Self-Regulated Phenomenon of Inorganic Artificial Solid Electrolyte Interphase for Lithium Metal Batteries

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ABSTRACT: Solid electrolyte interphase (SEI) is crucial for suppressing Li dendrite growth in high-energy lithium metal (LiM) batteries. Unfortunately, the naturally formed SEI on the LiM anode surface in carbonate electrolytes cannot suppress Li dendrites, resulting in a continuous consumption of electrolytes and LiM during cycling. Artificial SEI normally lacks self-healing and self-regulating capability, gradually losing the effectiveness during cycling. In this work, we report the self-regulating phenomenon of LiRAP-AEI that can effectively suppress Li dendrites and is investigated using in situ optical microscopy and COMSOL multiphysics simulation. The effectiveness of self-regulated LiRAP-AEI is further evaluated in the most aggressive Li/sulfur cells with a lean electrolyte (10 μL mAh⁻¹) and LiRAP-AEI/LiM (2.5-fold excess of LiM). The LiRAP@Cu|sulfur@C cells show a stable 3000 cycle life at a current density of 11.5 mA cm⁻². The self-regulated phenomenon holds great promise for the development of high-energy-density LMBs.

KEYWORDS: self-regulated phenomenon, inorganic artificial SEI, cryogenic electron microscopy, lithium metal batteries

Li-ion batteries have been widely applied in various engineering systems (e.g., mobile devices, vehicle electrification, and grid storage). To further increase the energy density, high-capacity electrode materials (Li metal anodes (LiM), silicon anodes, and sulfur cathodes) have been intensively investigated. Among anode materials, LiM is the most promising anode for high-energy batteries due to the high capacity and low potential. However, the implementation of LMBs has been seriously impeded because the LiM with lower electrochemical potential spontaneously reacted with electrolytes, forming a solid electrolyte interphase (SEI). The SEI from carbonate and ether electrolytes is not robust enough to accommodate the large volume changes forming Li dendrites, which continuously consumed electrolytes and LiM, limiting the lifespan of LiM batteries (LMBs) and even short-circuit.

Artificial SEI has been used to suppress Li dendrite growth. Polymer solid electrolytes hold great potential for the artificial SEI film due to the relatively high flexibility. However, most polymer solid electrolytes have low lithium ion conductivity and are not stable with Li metal. Some polymer solid electrolyte swells liquid electrolytes, and the liquid electrolyte will contact the LiM anodes, which leads to the formation of an unstable SEI film and the continuous consumption of electrolytes and LiM. In addition, polymer normally has a low mechanical strength and low interface energy with Li, which cannot effectively suppress Li dendrite growth. In contrast, some inorganic solid electrolytes have dense structure, superionic conductivity, high mechanical strength, and high interface energy with Li and are a promising artificial SEI for suppressing Li dendrites. Recently, Li-La₂Zr₂O₁₂ (LLZO) and lithium phosphorus oxynitride (LiPON) inorganic solid electrolyte films have been reported as an artificial SEI on LiM anodes. However, it is much challenged for coating a dense and super thin artificial SEI film on LiM anodes. For example, LiPON requires high vacuum coating technology, which increases the processing cost and limits the large-scale applications. Another challenge for artificial SEI is the lack of self-healing and self-regulating capability. The artificial SEI will gradually be damaged, losing the protection of LiM anodes because of the large volume changes of LiM during charge/discharge cycles. Therefore, the artificial SEI can only stabilize LiM anodes in the initial cycles due to the lack of self-regulating capability. To effectively...
suppress the Li dendrite growth, the artificial SEI has to be able to self-heal or self-regulate for repairing the damage.

