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# Bifunctional Interphase-Enabled Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> Electrolytes for Lithium–Sulfur Battery

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ABSTRACT:  $Li_{10}GeP_2S_{12}$  (LGPS) has a high ionic conductivity and compatibility with sulfur cathodes; however, the instability of LGPS against Li and Li dendrite growth still remains unsolved. Here, we solved these two challenges by forming a lithiophilic–lithiophobic gradient interlayer interphase layer between Li and LGPS through the sequential reduction of salts and solvent in Mg(TFSI)<sub>2</sub>-LiTFSI-DME liquid electrolyte at the LGPS/Li interface (TFSI = bis(trifluoromethanesulfonyl)imide; DME = dimethoxyethane). Mg(TFSI)<sub>2</sub>-LiTFSI is first reduced, forming a lithiophilic  $Li_xMg$  alloy-rich layer on the lithium surface and a lithiophobic LiF-rich layer on top of  $Li_xMg$ due to the lithiophobicity difference. The later reduced DME solvent forms a flexible organic polymer between the LiF-rich layer and LGPS. After evaporation of DME solvent, the Li/LGPS/Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub> all-solid-state battery shows a reversible capacity of 699.7 mAh g<sup>-1</sup> (1.07 mAh cm<sup>-2</sup>) based on the mass of Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub> at 100 mA g<sup>-1</sup> (0.26 mA cm<sup>-2</sup>). The rational design of a solid electrolyte interface between a Li anode and LGPS electrolyte opens a new opportunity to develop high-performance all-solid-state lithium batteries.

Solid-state lithium-sulfur batteries can achieve a high energy density and safety with a low cost, making them very attractive for large-scale energy storage systems.<sup>1</sup> The solid electrolytes in Li/S batteries can also prevent the shuttle reaction.<sup>2-4</sup> Among solid-state electrolytes,  $Li_{10}GeP_2S_{12}$ (LGPS) has a high ionic conductivity of 12 mS cm<sup>-1,5</sup> which is similar to those of liquid electrolytes. However, LGPS is thermodynamically unstable with metallic lithium.<sup>6</sup> The reduction of LGPS forms a mixed ionic/electronic conductive  $Li_2S-Li_3P-Li_xGe$  interface,<sup>6</sup> promoting lithium dendrite growth in solid electrolytes.<sup>7,8</sup> Besides, the reaction of LGPS with the metallic lithium anode results in cracking at the electrolyte/ lithium interface, increasing the interfacial resistance and reducing the cycle life.<sup>8,9</sup>

To prevent LGPS reduction and Li dendrite growth, an electronic insulating layer with a high interface energy against Li should be inserted between LGPS and Li. LiF has a very low

electronic conductivity and high interface energy with Li, making it the most promising interlayer for suppressing reduction of LGPS and growth of lithium dendrites.<sup>10,11</sup> However, the rigidity and lithiophobic nature of LiF between LGPS and Li also significantly increase the interfacial resistance at Li/LiF/LGPS. To reduce these interface resistances, a LiF-Li<sub>x</sub>M (M = metal) lithiophobic–lithiophilic gradient interlayer should be *in situ* formed between LGPS and Li and a flexible polymer should also be generated between rigid LGPS and LiF as a binder. The lithiophilic Li<sub>x</sub>M layer

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Figure 1. (a) Illustration of *in situ* formation of the Li<sub>x</sub>Mg/LiF/polymer (lithiophilic–lithiophobic) solid electrolyte interphase between Li and LGPS after dropping 1.0 M LiTFSI-Mg(TFSI)<sub>2</sub>-DME liquid electrolyte onto the LGPS membrane surface. (b) Galvanostatic cycling of the Li/LGPS/Li cell using different LiTFSI-Mg(TFSI)<sub>2</sub>-DME-treated LGPS at a constant current density of 0.2 mA cm<sup>-2</sup> with a fixed capacity of 0.2 mAh cm<sup>-2</sup>. The thickness of the LGPS pellet is 1000  $\mu$ m.



