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Sustainable Solid Electrolyte Interphase Enables High-Energy-Density Lithium Metal Batteries Under Practical Conditions

Xue-Qiang Zhang⁺, Tao Li⁺, Bo-Quan Li, Rui Zhang, Peng Shi, Chong Yan, Jia-Qi Huang, and Qiang Zhang^{*}

Abstract: Secondary lithium metal batteries afford great promises for future energy storage applications. However, high-energy-density Li metal batteries suffer from short lifespan under practical conditions including limited lithium, high cathode loading, and lean electrolyte due to the absence of appropriate solid electrolyte interphase (SEI). Herein, a sustainable SEI was designed rationally by combining fluorinated co-solvents with sustained-release additives in response to challenges from practical conditions. The intrinsically uniform SEI and the constant supplements of building blocks of SEI jointly afford to sustainable SEI. Particularly, specific spatial distributions and abundant heterogeneous grain boundaries of LiF, LiN_xO_y, and Li₂O in SEI effectively regulate uniformity of Li deposition, becoming the foundation of sustainable SEI. In a lithium metal battery with ultrathin Li anode (33 µm), high loading LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode (4.4 mAh cm⁻²), and lean electrolyte (6.1 g Ah⁻¹), 83% of initial capacity retains after 150 cycles with sustainable SEI compared to 4 cycles with pristine SEI. Furthermore, a pouch cell (3.5 Ah) demonstrated a specific energy of 340 Wh kg⁻¹ for 60 cycles with lean electrolyte (2.3 g Ah⁻¹) based on sustainable SEI. This work affords a fresh guidance to the design principles of SEI in practical Li metal batteries.

Introduction

The rapidly increasing demands from portable electronics, electric vehicles, and smart grids have driven intensive researches on secondary high-energy-density batteries. Lithium (Li) metal anode provides various opportunities for high-energy-density battery systems due to its high theoretical specific capacity (3,860 mAh g⁻¹) and low reduction potential (-3.04 V vs standard hydrogen electrode).^[1-2] One of the most promising practical Li metal battery systems is to couple Li metal anode with high-voltage and high-capacity nickel (Ni)-rich LiNi_xCo_yMn_{1-x-y}O₂ (NCM) cathode.^[3-4]

For practical Li metal batteries with a specific energy of more than 300 Wh kg⁻¹ at cell level with Ni-rich NCM cathode, practical conditions including ultrathin Li anode (< 50 μ m), high loading cathode (> 4 mAh cm⁻², i.e., high cycling capacity of Li per cycle), and lean electrolyte (< 3 g Ah⁻¹) are necessary.^[5-6] However, mild conditions, including thick Li anode (>200 μ m),

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low loading cathode (< 1 mAh cm⁻²), and flooded electrolyte (>30 g Ah⁻¹), are currently employed, which contributes to fundamental understanding and the pioneer design of SEI on Li metal anode (**Figure 1a**).^[4, 7] Compared with the stable SEI on graphite anode during thousands of cycles, the SEI on Li metal anode crumbles easily due to Li dendrites, which severely is aggravated under practical conditions.^[8] Consequently, the gap between academical researches and practical applications in designing SEI for Li metal anode is far more challenged than graphite anode.^[9] Actually, the design of SEI under mild conditions is quite difficult to meet the demands of SEI under practical conditions,^[10-11] inducing extremely short lifespan of SEI on Li metal anode applied to practical conditions are highly required.

Generally, the formation of Li dendrites was induced by non-uniform SEI during the plating process in Li metal batteries.^[12-13] The growth of Li dendrites cracks fragile SEI during Li plating, and then induces side reactions between fresh Li and electrolyte,^[14] i.e., SEI precursors. Afterwards during Li stripping process, parts of the plated Li loses electronic contact with the current collectors forming dead Li due to uneven stripping rate,^[15] which also causes the depletion of fresh Li. Moreover, the depletion amount of fresh Li and electrolyte per cycle increase with the increasing cycling capacity, i.e., high cathode loading of practical conditions. Therefore, intrinsically uniform SEI is the footstone of the design principles of SEI under practical conditions to regulate Li deposition and mitigate the depletion of SEI precursors.