In this work, we report the self-regulating phenomenon of super-ion-conductive lithium-rich antiperovskites (LiRAP)\textsuperscript{31,32} as an artificial SEI for suppressing LiM dendrite growth for the first time. The self-regulating capability of LiRAP artificial SEI (LiRAP-ASEI) relies on the large difference in ionic conductivity between LiRAP-ASEI and new SEI from reduction of electrolytes in the cracked LiRAP. The self-regulating capability of LiRAP-ASEI ensures long-term cycling stability of Li anodes even at a high current density. The self-regulating mechanism of LiRAP-ASEI has been characterized by the in situ optical microscopy (OM) technique and COMSOL Multiphysics simulation. The self-regulating mechanism of LiRAP-ASEI has been characterized by the in situ optical microscopy (OM) technique and COMSOL Multiphysics simulation. The self-regulating LiRAP-ASEI enables the Li anode to achieve a high efficiency (99.5\%) over 1500 cycles at a current density of 0.5 mA cm\textsuperscript{−2} and capacity of 0.5 mAh cm\textsuperscript{−2}. In addition, a full cell with a sulfur@C cathode with a lean electrolyte of 10 μL mAh\textsuperscript{−1} and limited Li excess (2.5-fold excess of Li) exhibits a 3000 cycle life at a current of 11.5 mA cm\textsuperscript{−2}. Self-regulated LiRAP-ASEI provides a new method for Li dendrite suppression in lithium metal batteries, which is critical for development of next generation high-energy batteries.

\section*{RESULTS AND DISCUSSION}

\textbf{Fabrication and Characterization of the LiRAP/LiM/Cu Anode.} LiRAP was in situ formed and simultaneously coated on the surface of a copper foil in molten state at a high temperature of 340 °C. Its thickness was controlled by adjusting the height of the coating rod. The LiRAP coating process is shown in Figure S1 and Figure S2, which is scalable and can be adapted in large-scale manufacturing. As illustrated in Figure 1a, a thin layer (<1 μm) LiRAP with high Li-ion conductivity was conformably coated on the Cu surface, serving as an artificial SEI (ASEI). The cross-sectional morphology of LiRAP@Cu was characterized by scanning electron microscopy (SEM) (Figure 1c). Energy dispersive spectroscopy (EDS) mapping of the LiRAP/Cu shows Cl and Cu in the layers (Figure 1d,e), where the Cl element is present as Li\textsubscript{3}OCl (thickness of ∼1 μm) and the Cu element is present as copper foil (thickness of ∼10 μm). It is evident that a two-layer structure is formed. The surface morphology of LiRAP@Cu reveals a uniform distribution of a smooth LiRAP film (Figure 1f,g) on the surface of Cu foil, which is attributed to the good flow ability of LiRAP under high temperature and the formation of nanocrystalline structure during the rapid annealing process (Figure S2). The cryo-TEM image of LiRAP/LiM/Cu was observed in Figure 1h, and the HRTEM images of LiRAP-ASEI were observed within the red zone of Figure 1h and j. From Figure 1j, we observe a compact nanocrystalline structure and the size of the nanocrystals is 2–5 nm. The FFT in the inset of Figure 1i and the X-ray diffraction (XRD) pattern in Figure S3 show that the Li\textsubscript{3}OCl SSE has an antiperovskite structure.
The interface resistance of the LiRAP-ASEI layer was measured by electrochemical impedance spectroscopy (EIS) using symmetric LiRAP-ASEI@LiM/LiRAP-ASEI@LiM cells (Figure S4). The interface resistance of SEI/LiM||SEI/LiM was larger than that of a symmetric LiRAP-ASEI@LiM||LiRAP-ASEI@LiM, as shown in Figure S4. By fitting the impedance with an equivalent circuit in Figure S4, the semicircle of LiRAP-ASEI@LiM yields a normalized resistance of ~13 Ω. The lithium ionic conductivity of the LiRAP film with ~1.0 μm thickness is calculated to be ~1 × 10^{-9} S cm^{-1} (Figure S4). In contrast, the natural SEI layer with ~50 nm thickness shows 2 or 3 times larger interface resistance than that of LiRAP film (1 μm). The ionic conductivity of SEI formed from organic electrolytes is around ~1.0 × 10^{-9} S cm^{-1} \(^{19,31}\), which is 5 orders of magnitude lower than that of LiRAP. The LiRAP-ASEI is stable during cycling, as demonstrated by only a minor increase in resistance after 100 cycles (Figure S4).

