

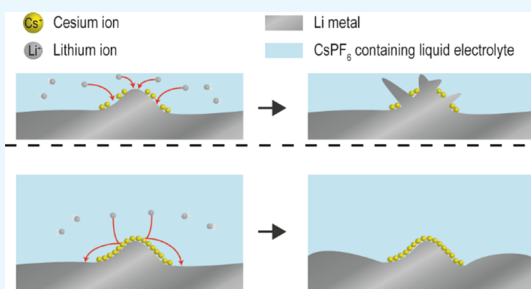
Effect of the Quantity of Liquid Electrolyte on Self-Healing Electrostatic Shield Mechanism of CsPF₆ Additive for Li Metal Anodes

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ABSTRACT: We used a cesium hexafluorophosphate (CsPF₆)-containing liquid electrolyte for surface-patterned Li metal anodes and confirmed that there is a synergistic improvement in the electrochemical performance such as cycle performance and rate capability. For instance, the surface-patterned Li metal maintains 91.4% of the initial discharge capacity after the 1000th cycle ($C/2 = 0.8 \text{ mA cm}^{-2}$ for charging, 1C for discharging). When a large quantity of the CsPF₆-containing liquid electrolyte (600 μL) is used, the bare Li metal and surface-patterned Li metal are more effectively stabilized in comparison with the case where 80 μL of electrolyte is used, resulting in improved electrochemical performance. Through systematic testing, we recognize that these results are because of the self-healing electrostatic shield mechanism, which is mainly dependent on the amount of Cs⁺ ions. A small amount of Cs⁺ ions cannot effectively counteract the incoming Li⁺ ions because they cannot form an effective electrostatic shield on the protrusions present on the Li metal surface.



INTRODUCTION

Commercialized Li secondary batteries are Li-ion batteries, which are based on intercalation chemistry (i.e., they use graphite as the anode material), and as a result of extensive research and development, these batteries are fast approaching their theoretical energy density limit.^{1,2} Therefore, a new active material based on new chemistry is the only way to solve this energy density issue. Li metal has been considered a promising anode material owing to its extremely high theoretical specific capacity (3860 mAh g⁻¹), low density (0.59 g cm⁻³), and lowest negative electrochemical potential (-3.040 V vs the standard hydrogen electrode).^{3–6}

During repeated plating/stripping, Li metal undergoes uncontrolled morphological changes such as the formation of the dendrite, granular Li, mossy Li, and finally, dead Li. Li metal anodes result in a reduction in the Coulombic efficiency and present safety issues, including a catastrophic safety failure accompanied by fire. This has prevented their use in practical battery applications over the past 4 decades.^{7–11}

Much effort has been made to suppress the uncontrolled Li formation during plating/stripping of Li.^{12–17} As an example of such efforts, we recently developed surface-patterned Li metal that guides the Li-ion plating space to prevent uncontrolled Li plating.^{5,13,18} On the other hand, CsPF₆ has been reported as a functional electrolyte additive, which can effectively control morphological changes on the surface of Li metal by inhibiting Li dendrite growth based on a unique self-healing electrostatic shield (SHES) mechanism.^{19,20} The detailed underlying

mechanism of SHES has been thoroughly demonstrated in previous CsPF₆-containing liquid electrolyte studies.^{19,21–24} Consequently, we recently reported the effect of CsPF₆ additives on surface-patterned Li metal when 80 μL of CsPF₆-containing liquid electrolyte was used.²⁵

In this study, we observed that the morphological properties of Li metal are largely dependent on the quantity of the CsPF₆-containing liquid electrolyte. We found that 80 μL of CsPF₆-containing liquid electrolyte did not form a smooth Li metal surface as reported in the previous study.¹⁹ When we decreased the amount of CsPF₆-containing liquid electrolyte below 80 μL , we still observed the same phenomena. This is why we compared 80 μL with the excess electrolyte (600 μL) used in most of previous studies reported by our group. Adjusting the amount of liquid electrolyte is one of the subtle art for Li battery manufacturers for guaranteeing the quality of their product. Practically speaking, however, the quantity of the liquid electrolyte used during the assembly of a unit cell may easily change depending on the researcher experimenting. The excess amount of liquid electrolyte is meaningless for practical use. Ironically, however, excessive amounts of liquid electrolytes are used in much scientific research and thus, should be carefully considered. We systemically investigate the effect of the quantity of the CsPF₆-containing electrolyte on the

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electrochemical performance of the unit cells and the surface properties of the Li metal anode using scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

For the same quantity of the CsPF₆-containing liquid electrolyte (80 μ L or 600 μ L), the surface-patterned Li metal exhibited improved cycle performance and rate capability over the bare Li metal (Figure 1a–d). This implies that there is a synergistic improvement effect of surface-patterned Li metal and CsPF₆-containing electrolytes.

