the stress by this additional layer would mitigate the stress that would otherwise accumulate in the SE and destroy the SE-electrode contact during cycling. Importantly, the ductility of this buffer layer was also expected to allow intimate contact between the SE and electrode even when the cell is being operated at low pressure.

The above-mentioned buffer zone was realized by inserting a high-ductility layer beneath the Mg film to construct a double protective layer. Our choice for this layer fell upon  $Ti_3C_2T_x$ , also known as MXene, a ceramic material with a 2D planar structure composed of a transition metal bonded to carbon or nitrogen. Synthesized by etching the anisotropic hexagonal MAX phase with a strong acid such as hydrofluoric acid (HF), hydrochloric acid (HCl), and ammonium hydrogen fluoride (NH<sub>4</sub>HF<sub>2</sub>),<sup>[19]</sup> MXene constitutes a structure consisting of layers of transition metal carbides with polar substituents such as -OH and -F on its surface. The functional groups and crystal structure of MXene were confirmed by Fourier-transform infrared spectroscopy (FT-IR) (Figure S2A, Supporting Information) and X-ray diffraction (XRD) results (Figure S2B, Supporting Information),

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**Figure 2.** A and B) Half-cell plating-stripping test of Mg thin film with various thicknesses at a current density of 1 mA cm<sup>-2</sup> and capacity of 3 mAh cm<sup>-2</sup>. Stack pressure = 10 MPa. A) Coulombic efficiency and B) time versus voltage profile. C,D) Full-cell evaluation with NCM811 cathode. Loading of the cathode is 32.5 mg cm<sup>-2</sup>. Stack pressure = 20 MPa. (C) First cycle voltage profile and (D) cycling performance at a current density of 0.1C.

respectively. This functionality imparts excellent binding capabilities to MXene, which readily forms hydrogen bonds with neighboring substances with polar substituents.<sup>[20]</sup> Due to its unique arrangement of 2D molecular nanosheets in a multilayer structure (Figure S3, Supporting Information), MXene has exceptional properties, such as high ductility and electrical conductivity, which most other ceramics do not offer simultaneously.<sup>[21]</sup> This combination of useful properties ensures that MXene is a highly promising material for a wide range of applications,<sup>[22]</sup> including post-Li-ion batteries.<sup>[23]</sup>

The double layer was fabricated by coating the anode current collector with a thin buffer layer of  $Ti_3C_2T_x$  MXene using the slurry casting method, after which a Mg thin film was sputtered on top of the MXene layer. Note that reduced graphene oxide (rGO) was incorporated in the MXene layer to enhance the dispersion of MXene. Top and cross-sectional scanning electron microscopy (SEM) images (Figure S4, Supporting Information) confirmed that the rGO was well distributed between the MXene flakes, thereby preventing the MXene from aggregating. The slurry was prepared in the form of an aqueous solution containing carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR). Details of the fabrication method appear in the Experimental Section. The MXene buffer layer had a thickness of  $\approx$ 5 µm, and energy-dispersive spectroscopy (EDS) imaging confirmed uniform coverage of the MXene layer by Mg (Figure S5, Supporting Information).

Nano-indentation analysis was employed to compare the ductility of the bare Mg film with that of the MXene/Mg double layer electrodes. The ductility of the electrodes was measured by applying a force of 0.07 mN to the electrodes, and the depth and force were then monitored while the tip was being released. The maximum depression depth for the simple Mg electrode was 41.4 nm, and the recovered depth was  $\approx 6.8$  nm when the force was released (Figure 3D). In contrast, the MXene/Mg electrode exhibited a depression depth of 274.9 nm, which was nearly 7 times greater than that of the bare Mg electrode, and reflected the superior ductility of MXene. The recovered depth of the electrode covered with the MXene/Mg double layer was also large at 216.0 nm (Figure 3E). The elastic recovery ratio is defined as the ratio of the recovered depth to the maximum depression depth (Equation 1):

Elastic recovery ratio 
$$=$$
  $\frac{\text{Recovered depth}}{\text{Max depression depth}}$  (1)