The LiRAP ASEI has a highly compact structure, which allows LiRAP-ASEI to effectively suppress Li dendrite penetration through LiRAP-ASEI. Even though the LiRAP-ASEI cracks during the Li plating/stripping cycles, the newly formed SEI in the crack with a much low ionic conductivity will reduce the lithium ion flux and thus reduce the LiM growth rate through the Li dendrite penetration in cracks, which self-regulate the SEI to suppress Li dendrite growth in the cracks. Therefore, self-regulated LiRAP-ASEI can maintain a high capability to suppress Li dendrites during LiM plating/stripping. In contrast (Figure 1b), during the LiM plating on Cu without LiRAP-ASEI, the lithium ion fluxes at these protuberant sites are much higher than the other intact sites in the LiM deposition process; the protuberant will quickly grow to form LiM dendrites (Figure 1b). The continuous growth of the dendritic LiM and reformation/growth of SEI during reiterative cycling will consume LiM anode and electrolyte, resulting in a fast capacity fading and a depressed Coulombic efficiency (CE).

**Electrochemical Performance of the LiRAP/LiM/Cu Anode.** The dendrite-suppressing ability of LiRAP-ASEI coated Cu and pristine Cu was evaluated at different currents by measuring the CE of their symmetric cells, respectively. As shown in Figure 2a–c and Figure S5, the Li reversibility and Li plating/stripping CE on LiRAP-ASEI@Cu are much higher than Cu in all currents from 0.5 to 4.0 mA cm^{-2} and all capacities from 0.5 to 4.0 mAh cm^{-2}. The average Li plating/stripping CE at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2} on LiRAP-ASEI@Cu is 99.5% with a high reversibility of over 1500 cycles, which is much higher than the cell with the Cu, which drops below 80% after only 200 cycles (Figure 2a). Further increasing the current density to 1 mA cm^{-2}, LiRAP-ASEI@Cu achieves an average CE of 99.1% over 600 cycles, whereas the CE of Cu decreases to 80% after only 100 cycles (Figure 2b). Even at the higher current density of 2 mA cm^{-2} and cycling capacity of 2 mAh cm^{-2} (Figure 2c) and 4 mA cm^{-2}/4 mAh cm^{-2} (Figure S5), the LiRAP-ASEI/Cu anode still maintains an average CE of 98.8% over 200 cycles and 98.5% over 50 cycles, respectively, whereas the CE of the control electrode drops below 80.0% after less than 40 cycles (Figure 2c and Figure S5). High Li reversibility and CE indicates the stable and higher efficiency Li migration onto the LiRAP-ASEI. The polarization voltages during galvanostatic LiM plating/stripping are presented in Figure S6. The LiRAP-ASEI only slightly increases the overvoltage, but the over-voltage of the LiRAP-ASEI/Cu electrode is much more stable than uncoated Cu electrodes, as demonstrated in Figure S6. Parts d, f, and h of Figure 2 show the SEM images of the...
LiRAP-ASEI/Cu after 20 cycles. The regions between the red lines represent the cross-section of the LiRAP-ASEI/LiM/Cu (Figure 2d,j,h) and LiM/Cu (Figure 2e,g,i). LiRAP-ASEI/LiM/Cu shows more uniform and dense electrodeposits of LiM (Figure S7a,b), while the Li deposited on Cu has a rough and porous dendrite structure (Figure S7c,d). The long cycling stability and high CE of LiRAP-ASEI/Cu is attributed to the self-regulation capability of LiRAP-ASEI.