Figure 2. XPS depth profiling spectra of SEI composition formed on Li after cycling in LiTFSI-Mg(TFSI)<sub>2</sub>-DME liquid electrolyte for 10 cycles. Curves from bottom to top represent the spectra acquired after sputtering for 0, 120, and 180 s; the etching depth was 10 nm when sputtering for 1 min.

that is separated from LGPS by a lithiophobic LiF layer is essential for suppressing LGPS reduction and Li dendrite growth because the lithium deposits only under the lithiophilic layer in each cycle, preventing the direct contact of deposited Li with LGPS. The lithiophilic Li<sub>x</sub>M layer can also reduce the interface resistance at the Li/LiF interface. To reduce the solid-solid interface resistance at LiF/LGPS, a Li-ion conducting polymer should be added as a binder between LiF and LGPS. We successfully formed a lithiophiliclithiophobic-polymer three-part layer by using a lithiophilic graphite-Bi substrate and forming a lithiophobic LiF/polymer solid electrolyte interface (SEI) on the Li surface using 2.0 M LiPF<sub>6</sub>-mix THF liquid electrolyte, which enabled the Li anode to achieve a record Coulombic efficiency of 99.8% at a current of 0.5 mA cm<sup>-2</sup> and a capacity of 1.0 mAh cm<sup>-2, 12,13</sup> Actually, the lithiophilic layer can also be directly formed from reduction of metal salts  $(Mg(TFSI)_2, ZnCl_2, AgTFSI; TFSI = bis-$ (trifluoromethanesulfonyl)imide) in liquid organic electrolytes.

Therefore, by rational design of the electrolytes, it is possible to directly form a lithiophilic Li<sub>x</sub>M/lithiophobic LiF/polymer composition layer by reduction of the electrolytes.

Herein, a bifunctional lithiophilic–lithiophobic/polymer SEI was *in situ* formed between LGPS and Li by coating/infiltrating a few drops of LiTFSI-Mg(TFSI)<sub>2</sub>-DME (DME = dimethoxy-ethane) electrolytes onto the LGPS membrane surface and then pressing it to Li anode. The reaction of the Li anode with LiTFSI-Mg(TFSI)<sub>2</sub>-DME electrolyte forms a Li<sub>x</sub>Mg/LiF/ polymer composite layer, where the lithiophilic Li<sub>x</sub>Mg-rich sublayer bonds to the surface of lithium and a lithiophobic LiF-rich layer bonds to the LGPS solid electrolyte through an organic polymer layer. The formation of the Li<sub>x</sub>M/LiF/ polymer composite layer is attributed to the decreasing reduction potentials of Mg(TFSI)<sub>2</sub> > LiTFSI > DME and the lithiophilicity difference between the Li<sub>x</sub>Mg and LiF components. The later formation of CH<sub>2</sub>CHOCO<sub>2</sub>Li and CH<sub>2</sub>CHOLi polymer species on top of the LiF-rich layer is



Figure 3. (a) Crater sputtered by a Ga<sup>+</sup> ion beam for the cycled LGPS in Li/Mg(TFSI)<sub>2</sub>-LiTFSI-DME@LGPS/Li cell. (b) ToF-SIMS analysis for F element in the cycled Li of Li/Mg(TFSI)<sub>2</sub>-LiTFSI-DME@LGPS/Li cell. (c) F element distribution of cycled Li in Li/Mg(TFSI)<sub>2</sub>-LiTFSI-DME@LGPS/Li cell.

attributed to (1) the low reduction potential of DME and (2)the high solubility of these organic compounds in DME solvent. During Li plating, the lithium is guided to deposit preferentially at the bottom of the lithiophilic LixMg-rich layer, away from LGPS that is separated by a lithiophobic LiF-rich layer. The lithiophobic LiF-rich layer with high interface energy against Li suppresses Li dendrite growth, and the low electronic conductivity of the LiF/polymer layer also prevents reduction of LGPS. The composition gradient in the composite interphase layer ensures a low contact resistance and high capability for Li dendrite suppression. LiTFSI-Mg(TFSI)<sub>2</sub>-DME electrolyte modification increased the critical current density from 0.6 mA  $cm^{-2}$  (0.6 mAh  $cm^{-2}$ ) for bare LGPS to 1.3 mA cm<sup>-2</sup> (1.3 mAh cm<sup>-2</sup>), which is the highest critical current density in LGPS solid electrolytes reported to date.9,14-16