The elastic recovery ratio of the bare Mg was only 16.5%, whereas that of the MXene/Mg was far higher at 78.6%. In the case of MXene/Mg, the recovered depth exceeded the non-recovered depth (Figure S6, Supporting Information), revealing the elasticity of the buffer. Another parameter that provides a useful assessment of the elasticity is the amount of energy conserved, where the integrated area under the curve of the load versus indentation depth corresponds to the energy consumed during indentation and unindentation. The difference between the integrated areas of the loading and unloading curves represents the plastic work (P), whereas the integrated area below the unloading curve represents the elastic work (E).<sup>[24]</sup> The detailed parameters are summarized in the Supporting Information (Table S1, Supporting Information). The ratio of elastic work to plastic work can be defined as

Elastic work / Plastic work ratio  $(E/P \text{ ratio}) = \frac{Elastic \text{ work}}{Plastic \text{ work}}$  (2)

The E/P ratio of the bare Mg was calculated to be 0.097, indicating that the plastic deformation force of Mg is more than ten SCIENCE NEWS \_\_

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Figure 3. Schematic illustration of lithiation with A) bare current collector, B) Mg thin film, and C) MXene/Mg double-layer. Nanoindentation profiles of D) Mg and E) MXene/Mg anode-less electrodes.

times as strong as the elastic recovery force. However, the addition of the MXene layer underneath Mg resulted in an E/P ratio of 3.744. Thus, the MXene/Mg double layer electrode amplified the elastic recovery compared to the plastic deformation based on the ductility of MXene.

The electrochemical performance of the MXene/Mg electrode was evaluated in comparison with its bare Mg counterpart. Initially, a half-cell Li plating-stripping test was conducted at room temperature under high pressure of 10 MPa. The results showed that the CEs of both MXene/Mg and Mg were similar throughout cycling (Figure S7A, Supporting Information). However, the lifespan of MXene/Mg before short-circuiting was shorter at 350 h, decreasing from 1100 h for Mg (Figure S7B, Supporting Information). The inferior durability of MXene/Mg is attributed to the roughened surface resulting from the addition of the MXene layer, which could more easily give rise to short circuits under high pressure. In this regard, the flatter surface of the bare Mg metal layer deposited by sputtering (Figure S8, Supporting Information) would be more tolerant and experience less shortcircuiting at high pressure. These results suggested that increasing the ductility of the current collector of the anode-less cell may not necessarily be beneficial for improving the key performance indicators of an anode-less ASSB cell under high pressure conditions.

As the next step, we proceeded to lower the stack pressure and found the trend to reverse itself. The half-cell plating-stripping tests at 2 MPa indicate that MXene/Mg is conspicuously superior to Mg in terms of both its Coulombic efficiency and lifespan. At a current density of 0.2 mA cm<sup>-2</sup> and capacity of 0.5 mAh cm<sup>-2</sup> (Figure S9, Supporting Information), the ICE of Mg was 60.8%, whereas that of MXene/Mg was 75.4%, and the lifespan until the point of short-circuiting was 130 and 380 h, respectively. These results reveal the significance of the ductility of anode-less electrodes when operated at low pressures. The same trend was observed even with a current density of 0.5 mA cm<sup>-2</sup> and capacity of 1.0 mAh cm<sup>-2</sup> (Figure S10, Supporting Information). We extended the electrochemical testing to full-cells by pairing with an NCM811 cathode while retaining the hitherto established



**Figure 4.** Full-cell evaluation of Mg thin film-based anode-less electrode with NCM811 cathode at room temperature (25 °C) and low stack pressure (2 MPa). Loading of the cathode is 20 mg cm<sup>-2</sup>. Voltage profiles of 1<sup>st</sup> and 30<sup>th</sup> cycle, with A) Mg and B) MXene/Mg anode-less electrode. C) Cycling performance of the corresponding test with a current density of 0.1 C. EIS Nyquist plots of the full-cells D) before cycling and E) after 10 charge-discharge cycles.