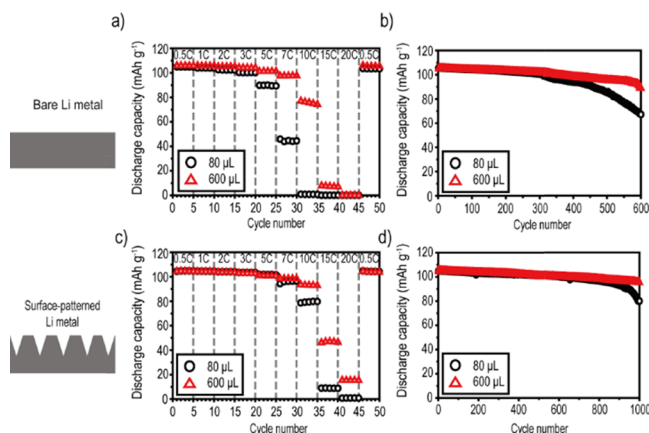


Figure 1. (a–d) Rate capabilities and cycle performance of unit cells (LMO/Li metal) containing (a, b) bare Li metal and (c, d) surface-patterned Li metal, each with 80 and 600 μ L of CsPF₆-containing liquid electrolyte, respectively.

The unit cells containing bare Li metal and surface-patterned Li metal showed improved cycle performance and rate capability when a larger quantity of the CsPF₆-containing liquid electrolyte (600 μ L) was used. These results are reasonable because a newly formed Li metal surface subjected to uncontrolled Li metal formation consumes liquid electrolytes to form a solid electrolyte interphase (SEI).^{26,27} A larger quantity of the liquid electrolyte can provide more Li ions and solvent to Li metal anodes.

The surface morphological changes of Li metal were investigated after precycling.

In the case of bare Li metal, the surface of the Li metal in unit cells containing 80 μ L of CsPF₆-containing liquid electrolyte was filled with uncontrolled Li growth (Figure 2a,b). In contrast, the Li metal in unit cells containing 600 μ L of CsPF₆-containing liquid electrolyte showed a smooth surface morphology (Figure 2c,d). Considering the previously reported results that the CsPF₆-containing liquid electrolyte effectively reduces the formation of uncontrolled Li during plating,^{19–21,28} the Li metal in unit cells containing 80 μ L of CsPF₆-containing liquid electrolyte is a rarity.

In the case of surface-patterned Li metal, 80 μ L of CsPF₆-containing liquid electrolyte again did not show a uniform surface morphology (Figure 3a,b). Uncontrolled Li filled the pattern holes, and flat Li was formed sporadically between the surface patterns. In contrast, the surface-patterned Li metal of the unit cells containing 600 μ L of CsPF₆-containing liquid electrolyte showed a smooth surface morphology, and the surface patterns were uniformly filled with Li metal (Figure 3c,d).

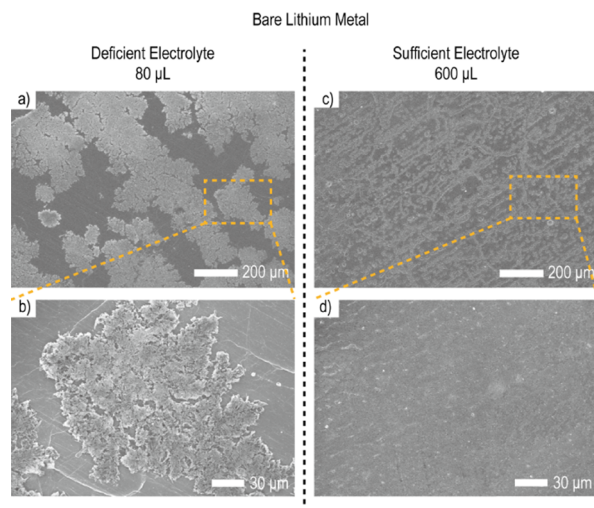


Figure 2. (a–d) SEM images of the bare Li metal surface after precycling when different quantities of the CsPF₆-containing liquid electrolyte were used: (a, b) 80 μ L of CsPF₆-containing liquid electrolyte and (c, d) 600 μ L of CsPF₆-containing liquid electrolyte.