Adequate supplements of SEI precursors must be taken into consideration in addition to the intrinsic uniformity SEI when comes to repeated plating/stripping processes under practical conditions. The cracks and reconstructions of SEI are hardly to avoid with large amounts of cycled Li during repeated cycles due to Li dendrites and large volume change, which depletes SEI precursors continuously. At subsequent cycles, uniform SEI formed at initial cannot maintain once any indispensable component of SEI precursors uses up, especially with limited Li and lean electrolyte in practical Li metal batteries, which leads to rapidly irreversible battery decay.^[16] Therefore, a sustainable SEI, which concurrently ensures the intrinsic uniformity of SEI and the adequate supplements of building blocks of SEI, emerges as a fresh design principle of SEI for practical Li metal batteries.

Although the application of artificial films^[17-20] and structured hosts^[21-24] can mitigate Li dendrites growth effectively, yet the intrinsic SEI remains unchanged and becomes the bottleneck of practical Li metal batteries. Electrolyte plays a vital role in regulating the uniformity of SEI.^[25-29] Tremendous efforts have been devoted to constructing intrinsically uniform SEI by regulating the electrolyte solvation, i.e., the components and structure of electrolyte, such as concentrated electrolyte,^[30-34] fluorinated electrolyte,^[35-37] and sacrificial additives.^[38-40] Among various approaches, LiF-rich SEI (F-SEI) and LiN_xO_y-contained

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SEI (N-SEI) have arisen as exemplary methods to stabilize Li metal under mild conditions recently. F-SEI is generated by fluorinated solvents or Li salts^[37, 41-45] and N-SEI is constructed by LiNO₃ additives in carbonate or ether electrolyte,^[40, 46-51] respectively. Generally, F-SEI and N-SEI are formed by additives as SEI precursors (< 5%, by weight or volume), which cannot maintain sustainable due to irreversible exhaustion of limited additives under practical conditions.^[52-53] In order to avoid the rapid depletion, F-SEI induced by co-solvent^[45] and N-SEI formed by sustained-release method^[49, 54] have been put forward. Nevertheless, the sustainability of F-SEI or N-SEI under practical conditions (Figure 1a), including ultrathin Li anode (50 µm), high loading NCM523 cathode (> 4 mAh cm⁻², measured value) and lean electrolyte (< 3 g Ah⁻¹), has never been evaluated. Furthermore, sustainable SEI by combining of F-SEI and N-SEI in carbonate electrolyte remains an unexplored area in practical Li metal batteries, especially in pouch cells.

In this contribution, sustainable SEI was proposed as a fresh design principle in response to challenges from practical conditions. The sustainability of F-SEI generated bv fluoroethylene carbonate (FEC) as co-solvent and N-SEI formed by sustained-release of LiNO₃ was firstly investigated under practical conditions owing to the huge difference in battery performance between practical and mild conditions (Figure S1). Then, the rational combination of F-SEI and N-SEI to construct sustainable fluorinated-nitrided SEI (FN-SEI) in carbonate electrolyte was developed. In a Li metal battery composed of ultrathin Li anode (33 µm), high loading LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM523) cathode (4.4 mAh cm⁻²), and lean electrolyte (6.1 g Ah⁻¹), FN-SEI contributed to a capacity retention of 83% after 150 cycles compared to 4 cycles by pristine SEI. Based on the analysis of components and structure of FN-SEI, LiF, LiN_xO_y, and Li₂O dominate in the components of SEI and exhibit specific spatial distributions vertically. The abundant heterogeneous grain boundaries among LiF, LiNxOy, and Li2O contribute to uniform and rapid diffusion of Li ions through SEI, which guarantees uniform Li depositions. The intrinsically uniformity of SEI and the constant supplements of building blocks of SEI jointly afford to sustainable SEI compatible with practical conditions. Consequently, the effect of sustainable FN-SEI was demonstrated in an aggressive pouch cell with specific energy of 340 Wh kg⁻¹ at cell level (including all parts of a pouch cell) with lean electrolyte (2.3 g Ah⁻¹) while no external pressure was employed. Furthermore, the generality of sustainable SEI was also verified by the rational design of fluorinated-sulfurized SEI (FS-SEI) in practical Li metal batteries.