conditions of room temperature and 2 MPa. The cross-sectional SEM images of the as-fabricated full-cell (Figure S11, Supporting Information) and the elemental mapping of the anode interface therein (Figure S12, Supporting Information) jointly indicate that the MXene/Mg bilayer structure remained intact even after pressuring the cell assembly during the fabrication. The initial discharge capacities of the Mg and MXene/Mg cells were 134 mAh g<sup>-1</sup> (Figure 4A) and 132 mAh g<sup>-1</sup> (Figure 4B), respectively. Despite the similar charge and discharge profiles, the overpotential of the Mg cell rapidly increased with cycling,

which explains its more severe capacity decay (Figure 4C). At this point, we need to emphasize that the low pressure operation of anode-less ASSBs has been rarely reported thus far owing to the weakened SE-anode contact (Table S2, Supporting Information). Cross-sectional SEM images of the MXene/Mg cell after charging at 2 MPa revealed uniform distributions of Mg and Li deposits above the MXene layer (Figure S13, Supporting Information), highlighting the role of the MXene layer in relieving the stress caused by the volume change of plated Li and therefore minimizing the increase in the interfacial resistance. A control www.advancedsciencenews.com

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Figure 5. X-ray microscopy (XRM) with microcomputed tomography ( $\mu$ CT) of the anode-SE interfaces after 10 cycles of full-cell operation at room temperature and stack pressure of 2 MPa.

electrode with only bare MXene layer without the Mg metal layer showed severe capacity fading (Figure S14, Supporting Information), highlighting the importance of the synergistic effect of the two layers in achieving uniform deposition and stripping of Li under low stack pressure.

The impact of the MXene buffer layer on the internal cell resistance was investigated by conducting electrochemical impedance spectroscopy (EIS) analysis of the full-cell at room temperature and low pressure. In the Nyquist plots (Figure 4D,E), the x-axis intercept represents the bulk electrolyte resistance  $(R_{\rm h})$ , whereas the semi-circle corresponds to the charge transfer resistance  $(R_{CT})$ .<sup>[25]</sup> Before cycling (Figure 4D), the  $R_b$  and  $R_{CT}$  of bare Mg were 140.2  $\Omega$  cm<sup>2</sup> and 38 k $\Omega$  cm<sup>2</sup>, respectively. The equivalent circuits that were used to fit the Nyquist plots and the corresponding EIS fitting curves are presented in Figure S15 (Supporting Information). For the MXene/Mg, interestingly, we observed an additional semi-circle at early frequencies (enlargement in Figure S15A, Supporting Information). We attributed this semi-circle to the additional R<sub>CT</sub> contributed by the MXene layer beneath the Mg film and denoted it  $R_{CT1}$  while the second main semi-circle corresponding to the overall R<sub>CT</sub> was designated  $R_{CT2}$ . Our fitting with this equivalent circuit yielded  $R_{CT1}$  and  $R_{CT2}$  values of 1151  $\Omega$  cm<sup>2</sup> and 32 k $\Omega$  cm<sup>2</sup>, respectively. The kilo-ohm level of  $R_{CT}$  can be explained by the cell stack pressure as low as 2 MPa, which limits physical contact between the solid components inside the cell before cycling. These resistances decreased to a few hundred ohms once the cell was electrochemically cycled, as the Li occupied the voids inside the cell. For example,  $R_{CT}$  decreased to 571 and 293  $\Omega$  cm<sup>2</sup> for Mg and MXene/Mg, respectively, after 10 cycles (Figure 4E). These values indicate that  $R_{CT}$  of the two cells became quite distinct during cycling even though their original values were not significantly different before cycling. R<sub>CT</sub> reflects the physical contacts among the cell components in a way that the loss of physical contacts disrupts the pathway for efficient electron transfer, resulting in an increase in  $R_{CT}$ .<sup>[25,26]</sup> The distinct  $R_{CT}$  values point to the fact that the MXene buffer layer effectively mitigates the increase in  $R_{CT}$ caused by inter-particle contact loss under low pressure. Additionally,  $R_{CTI}$ , which reflects the MXene layer before cycling, disappeared after 10 cycles, resulting in only one semicircle, similar to the bare Mg cell. This phenomenon is ascribed to the fusion of the MXene layer with Mg and Li on top during cycling, which unified the charge transfer mode.

(A, B, and C) XRM images of Mg anode-less electrode: (A) 3D image, (B) pore mapping, and (C) 2D image of the anode-SE interface.