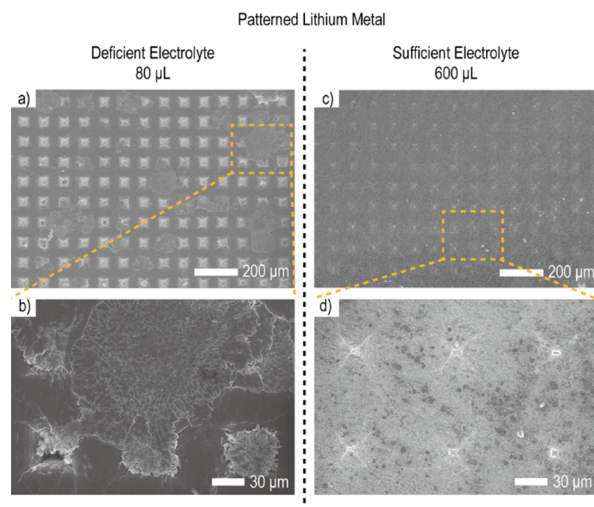


Figure 3. (a–d) SEM images of the surface-patterned Li metal surface after precycling when different quantities of the CsPF₆-containing liquid electrolyte were used: (a, b) 80 μ L of CsPF₆-containing liquid electrolyte and (c, d) 600 μ L of CsPF₆-containing liquid electrolyte.

The CsPF₆-containing liquid electrolyte is composed of organic solvents, Li salt (lithium hexafluorophosphate, LiPF₆), and CsPF₆. Considering this, it can be deduced that the amount of components other than CsPF₆ may affect the morphological change of Li metal during Li plating. To confirm this, a liquid electrolyte that did not contain CsPF₆ was used to monitor the surface change of bare Li metal after Li plating. The morphological characteristics of Li metal operated with pure LiPF₆ were almost identical for 80 μ L (Figure 4a,b) and 600 μ L (Figure 4c,d) of the liquid electrolyte. In both cases, the Li surface was filled with uncontrolled Li growth. Considering this, it can be deduced that the morphological change of Li metal observed in Figures 2 and 3 solely depends on the amount of CsPF₆ in the electrolyte.

The amount of Cs⁺ cations plays a vital role in the SHES mechanism,¹⁹ which implies that the amount of Cs⁺ cations is the key to determining the Li surface condition during Li

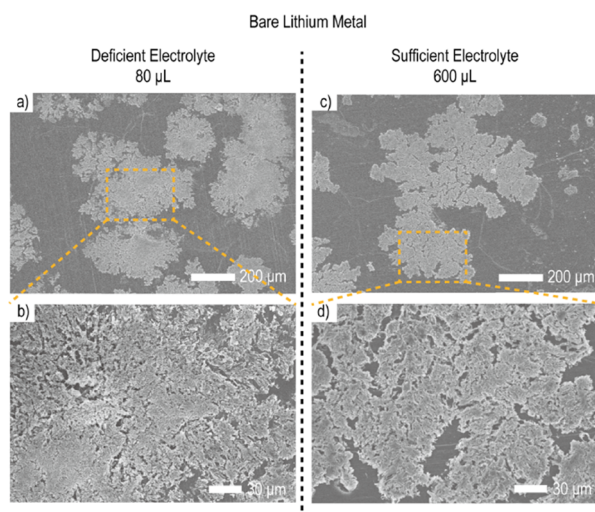


Figure 4. (a–d) SEM images of bare Li metal after precycling when different quantities of the CsPF₆-free liquid electrolyte [1 M LiPF₆ + EC/PC/EMC (5/2/3 by vol)] were used: (a, b) 80 μL of liquid electrolyte and (c, d) 600 μL of liquid electrolyte.

plating. Although the effect of CsPF₆ concentration in the electrolyte on the morphological change of Li metal during Li plating was discussed in a previous study,¹⁹ the effect of the quantity of the CsPF₆-containing liquid electrolyte has not been considered in detail. The latter is a critical issue that should be addressed because the importance of the quantity of the liquid electrolyte has been underestimated. For instance, specific information regarding the quantity of the liquid electrolyte is rarely detailed in the [Experimental Section](#) of battery-related studies.¹⁹ More practically, the quantity of the liquid electrolyte used during the assembly of a unit cell may easily change depending on the researcher conducting the experiment.

The effect of the amount of Cs⁺ ions on the SHES mechanism is illustrated in [Figure 5](#). Because of the lower

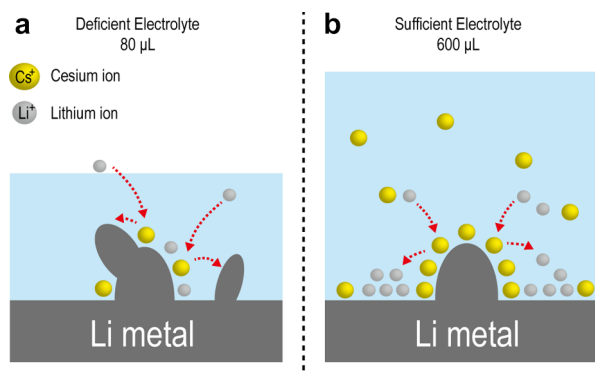


Figure 5. Effect of the amount of Cs⁺ ions necessary for the SHES mechanism to stabilize the Li metal surface during Li plating: (a) 80 μL of deficient electrolyte and (b) 600 μL of sufficient electrolyte.