Results and Discussion

Appropriate electrolyte systems are required to evaluate the sustainability of F-SEI and N-SEI under practical conditions. Specially, 1.0 M hexafluorophosphate (LiPF₆) in FEC / dimethyl carbonate (DMC) (1:4, by volume) and 1.0 M LiPF₆ in ethylene carbonate (EC) / diethyl carbonate (DEC) (1:1, by volume) with a LiNO₃ sustained-release membrane (**Figure S2**) were chosen to obtain F-SEI and N-SEI, respectively. FEC as co-solvent and the sustained-release of LiNO₃ were chosen to avoid the rapid

depletion of SEI precursors. The thickness of Li anode, the cathode loading, and the amount of electrolyte are the key parameters that dictate the cycling performance and specific energy of Li metal batteries. In this section, practical conditions, including ultrathin Li anode (33 µm), high loading NCM523 cathode (4.4 mAh cm⁻², measured value) and lean electrolyte (6.1 g Ah⁻¹) were applied to evaluate the performance of SEI in practical Li metal batteries. The cycle life under practical conditions is one-eighth of that under mild conditions in most previous reports (Figure 1a; Figure S1), including thick Li anode (>200 µm), low cathode loading (<1 mAh cm⁻²) and flooded electrolyte (>30 g Ah⁻¹). Batteries with electrolyte (< 6.1 g Ah⁻¹) cannot work normally in coin cells but work well in pouch cells because there is more useless space in coin cells to absorb electrolyte. Therefore, the battery performance in coin cells under above practical conditions is recommended to predict the performance of electrolyte or other strategies in pouch cells in order to bridge the gap between academic achievements and practical applications.



Figure 1. a) Comparison between practical conditions and mild conditions in a coin cell. b) Cycling performance of Li | NCM523 batteries with different types of SEI at 0.4 C after two formation cycles at 0.1 C. The red dash line indicates 80% capacity retention of the initial discharge capacity at 0.4 C. Corresponding voltage profiles of Li | NCM523 batteries after 3 and 60 cycles with c) F-SEI, d) N-SEI, and e) FN-SEI.

Under practical conditions, Li | NCM523 batteries using common electrolyte (1.0 M LiPF₆ in EC/DEC, 1:1 by volume, denoted as pristine EC/DEC) failed rapidly after only 4 cycles (**Figure 1b**). The benchmark of cycle life is based on the 80% capacity retention of the initial discharge capacity at 0.4 C. The fresh Li has been totally depleted to form thick dead Li, which accounts for drastic capacity decay (**Figure S3**). The thickness of dead Li is nearly 5 times of initial fresh Li. The Li | NCM523 batteries with F-SEI decayed after 64 cycles, and the Li | NCM523 batteries with N-SEI slumped after 53 cycles. Both F-SEI and N-SEI exhibited rapid increase of cell overpotentials during cycling (**Figure 1c, d**), indicating that the sustainability of sole F-SEI or N-SEI is limited.

Notably, the cycle life of Li | NCM523 batteries with FN-SEI was extended significantly, which demonstrates a capacity retention of 83% after 150 cycles. Moreover, the increase of overpotential within the first 60 cycles was effectively decreased (**Figure 1e**). Li metal anode was protected primely so that the cycled Li anode with FN-SEI after 150 cycles also worked well when pairing with fresh NCM523 cathode (**Figure S4**), further illustrating the sustainability of FN-SEI. In addition, improved rate performance was also achieved with FN-SEI. With the rate increasing from 0.1 C to 2.0 C, Li | NCM523 batteries with FN-SEI showed better rate performance than F-SEI and N-SEI (**Figure S5**). The above results confirm the significant sustainability of FN-SEI in improving the lifespan of Li metal batteries.