In addition to the Li anode, the lithium sulfide cathode in Li/LGPS/Li<sub>2</sub>S solid-state batteries also needs to be optimized to achieve high performance. Since lithium sulfide has very low electronic and ionic conductivity, the electrochemical lithiation/delithiation reaction occurs only on triple-phase boundaries of Li<sub>2</sub>S/electronic additive/solid electrolyte. Once Li<sub>2</sub>S loses contact with the electronic additive or solid electrolyte, the electrochemical reaction will stop.<sup>17</sup> To maximize the triple-phase boundaries, we designed an in situ formed Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub> cathode, where high electronic conductivity Ni atoms and Li2S active materials were homogeneously distributed in a mixed conductor amorphous LiTiS<sub>2</sub> matrix,<sup>18</sup> thus enhancing the utilization and reaction kinetics of Li<sub>2</sub>S. This rational design of Li/LGPS/Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub> solid-state batteries shows excellent cycling stability with reversible capacity of 400.6 mAh  $g^{-1}$  based on the mass of Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub> after 120 cycles at a current density of 100 mA  $g^{-1}$ .

Composition Optimization of LiTFSI-Mg(TFSI)<sub>2</sub>-DME Liquid Electrolytes. LGPS solid electrolyte powders were

pressed at 360 MPa to form a thin pellet, and then a drop of LiTFSI/Mg(TFSI)<sub>2</sub> electrolyte (~20  $\mu$ L) was added on both sides of the LGPS pellet, followed by pressing two lithium foils on both sides of the LGPS (Figure 1a) and then drying to evaporate the unreacted DME solvent. All the processes were performed in an argon-filled glovebox. To optimize the two salt concentrations, the mole ratios of the LiTFSI/Mg(TFSI)<sub>2</sub> salt were varied at 4:0, 3:1, 2:2, 1:3, and 0:4, while the total salt concentration of LiTFSI-Mg(TFSI)<sub>2</sub> in the electrolyte was fixed at 1.0 M. The corresponding electrolytes at the salt mole ratios of 4:0, 3:1, 2:2, 1:3 and 0:4 are abbreviated as LiMg40, LiMg31, LiMg22, LiMg13, and LiMg04, respectively. For comparison, a Li/LGPS/Li symmetric cell using bare LGPS (without addition of liquid electrolyte) was also assembled using the same procedures. As illustrated in Figure 1a, the bifunctional Li, Mg-LiF-polymer lithiophilic-lithiophobic SEI was in situ formed between Li and LGPS once Li was attached onto the LiTFSI-Mg(TFSI)2-DME electrolyte-infiltrated LGPS.

The stability of LGPS in LiTFSI-Mg(TFSI)<sub>2</sub>-DME organic electrolyte was investigated. As shown in Figure S1, 10 days after mixing LGPS powder with LiTFSI-Mg(TFSI)<sub>2</sub>-DME organic electrolyte, the X-ray diffraction (XRD) pattern of the mixed LGPS was similar to that of the pristine LGPS after DME was evaporated, which means LGPS was stable in the minor amount of organic electrolyte. To optimize the liquid electrolytes, LGPS membranes were treated with different liquid electrolytes (LiMg40, LiMg31, LiMg22, LiMg13, and LiMg04), and the Li plating/stripping performances of these five LGPS membranes were evaluated using Li/LGPS/Li symmetric cells at current density of 0.2 mA cm<sup>-2</sup> and a fixed capacity of 0.2 mAh cm<sup>-2</sup>. As shown in Figure 1b, the lithium stripping/plating overpotential decreases with increasing mole ratio of Mg(TFSI)<sub>2</sub>/LiTFSI due to the gradually increased lithiophilicity of the SEI. However, the overpotential difference among LiMg22, LiMg13, and LiMg04 is small, and reduction