In situ optical microscopy (IS-OM) (Figure S8) has been used to investigate the self-regulating mechanism of LiRAP-ASEI. Although the LiRAP-ASEI film has high mechanical strength, the large volume change during LiM plating/stripping can still lead to breaking and cracking of ASEI (Figure S10) especially at high current and capacity (Figure 3a), which cause LiM penetration into/across LiRAP-ASEI, forming a Li protrusion. At the same time, the new SEI will be immediately formed on the Li protrusion surface. Due to the much lower Li-ion conductivity (\(\sigma \approx 1.0 \times 10^{-9} \text{ S cm}^{-1}\)) of the newly formed SEI than that (\(\sim 10^{-4} \text{ S cm}^{-1}\)) of LiRAP-ASEI, the Li flux to the Li protrusion is lower than the noncrack domain, which suppresses the Li protrusion to develop further into a Li dendrite (Figure 3a). This self-regulating process will yield uniform deposition of LiM. Moreover, the newly formed natural SEI film in the crack can adhere and repair the original LiRAP-ASEI film fragments and contributes to the integrity of the film (Figure 3a). The self-regulating mechanism is
conformed using the optical microscopy images exhibited. As shown in Figure S11a, the surface of Cu foil exhibits an increasing number of LiM dendrites with continuous plating for 60 min at a current density of 2.0 mA cm\(^{-2}\). On the contrary, no dendrites can be observed in LiRAP/Cu after a continuous plating of 60 min (Figure 3b and Figure S11b), indicating that the LiRAP film can be employed as a stable protection layer for LiM and suppress the formation of LiM dendrites. Moreover, as shown in Figure 3b, the surface of the LiRAP-ASEI/LiM/Cu work electrode initially displays a LiM hump within the first 45 min. However, with continuous plating, the LiM hump ultimately disappears and uniform deposition for LiM is obtained. The self-regulated effect of LiRAP-ASEI film in the stabilization of LiM anode was also simulated using COMSOL (Figure 3c,d). For Li plating on a Cu foil anode (Figure 3d), when a pinhole (crack) of 0.2 μm in diameter is formed by the stress concentration, a small LiM protrusion grows at the crack and a natural SEI with a low ionic conductivity of \(\sigma \approx 1.0 \times 10^{-9} \text{ S cm}^{-1}\) is immediately formed on the protrusion surface due to the reduction of the liquid electrolytes. Although the SEI on the protrusion is the same as the other place, the Li concentration in front of the Li protrusion is much higher than other locations, which self-promote the Li protrusion to grow into a large pillar-like LiM whisker out of the pinhole as a LiM dendrite. For the LiRAP-ASEI/Cu anode (Figure 3c), even if a pinhole crack with the same size is formed in the LiRAP film during Li plating, a small LiM protrusion appeared at the defect. However, the LiM protrusion and the electrolyte then reacted electrochemically, forming a new natural SEI film on the LiM protrusion. Because the ion conductivity of LiRAP-ASEI (\(\sigma \approx 1.0 \times 10^{-4} \text{ S cm}^{-1}\)) is higher than that of the natural SEI layer (\(\sigma \approx 1.0 \times 10^{-9} \text{ S cm}^{-1}\)) \(^{19,31}\), the LiM deposition rate of LiM is suppressed at the new SEI film covered crack, achieving a uniform deposition of LiM. Both COMSOL simulation (Figure 3c) and in situ optical microscopy (IS-OM) (Figure 3b) provide evidence for the self-regulated mechanism shown in Figure 3a.

The LiM plated LiRAP-ASEI/Cu at different cycling numbers were detected using XRD spectra and surface XPS spectra. Due to the stress generated during LiM deposition, the LiRAP-ASEI is expected to experience repeated cracking and self-regulation (Figure 4a). In situ XRD (see Figure 4b and Figure S9) demonstrated that the LiM peaks are gradually enhanced and the LiRAP peaks remain stable in the electrochemical deposition process from 0 to 6 mAh cm\(^{-2}\). During the Li stripping from 6 to 0 mAh cm\(^{-2}\), the LiRAP peaks are basically unchanged and the LiM peaks are weakened. Therefore, the process of LiM plating/stripping on the LiRAP/LiM/Cu anode is reversible, which contributes to the cycling stability of the LiRAP SEI layer during LiM plating/stripping cycles. The long cycling stability of LiRAP-ASEI was also evaluated using the ex situ XRD spectra. As shown in Figure 4c and d, the fresh LiRAP-ASEI/Cu (soaked in the electrolyte solution for 10 h) displays a crystal structure of standard antiperovskite Li3OCl and a uniform SEM image of a