The uniformity of SEI is the prerequisite for sustainable SEI and Li deposition morphology is the direct evidence for the uniformity of SEI.^[12, 55-56] Li deposition morphology after the first Li plating process was investigated by scanning electron microscopy (SEM) to gain insights into the uniformity of SEI. Remarkable differences in Li deposition morphology were observed. Li whisker with a diameter of 2 µm was observed in pristine EC/DEC electrolyte (Figure S6). In case of F-SEI, the diameter of Li whisker was 6 folds larger than that in pristine EC/DEC electrolyte although the Li deposition remained whisker-shaped (Figure 2a). For N-SEI, Li depositions are whisker-like but the compactness is significantly inferior to that with F-SEI (Figure 2b). In the case of FN-SEI, compact deposition of large Li nodules (25 µm in diameter) were observed (Figure 2c), which is considered to greatly mitigate the parasitic reactions with electrolyte due to decreased reaction surface area and is less likely to penetrate separators. The thickness of dead Li with F-SEI was 180 µm after 100 cyles and N-SEI was 153 µm only after 45 cycles (Figure 2d, e). In comparison, Li metal anode with a sustainable FN-SEI demonstrated a much less thickness of dead Li (133 µm) even after 200 cycles (Figure 2f). The fresh Li nearly becomes dead Li and induces large volume change when batteries fail (Figure S7). Obviously, FN-SEI demonstrates the minimum volume expansion, which reconfirms that less dead Li and side reactions generate in case of FN-SEI due to much compact Li deposition. FN-SEI contributes to higher Coulombic efficiency, less dead Li formation, and higher safety compared with F-SEI and N-SEI.

The interfacial evolution of Li | NCM523 batteries with different types of SEI was further investigated bv electrochemical impedance spectroscopy (EIS), where the semicircle in the high-frequency region is designated to the migration of Li ions through SEI (R_{SEI}) and the semicircle in middle-frequency region is the resistance of charge transfer (R_{ct}).^[57] In general, NCM cathode is relatively stable when charged to 4.3 V. Therefore, the deterioration of Li metal anode affords the dominated interfacial impedance change in Li | NCM523 batteries. Both R_{SEI} and R_{ct} increased from the 1st to the 100th cycle in the following order: N-SEI > F-SEI > FN-SEI (Figure 2g, h, Figure S8, and Table S1). The larger increase in R_{SEI} occurs with F-SEI and N-SEI due to continuous side reactions on Li metal. The accompanying drastic increase in R_{ct} is from the accumulation of porous and thick dead Li, which resembles to the results in Li | Li symmetric cells (**Figure S9**). In contrast, the increase in R_{SEI} and R_{ct} with FN-SEI is much smaller. The results of interfacial evolution further demonstrate that FN-SEI significantly decreases the interfacial resistance via enhancing the uniformity of Li depositions and suppressing the formation of dead Li.



Figure 2. Li deposition morphologies in Li | NCM523 batteries with different types of SEI. The Li deposition morphologies of a) F-SEI, b) N-SEI, and c) FN-SEI after the first deposition process. The deposition was carried out at a current density of 0.15 mA cm⁻² with a capacity of 2.5 mAh cm⁻² in Li | NCM523 batteries. Cross-sectional views of cycled Li metal anode retrieved from Li | NCM523 batteries with d) F-SEI, e) N-SEI, and f) FN-SEI after cycles. The evolutions of interfacial resistance of Li | NCM523 batteries with different types of SEI after g) 1 and h) 100 cycles (45 cycles for N-SEI).