(D, E, and F) XRM images of the MXene/Mg anode-less electrode: (D) 3D image, (E) pore mapping, and (F) 2D image of the anode-SE interface.

To evaluate the degree of contact loss relaxation at the interfaces, X-ray microscopy (XRM) was employed in conjunction with micro-computed tomography (µ-CT). In particular, we visualized the three-dimensional (3D) morphology of the anode interface. By capturing a series of 2D transmission images of a rotating sample, it is possible to reconstruct an X-ray CT image and visualize the high-resolution 3D structure of the sample.<sup>[27]</sup> After 10 cycles of full-cell operation under 2 MPa stack pressure, the cell was disassembled, and the interface between the anode and the SE layer was analyzed in detail. Severe contact loss resulting from the volume change during charging and discharging was observed in the Mg electrode (Figure 5A), and mapping of the internal pores revealed a porosity of  $\approx 28\%$  (Figure 5B). Additionally, the 2D SEM image (Figure 5C) showed that the interface between the anode and SE had been roughened, indicating severe damage to the contact at the interface. In contrast, for the MXene/Mg electrode, the contact between the anode and SE ADVANCED SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com

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was much smoother (Figure 5D) because of the stress released by the MXene buffer layer, resulting in an internal porosity of only 6% (Figure 5E). Furthermore, the 2D image indicates that the anode-SE interface remained largely flat (Figure 5F), which points to the fact that its superior capacity retention is associated with sustained anode-SE contact.

## 3. Conclusion

In summary, this paper reports a dual thin film as a protective layer for sulfide-based anode-less ASSBs. Mg was chosen for the upper layer from among the lithiophilic metal candidates that can form an alloy with Li to allow the cell to operate at room temperature based on the low energy barrier of this metal for lithiation. As the Mg layer alone cannot adapt to the volume change of the electrode during Li plating and stripping, a ductile MXene layer was integrated and inserted underneath to release the mechanical stress and therefore enable the cell to operate at low pressure (i.e., 2 MPa). The 2D and 3D microstructural analyses verified that the highly ductile double layer structure sustains the anode-SE interface by buffering the stress. The proposed double-layer strategy plays a key role in realizing the first anode-less ASSBs to date operating simultaneously at room temperature and low pressure and offers useful insights regarding the need to take both chemical and mechanical considerations into account together to achieve practically viable anode-less ASSBs capable of simultaneously operating at room temperature and low pressure.

#### 4. Experimental Section

Synthesis of  $Ti_3C_2T_x$  MXene:  $Ti_3C_2T_x$  MXene flakes were synthesized using a bifluoride-based etching method as previously reported.<sup>[19]</sup> Briefly, 1 g of  $Ti_3AlC_2$  MAX phase was added to 20 mL of 2 M NH<sub>4</sub>HF<sub>2</sub> and continuously stirred for 24 h at room temperature. The resulting mixture was then subjected to centrifugation using deionized (DI) water at 3500 rpm. Each centrifugation of 5 min was repeated 5 times, followed by vacuum-assisted filtration through a 0.22 µm pore size PVDF filter membrane and rinsing with DI water. The obtained  $Ti_3C_2T_x$  powder was then vacuum-dried at 120 °C for 24 h.

Preparation of Electrode: The Mg electrode was fabricated using the sputtering method to deposit a layer of elemental Mg on a stainless steel (SUS316L-H foil, Wellcos) current collector. The MXene/Mg electrode was also fabricated by sputtering the Mg on the MXene layer. The MXene layer was coated using MXene ink that was prepared by following the reported procedure;<sup>[23b]</sup> 15 mL of DI water was added to the  $Ti_3C_2T_x$  MXene followed by vigorous shaking using a vortex machine. The resulting mixture was then centrifuged at 3500 rpm for 30 min, and the top 80% supernatant was collected and further centrifuged at 5000 rpm for 30 min. The resulting sediment was re-dispersed in 15 mL of DI water by vigorous shaking, resulting in a viscous MXene ink. The slurry was then prepared by dispersing the MXene ink, rGO (rGO-V20, Standard Graphene), and CMC-SBR binder in DI water solvent. The weight ratio of the slurry composition was MXene:rGO:CMC:SBR = 70:20:5:5. The slurry was cast onto SUS using the doctor blade method, followed by drying under vacuum at 60 °C overnight. A reference MXene electrode was fabricated using the same procedure, but without adding rGO, and the thickness of the MXene layer was  $\approx$ 5 µm. The composite cathode was fabricated by first dispersing LiNbO<sub>3</sub>-coated NCM811, LPSCl, vapor-grown carbon fiber (VGCF), and poly(tert-butyl acrylate)-b-poly(1,4-butadiene) binder in butyl butyrate with a weight ratio of 70:26:1.5:2.5, followed by casting on Al foil and drying at 100 °C for 15 h. The binder was then deprotected through heat treatment at 160 °C for 15 h for in situ deprotection and then maintained at room temperature under vacuum for 24  $h.^{[28]}$ 