Figure 4. Schematic of long-cycling stability of the self-regulated LiRAP-ASEI layer. (a) Schematic illustration of the production process of the self-regulated LiRAP SEI layer after long cycling in the LiRAP/LiM/Cu alloy anode. (b) In situ XRD spectra of LiRAP/LiM/Be foil with different Li deposition capacities (0 mAh cm\(^{-2}\) discharge to 6 mAh cm\(^{-2}\) charge to 0 mAh cm\(^{-2}\) at a current rate of 2 mA cm\(^{-2}\)). (c) XRD spectra of the self-regulated LiRAP SEI layer with different cycle numbers (0 cycles, 1 cycle, 10 cycles, and 100 cycles at a current rate of 2 mA cm\(^{-2}\) and a capacity of 2 mAh cm\(^{-2}\)). (d) SEM image of the self-regulated LiRAP SEI layer with different cycle numbers (current rate of 2 mA cm\(^{-2}\) and capacity of 2 mAh cm\(^{-2}\)).
smooth LiRAP film. After one cycle of electrochemical cycling, the LiRAP-ASEI breaks and cracks and the new natural SEI will be immediately formed on the crack of LiRAP-ASEI (Figure 4d), and the standard peak of Li$_3$OCl remains unchanged with the appearance of LiCl peaks, which is mainly derived from the decomposition of Li$_3$OCl (Figure 4d) and contributes to suppress Li dendrites.33,34 As indicated in Figure 4c, after electrochemical discharge/charge for 10 and 100 cycles, the peak intensity of LiCl is almost unchanged and the structure of LiRAP-ASEI film is still maintained stable.

**Figure 5.** Electrochemical performance of the LiRAP/LiM/Cu anode and LiM/Cu anode in the Li−S full cell. (a–d) Cycling profiles of gravimetric capacity and areal capacity of the LiRAP/LiM/Cu anode and LiM/Cu anode with the sulfur cathode, at charging/discharging C rates of (a) 0.5 C/0.5 C, (b) 1 C/1 C, (c) 2 C/2 C, and (d) 5 C/5 C with an operating voltage window of 1.7−3.0 V. SEM images showing the surface morphologies of (e) LiRAP/LiM/Cu and (f) Li/Cu after 200 cycles of the Li−S full cell.
The surface composition of LiRAP/LiM/Cu and LiM/Cu was analyzed by X-ray photoelectron spectroscopy (XPS) (Figures S12 and S13). Significant differences are observed between the two anodes, including Cl 2p (Figure S12a), F 1s (Figure S12b), and Li 1s (Figure S12c) peaks for LiRAP/LiM/Cu and LiM/Cu anodes. For the LiRAP/LiM/Cu anode after 1 cycle, deconvolution of the Cl 2p peak at 199.0 eV verifies the presence of LiRAP and LiCl with binding energies of 198.5 and 199.8 eV, respectively. When the LiRAP/LiM/Cu anode was charged/discharged for 100 and 100 cycles, the presence of C–Cl with binding energies of 200.5 eV was observed. The binding energies of 198.5, 199.8, and 200.5 eV for the presence of Li3OCl, LiCl, and C–Cl are unchanged after 10 and 100 cycles, suggesting that the formed LiCl protected LiRAP-ASEI from further reduction. The F 1s peak for the LiRAP-ASEI layer shows the presence of LiF and C–F bond with binding energies of 198.5 eV, respectively (Figure S12b).