X-ray photoelectron spectroscopy (XPS) analysis was carried out on the cycled Li metal to further disclose the features of SEI. The organic layer exists on the top surface of SEI (Figure S10-S12). The types and spatial distribution of inorganics vary with the types of SEI beneath the organic layer. In F-SEI, LiF distributes uniformly at different depths (Figure 3a, d), which is mainly from the decomposition of FEC as reported.^[45, 52] LiF has been known to increase the uniformity of Li deposition.[35, 58] In N-SEI, the content of LiF significantly reduces according to the atomic concentration of F (Figure S13) because the formation of LiF only depends on the decomposition of LiPF₆. The emerge of LiN_xO_y indicates that LiNO₃ engages in the formation of SEI, and thus sustainedrelease of LiNO₃ is effective in SEI modification (Figure 3b).^[54] LiN_xO_y also has a positive effect on improving the ion transport property of SEI.^[40, 53] The content of LiF and LiN_xO_v demonstrates negligible changes with depth in F-SEI and N-SEI, respectively. In contrast, the spatial distribution of inorganics in FN-SEI varies greatly with depth (Figure 3c, f). The content of LiF decreases with increasing depth although the relative amount of LiF is very high. On the contrary, the content of Li₂O increases with the rise of depth in FN-SEI. Compared with F-SEI,

it is inferred that LiNO₃ additives greatly alters the components and the spatial distribution of inorganics in F-SEI to form FN-SEI. Moreover, the introduction of LiNO₃ promotes the generation of much Li₂O in the closest vicinity of Li metal in the formation processes of FN-SEI. LiF, LiN_xO_y, and Li₂O dominate in the components of SEI and display specific spatial distributions in SEI, which improve the intrinsic uniformity and ion transport capability of SEI significantly.



Figure 3. XPS spectra depth profiles of a) F-SEI, b) N-SEI, and c) FN-SEI on Li metal anode after etching. The peak area ratio of LiF, LiN_xO_y, and Li₂O in d) F-SEI, e) N-SEI, and f) FN-SEI. g) High-resolution TEM image of the FN-SEI on Li metal retrieved from Li | NCM523 batteries after one formation cycles. h) Tafel plots obtained from a cyclic voltammetry test in Li | Li cells with a scan rate of 1.0 mV s⁻¹.

FN-SEI was further detected via transmission electron microscopy (TEM) equipped with double spherical aberration correctors (Figure 3g), in which different crystalline inorganics (ca. 5 nm in diameter), mainly LiF and Li₂O, can be identified evidently. No N-containing crystalline inorganic compound was observed but N element can be detected via the energy dispersion spectrum elemental mappings (Figure S14). LiF, LiN_xO_v , and Li_2O are mixed in spatial, forming abundant heterogeneous grain boundaries. The grain boundaries between inorganics significantly impact the diffusion of Li ions in SEI.[15, 55] There are much different grain boundaries in SEI, mainly including heterogeneous and homogeneous grain boundaries. The heterogeneous grain boundaries are proven to exhibit the faster diffusion of Li ions than the homogeneous grain boundaries.^[59] The diffusion of Li ions in SEI are positively correlated with exchange current density (I₀, Figure 3h).^[60-61] The exchange current density of FN-SEI ($I_0 = 5.21 \text{ mA cm}^{-2}$) is much larger than that in F-SEI ($I_0 = 0.15 \text{ mA cm}^{-2}$) and N-SEI (I_0 = 0.06 mA cm⁻²). Compared with F-SEI and N-SEI, more abundant heterogeneous grain boundaries among LiF, LiNxOy, and Li2O in FN-SEI in the closest vicinity of Li metal contribute to rapid Li ions transport definitively. Furthermore, the abundant heterogeneous grain boundaries also benefit uniform Li ions diffusion, which have been proved by uniform Li deposition.