Characterization Method: The chemical bond characteristics of the synthesized Ti<sub>3</sub>C<sub>2</sub>T<sub>v</sub> MXene were analyzed by FT-IR (Tensor27, Bruker). Top- and cross-sectional images of the electrode were acquired using field emission-SEM (JSM-7800F Prime, JEOL, Japan) and focused ion beam (FIB) (Helios 650, FEI, USA), respectively. To measure the mechanical properties of the electrodes, nano-indentation tests were performed using an ultra-precision surface mechanical analyzer (Anton Paar, Austria) with an indentation load of 0.07 mN at five different positions on each electrode. The 3D distribution and porosity of the interfaces were analyzed using a system that combined high-resolution 3D X-ray microscopy (XRM) and computed tomography (Xradia 620 Versa, Carl Zeiss, USA) installed at the national center for inter-university research facilities (NCIRF) at Seoul National University. After 10 cycles at room temperature and stack pressure of 2 MPa, the pellet in each NCM/anode-less full-cell was carefully separated. The anode-SE interface was then selectively subjected to X-ray beam for 4 h. The conditions of the X-ray beam were as follows: 80 kV (voltage), 125 µA (current), and 10 W (power). The resolution of the image was 0.5 pixels per unit. Next, the obtained raw data was processed to reconstruct the 3D structure of the anode-SE interface using the advanced imaging software (Dragonfly, Object Research Systems (ORS)). The porosity of the samples was also obtained using the same software based on the contrast difference.

Electrochemical Characterization: The cell assembly of the all-solidstate half-cells was fabricated by first pelletizing 150 mg of LPSCI onto the SE layer with a diameter of 13 mm by cold-pressing it at 150 MPa, followed by positioning the as-prepared Mg-based anode-less electrode underneath the SE layer. Subsequently, the assembled cell was compressed at a pressure of 380 MPa. The Li foil was then placed on top of the SE layer. SUS foils were used as the current collectors for the electrodes on both sides. After the compression, the cell was positioned in a housing case that was custom-fabricated for pressure control during cell testing. The cell pressing pressure was precisely controlled to either 10 MPa or 2 MPa by incorporating a spring with a specific spring constant (Shinheung Indus.) inside the housing case and adjusting the pressing depth. The all-solid-state full-cells were fabricated by preparing the SE layer using the same procedure as for the half-cells. The as-prepared cathode and anodeless electrode were placed on each side of the SE pellet, and the whole assembly was then compressed at 380 MPa. Following compression, the cell was inserted into a housing case with a spring, applying a stack pressure of either 20 MPa or 2 MPa, using the same procedure as the half-cells. All assembly processes were carried out in an Ar-filled glove box. Electrochemical evaluations were conducted at 25 °C. The areal capacity of the half-cell plating-stripping test was determined by the duration of plating with the stripping cutoff voltage of 0.1 V (vs Li/Li<sup>+</sup>) using a battery cycler (WBCS 3000, WonATech, South Korea). The electrochemical performance of full-cells was assessed in constant current (CC) mode for both charge and discharge with a current density of 0.1 C in the potential range of 2.5-4.2 V (vs Li/Li<sup>+</sup>), using the same battery cycler as for half-cell evaluation.

## **Supporting Information**

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

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## **Conflict of Interest**

The authors declare no conflict of interest.

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### **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 batteries, anode-less, magnesium thin film, MXene, sulfide solid electrolytes

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