**Electrochemical Performance of the Full Cells.** The electrochemical performance of self-regulated LiRAP-ASEI/LiM/Cu anodes was evaluated in LiI/Li full cells. The LiI is deposited on the copper electrode or LiRAP-ASEI/Cu electrode by a process of electrochemical deposition. The LiRAP-ASEI/LiM/ITO@C cells were cycled with electrolyte (1 M LiTFSI in DOL:DME (1:1 vol %) with 1 wt % LiNO3) under lean electrolyte (10 μL mAh−1) and limited Li excess (2.5-fold excess of Li) conditions. As demonstrated in Figure S15 and Figure 5a–d, LiRAP-ASEI/LiM/ITO@C cells exhibit a much better cycle stability than Li/ITO@C cells in all currents from 0.2 to 1 C. The corresponding voltage profile of LiRAP-ASEI/LiM/ITO@C and LiM/CuITO@C cells in Figure 5c is shown in Figure S16. At 2 C rate (Figure 5c), LiRAP-ASEI/LiM/ITO@C cells maintain 80% capacity retention at 2 C after 1000 cycles and a high Coulombic efficiency of 99.45% (Figure S17). At a higher rate of 3 C (11.5 mA cm−2), the LiRAP/LiM/CuITO@C cell was stably cycled for over 3000 cycles with capacity retention above 80% (Figure 5d) and a high Coulombic efficiency of 99.84% (Figure S17). Such a high performance of LiITO@C cells in a lean electrolyte and limited Li have never been reported before. In sharp contrast, the Coulombic efficiency of LiM/CuITO@C cells quickly dropped to 90% under 100 cycles (Figure S17). The surface features of the cycled LiM/Cu and LiRAP/LiM/Cu anodes were examined by SEM. For the cycled LiM/Cu (Figure 5f), thick and porous structures are observed after 200 cycles. Therefore, a large volume expansion as well as severe dendrite formation occurred after the cycling of the pristine Li anode. In Figure 5e, the cycled LiRAP/LiM/Cu anode shows compact and dendriteless morphologies. The SEM image supports that the LiRAP-ASEI is in its intact form with the LiRAP-ASEI’s mechanical stability preserved after the cycles.

**CONCLUSIONS**

In conclusion, we report the self-regulating phenomenon of inorganic ASEI for the stabilization of a LiM anode after the fracture of the ultrathin inorganic ASEI during early cycling. The self-regulating capability of LiRAP-ASEI was demonstrated by in situ OM and COMSOL simulation, suggesting its potential as an excellent adaptive interfacial layer for suppressing the growth of LiM dendrites. Moreover, after entering the long cycles, the LiRAP-ASEI compound film serves as a superionic conductive, chemically stable, and mechanically robust protective layer, leading to an ultrahigh current density for the LiM anode during the long-time cycling. The constructed LiRAP-ASEI/LiM/Cu||S|C full cell can operate stably over 3000 cycles under a current density up to 11.5 mA cm−2 in 10 μL mAh−1 electrolyte and only shows a 2.5-fold excess of LiM. Our work clarifies the self-regulated phenomenon of the ultrathin inorganic solid electrolyte ASEI and reveals the underlying microscopic mechanism, holding great promise for the commercialization of inorganic solid electrolyte as an ASEI for LiM batteries.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.nanolett.0c01400](https://pubs.acs.org/doi/10.1021/acs.nanolett.0c01400).

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Author Contributions
C.W., Y.Z., H.Z., B.H., and Y.D. conceived and supervised the study. B.H., D.F., S.L., and Z.Z. designed the experiments and analyses. B.H., D.F., and Y.Z. performed the anodes and the electrochemical tests. B.H., D.F., and Z.Z. investigated the morphology and physical properties of the obtained anodes. All authors took part in the data analysis and interpretation. K.X., H.M., and M.G. participated much in the discussion and interpretation of the results. C.W., H.Z., B.H., C.W., and Y.D. contributed to the writing of the manuscript.

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Notes
The authors declare no competing financial interest.

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