Figure 4. (a) Galvanostatic cycling of a Li/LGPS/Li cell at a constant current density of 0.05 mA cm<sup>-2</sup> under a fixed capacity of 2 mAh cm<sup>-2</sup>. The thickness of the LGPS pellet is 1000  $\mu$ m. (b) Galvanostatic cycling of a Li/LGPS/Li cell at step-increased current density under a fixed capacity of 1 mAh cm<sup>-2</sup>. The thickness of the LGPS pellet is 300  $\mu$ m. (c) Galvanostatic cycling of Li/LGPS/Li cells using LGPS with and without LiMg22 treatment at step-increased current densities. The time for each charge and discharge process is 1 h. The thickness of the LGPS pellet is 300  $\mu$ m.

of the amount of LiTFSI will reduce the LiF content in the SEI. By balancing the interface resistance and Li dendrite suppression capability, we selected LiMg22 for further investigation. The larger overpotential of the Li/LGPS/Li cell with LiMg22 liquid electrolyte treatment in the first few cycles is attributed to the formation of a SEI after mixing LGPS with liquid electrolyte, as evidenced by the semicircle at high frequency in the impedance spectra of LGPS-LiMg22 electrolyte (Figure S2).

**Characterization of Lithiophilic–Lithiophobic Composition Interlayer.** Since the SEI composition in liquid electrolyte-treated LGPS should be the same as that formed in the liquid electrolyte with the same composition, the composition of the lithiophilic–lithiophobic SEI that formed in LiTFSI-Mg(TFSI)<sub>2</sub>-DME (LiMg22) liquid electrolyte was characterized by X-ray photoelectron spectroscopy (XPS). As shown in Figure 2, no signal of reduced  $Mg^0$  was observed on the SEI surface, while the concentration of  $Mg^0$  gradually increased with increasing etching time in the Mg 2p spectra, implying that the lithiophilic Li<sub>x</sub>Mg is bonded to the bottom Li (Figure 1a). For C 1s spectra, the concentration of the organic component is higher on the SEI surface and then gradually decreases with increasing sputtering time, suggesting the organic polymer is rich on the SEI surface. In the F 1s spectra, peaks stemming from LiTFSI and LiF were observed on the SEI surface and then the concentration of LiF increased when the etching time increased. The XPS characterization demonstrated that a Li<sub>x</sub>Mg/LiF/polymer composite SEI was formed on Li anodes in 1.0 M LiTFSI-Mg(TFSI)<sub>2</sub>-DME electrolyte.

The SEI formed between Li/LGPS with and without liquid electrolyte treatment was also evaluated using XPS. Li/LGPS/ Li cells with and without LiMg22 liquid electrolyte treatment were charged/discharged at a current density of 0.2 mA cm<sup>-2</sup> and a capacity of 0.2 mAh cm<sup>-2</sup>. After 10 cycles, both Li/ LGPS/Li cells with and without liquid electrolyte treatment were disassembled and the surface composition of LGPS and Li was analyzed using XPS. For Li/LGPS/Li cells without liquid electrolyte treatment, LGPS was reduced by lithium, as proved by the presence of Ge<sup>0</sup> (Figure S3a) and Li<sub>2</sub>S (Figure \$3b)<sup>6,19</sup> on the LGPS surface. For the Li/LGPS/Li cells with LiMg22 liquid electrolyte treatment, a lithiophilic-lithiophobic gradient SEI was formed between Li and LGPS. However, the SEI was scratched during separation of Li from LGPS, and the composition on the surface of Li and LGPS varied from spot to spot. XPS on the Li surface showed both  $LiF^{10}$  (Figure S3c) and Mg<sup>0 20</sup> (Figure S3d). On the surface of LGPS, the most XPS showed only the LiF (Figure S3e) peak, but no signal for Mg<sup>0</sup> was detected (Figure S3f), implying lithiophilic Mg<sup>0</sup> was rich on the surface of Li at the LGPS-LiMg22/Li interface. Additionally, Li<sub>2</sub>CO<sub>3</sub> and some organic species, LiO-(CH<sub>2</sub>)O<sub>n</sub>-Li<sup>21</sup> derived from the reduction of DME by the lithium were also observed (Figure S3g) on the surface of LGPS. Furthermore, on the LGPS surface after removal of the SEI, only a large amount of LiTFSI with a trace of LiF (Figure S3h) could be detected, suggesting that Li did not contact to LGPS. The large amount of LiTFSI inside LGPS can also consume lithium dendrites, even though lithium dendrites break through the interphase.