reduction potential of Cs⁺ ions than Li⁺ ions, the Cs⁺ ions are accumulated near the tip to form an electrostatic shield. If the number of Cs⁺ ions is low, they cannot form a stable electrostatic shield and cannot effectively repel the incoming Li⁺ ions from the protrusion ([Figure 5a](#)). As a result, Li⁺ ions will form uncontrolled Li growth during plating. On the other hand, if the number of Cs⁺ ions is high enough to form a solid

positive shield, the SHES can effectively disrupt the uncontrolled Li formation and result in a smooth Li surface ([Figure 5b](#)).

CONCLUSIONS

A large quantity of the CsPF₆-containing liquid electrolyte (600 μL) effectively stabilized the Li metal anode in comparison with the case where a smaller quantity of the electrolyte was used (80 μL). The formation of uncontrolled Li metal growth, such as dendrites, mossy Li, and granular Li, was diminished by applying 600 μL of CsPF₆-containing liquid electrolyte, resulting in improved electrochemical performance such as cycle performance and rate capability. Considering these results, it can be deduced that a sufficient number of Cs⁺ ions is essential for the normal operation of the SHES mechanism of CsPF₆ to stabilize the Li metal anode.

EXPERIMENTAL SECTION

Materials and Characterization. LiPF₆, propylene carbonate (PC), ethylene carbonate (EC), and ethyl methyl carbonate (EMC) were purchased (battery grade, Enchem Co., Ltd., Republic of Korea) and used as received. CsPF₆ (>99.0%, anhydrous, SynQuest Laboratories) was dried at 60 °C for 4 days under vacuum inside the antechamber of an Ar-filled glove box. The CsPF₆-containing electrolyte was prepared by mixing 0.05 M CsPF₆ with a mixture of EC, PC, and EMC (5/2/3 by weight) containing 1 M LiPF₆. Each step of the preparation process was performed in the Ar-filled glove box (dew point below −70 °C).

Lithium manganese oxide (LiMn₂O₄, Iljin Materials, Republic of Korea), conductive carbon (Super P Li, Imerys, Belgium), poly(vinylidene fluoride) (PVDF, KF-1300, Kureha, *M_w* = 350,000), *N*-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, Republic of Korea), and Al current collector foil (15 μm, Sam-A Aluminium, Republic of Korea) were used as the cathode. A polyethylene microporous film (ND420, Asahi Kasei E-Materials, Japan) was used as the separator. The LiMn₂O₄ cathode was prepared by coating slurry consisting of 90 wt % LiMn₂O₄, 5 wt % Super P Li, and 5 wt % PVDF in the NMP solvent onto Al foil. Surface-patterned Li metal (200 μm, Honjo, Japan) was prepared following the same procedure reported in our previous studies.^{13,18} The 2032 coin-type unit cells (LMO/PE separator/Li metal) were assembled in the argon-filled glove box with different quantities of the electrolyte (80 and 600 μL).

The morphological feature of flat or patterned Li metal was analyzed by a field emission SEM (FE-SEM, S-4800, Hitachi, Japan). The unit cells were carefully disassembled in a glove box filled with Ar, and Li metal was detached from the cell. Li metal was gently rinsed with the DMC solvent followed by drying under vacuum (25 °C, 12 h) to remove the residual electrolyte on the Li metal surface.

Electrochemical Property Measurement. The unit cells were cycled at C/10 (0.16 mA cm^{−2}) followed by three additional cycles (stabilization cycles) at C/5 (0.32 mA cm^{−2}) in a constant current (CC) mode for both charging and discharging between 3.0 and 4.3 V versus Li/Li⁺ using a charge/discharge cycler (PNE Solution Co., Ltd., Korea) at 25 °C. This series of processes consisting of formation and stabilization steps was defined as precycling. After precycling, the rate capability of the unit cells was evaluated by varying the discharging current densities from C/2 to 20C (CC mode, C/

2, 1C, 2C, 3C, 5C, 7C, 10C, 15C, and 20C) while maintaining the charging current density of C/2 (CC/CV mode, 0.8 mA cm⁻²) between 3.0 and 4.3 V versus Li/Li⁺. The cycle performance of the precycled cells was tested between 3.0 and 4.3 V versus Li/Li⁺ at C/2 charge current density and 1C discharge current density (CC mode for charging and CC mode for discharging) at 25 °C.

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Notes

The authors declare no competing financial interest.

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