The composition depth profile of LiMg22 electrolyte-treated LGPS after 10 Li plating/striping cycles in Li/LGPS/Li cell was characterized using time-of-flight secondary ion mass spectrometry (ToF-SIMS; Figure 3). Figure 3a shows the side surface of the crater sputtered by Ga<sup>+</sup> ions. Fluorine content in the cycled LGPS with LiMg22 treatment is significantly high at the top surface layer (Figure 3b,c), implying a LiF-rich layer (~200 nm) was formed between LGPS and Li after cycling, which is consistent with the SEI component in LiTFSI-Mg(TFSI)<sub>2</sub>-DME liquid electrolyte. All these results demonstrate the successful formation of a lithiophilic-lithiophobic Li<sub>x</sub>Mg-LiF-polymer composite interface between the solid LGPS electrolyte and lithium anode by in situ decomposition of LiTFSI-Mg(TFSI)<sub>2</sub>-DME liquid electrolyte during electrochemical cycling, where a lithiophilic LixMg alloy-rich layer forms on the surface of lithium anode and a LiF-rich lithiophobic layer bonds to the side of the LGPS solid electrolyte through the organic polymer component.



Figure 5. (a) SEM images of bulk LGPS electrolyte in the Li/LGPS/Li cell after cycling. SEM image of bulk LGPS electrolyte in the Li/LGPS-LiMg22/Li cell (b) before cycling and (c) after cycling. (d) Cross-section images of LGPS/Li interphase in the Li/LGPS/Li cell after cycling. Cross-section images of LGPS/Li interphase in the Li/LGPS-LiMg22/Li cell (e) before cycling and (f) after cycling.



Figure 6. EDS mapping of the LGPS/Li interface in (a) Li/LGPS/Li and (b) Li/LGPS-LiMg22/Li cells after cycling.

Lithiophilic-Lithiophobic Interlayer for Li Dendrite Suppression. Li dendrite growth in LGPS electrolytes was evaluated using a Li/LGPS/Li symmetric cell. For a bare LGPS electrolyte (without liquid electrolyte treatment) with 1.0 mm thickness, the Li/LGPS/Li cell was shorted after three cycles at a low current of 0.05 mA  $cm^{-2}$  and a practical capacity of 2.0 mAh  $\text{cm}^{-2}$  (Figure 4a). When the thickness of the LGPS pellet was decreased from 1000  $\mu$ m to about 300  $\mu$ m and the Li/ LGPS/Li cell was cycled at a fixed capacity of 1.0 mAh cm<sup>-2</sup> with a step-increased current density (Figure 4b), shortcircuiting occurs at a low current density of 0.2 mA cm<sup>-2</sup>. All these results confirmed that LGPS electrolytes cannot be used for Li batteries due to the lithium dendrite growth and massive cell impedance increases. The effectiveness of a lithiophiliclithiophobic composite interphase for Li dendrite suppression was investigated by comparing the Li stripping/plating behavior of Li/LGPS/Li cells using 300  $\mu$ m LGPS with and

without LiMg22 liquid electrolyte treatment at a step-increased current but a fixed charge/discharge time of 1.0 h. For a bare LGPS, the Li/LGPS/Li cell was shorted at a current density of 0.6 mA cm<sup>-2</sup> and a capacity of 0.6 mAh cm<sup>-2</sup> (Figure 4c). After treatment with LiMg22 liquid electrolyte, the Li/LGPS/Li cell showed an increased critical current density of 1.3 mA cm<sup>-2</sup> with a capacity of 1.3 mAh cm<sup>-2</sup> (Figure 4c), which is one of the highest value for LGPS electrolytes at a similar Li plating/stripping capacity.<sup>9,14-16</sup>

For bare LGPS electrolytes, the continuous reactions between unconnected lithium dendrite and LGPS led to large volume expansion and fracture at the solid electrolyte and Li/LGPS interface (Figure 5a,d), which significantly increased the impedance of Li/LGPS/Li cells (Figure S4). In sharp contrast, no cracks were observed in the Li/LGPS/Li cells when treated LGPS was used (Figure 5c,f), which is similar to the LGPS before cycling (Figure 5b,e). The corresponding cell



Figure 7. Galvanostatic charge/discharge profiles of (a) Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub>/LGPS/Li and (b) Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub>/LGPS-LiMg22/Li all-solid-state batteries. (c) Galvanostatic cycling profiles of Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub>/LGPS-LiMg22/Li all-solid-state battery at a current density of 100 mA  $g^{-1}$ . (d) Rate capability of a Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub>/LGPS-LiMg22/Li all-solid-state battery.

impedance of Li/LGPS/Li cell using treated LGPS is about 4 times lower than that of the untreated Li/LGPS/Li cell (Figure S4). Short-circuiting of the Li/LGPS/Li cells was also demonstrated (Figure 6a) by the elemental mapping of a cross-section of the electrolyte after cycling, where the O element distribution from oxidized Li (Li<sub>2</sub>O) was observed across the LGPS electrolyte. However, for the Li/LGPS-LiMg22/Li cell, all the elements are homogeneously distributed (Figure 6b).

The impact of the in situ formed lithiophilic-lithiophobic composite SEI on the electrochemical performance of all-solidstate full cells was investigated using Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub> cathode, where high electronic conductivity Ni atoms and Li<sub>2</sub>S active materials were homogeneously distributed in a mixed conductor amorphous LiTiS<sub>2</sub> matrix to minimize the interface resistance and maximize the triple-phase boundary in the cathode layer. The Li<sub>2</sub>S cathode without LiTiS<sub>2</sub> matrix shows worse cycling stability (Figure S5). Figure 7a shows that shortcircuit characterized by unstable charge curves<sup>22</sup> began to occur at the 20th cycle for the Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub>/LGPS/Li cell without liquid electrolyte treatment. However, for the Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub>/LGPS/Li cell after liquid electrolyte treatment, the short-circuit phenomenon was not observed (Figure 7b), and a high reversible capacity of 400.6 mAh  $g^{-1}$  based on the weight of Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub> was maintained after cycling at a current density of 100 mA  $g^{-1}$  (0.26 mA cm<sup>-2</sup>) for 120 cycles (Figure 7c). The Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub>/LGPS/Li cell after liquid electrolyte treatment also shows excellent rate capabilities, with reversible capacities of 764.0, 606.3, 470.5, and 127.5 mAh g<sup>-1</sup> based on the weight of Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub> at 100, 200, 500, and 2000 mA  $g^{-1}$ , respectively (Figure 7d). When the current decreases back to 100 mA  $g^{-1}$ , the capacity could increase back to 620 mAh  $g^{-1}$ .

In summary, the addition of LiTFSI-Mg(TFSI)<sub>2</sub>-DME liquid electrolyte between solid LGPS electrolyte and lithium anode can effectively suppress dendrite growth and LGPS reduction

due to the formation of a bifunctional Li<sub>x</sub>Mg/LiF/polymer lithiophilic–lithiophobic composite solid electrolyte interface between Li and LGPS. Modification of the LiTFSI-Mg-(TFSI)<sub>2</sub>-DME liquid electrolyte significantly increased the critical current from 0.6 mA cm<sup>-2</sup> (capacity of 0.6 mAh cm<sup>-2</sup>) for bare LGPS to 1.3 mA cm<sup>-2</sup> (capacity of 1.3 mAh cm<sup>-2</sup>). The all-solid-state Ni-Li<sub>2</sub>S-LiTiS<sub>2</sub>/LGPS-LiMg22/Li full cell shows a high reversible capacity of 699.7 mAh g<sup>-1</sup> (1.07 mAh cm<sup>-2</sup>) at a current density of 100 mA g<sup>-1</sup>, with a cycle life of >120.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c02617.

Experimental details and Figures S1–S5, showing XRD of LGPS, EIS of LGPS before and after liquid electrolyte modification, XPS of LGPS/Li interface and impedance of Li/LGPS/Li cell with and without liquid electrolyte modification, cyclic performance of Ni-Li<sub>2</sub>S/LGPS-LiMg22/Li cell (PDF)

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## Notes

The authors declare no competing financial interest.

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