Sustainable FN-SEI was further employed in a practical Li | NCM523 pouch cell of 3.5 Ah with a specific energy of 340 Wh kg⁻¹ at cell level with lean electrolyte (2.3 g Ah⁻¹) in order to evaluate the potential of the fresh design principle. The mass of all parts of the pouch cell is included into the calculation of the specific energy (detailed pouch cell parameters see Figure S15 and Table S2). The Li | NCM523 pouch cell with the specific energy of 340 Wh kg⁻¹ at cell level was achieved and more than 60 stable cycles with a capacity retention of 90% were demonstrated without no external pressure (Figure 4c, d). The stable cycle for Li metal pouch cells is more challenged without external pressure than that with external pressure. The pouch cell was disassembled after 45 cycles to investigate the protection effect of FN-SEI on Li metal anode and analyze the decay mechanism of pouch cells. The cycled Li surface with sustainable FN-SEI maintained smooth and showed good metallic luster (Figure S16 and Figure S17a, b), while Li anode without FN-SEI exhibited highly porous and pulverized morphology (Figure S16 and Figure S17c, d). Base on the thickness estimation of remaining fresh Li (48 µm, Figure S17b), only 27% of the pristine Li (66 µm, double sides Li on current collector in pouch cells) was consumed after 45 cycles with FN-SEI protection, proving that sustainable FN-SEI suppresses the depletion of fresh Li effectively. Sustainable FN-SEI significantly protects Li metal and contributes to stable cycles of Li metal pouch cells, which make much sense for practical applications.



Figure 4. a) Schematic of a pouch cell under practical conditions—with ultrathin Li anode, lean electrolyte and high loading cathode. b) Digital image of a pouch cell with specific energy of 340 Wh kg⁻¹ at cell level and c) the corresponding cycling performance at 0.1 C after three formation cycles at 0.05 C. d) The voltage profiles of pouch cells at 1st and 50th cycle.

In order to further prove the generality of design principle of SEI in this work, another example, Li_2SO_4 , was rationally designed based on the above insights and understanding to construct sustainable FS-SEI. The cycle life of Li | NCM523

batteries with FS-SEI was extended significantly when compared with F-SEI (**Figure S18a**). The increase of overpotential within the first 60 cycles was also effectively decreased (**Figure S18b**, c), which confirms the effectiveness of sustainable SEI in Li metal batteries under harsh conditions. The components and the corresponding distribution in FS-SEI resemble to the features of FN-SEI (**Figure S19**). There are much LiF and Li₂O in FS-SEI, in which Li₂O increases and LiF decreases with the increasing depth. Moreover, there are lithium sulfates (LiSO_x) due to the decomposition of Li₂SO₄. The above analyses demonstrate the vital role of components and their distributions in regulating Li ion diffusion and deposition. The successful extension of FS-SEI and the fundamental understanding of SEI under practical applications.

Conclusion

Sustainable SEI under harsh conditions, including ultrathin Li anode (< 50 μ m), high cathode loading (> 4 mAh cm⁻²), and lean electrolyte (< 3 g Ah⁻¹), was proposed to promote the development of practical Li metal batteries in this work. A rational electrolyte strategy was developed to construct sustainable SEI, in which the intrinsically uniformity of SEI and the constant supplements of building blocks of SEI jointly afford to sustainable SEI. LiF, LiNxOv, and Li2O display specific vertically spatial distribution and the abundant heterogeneous grain boundaries in FN-SEI contribute to uniform and rapid Li ions transport. Much improved uniformity of SEI effectively regulates uniformity of Li deposition and decreases the depletion of SEI precursors per cycle, which is the foundation of sustainable SEI. In a practical Li metal battery, FN-SEI contributed to a capacity retention of 83% after 150 cycles compared to 4 cycles by pristine SEI, 64 cycles by F-SEI, and 53 cycles by N-SEI, respectively. More important, a practical pouch cell with specific energy of 340 Wh kg⁻¹ at cell level maintained more than 60 cycles with 90% capacity retention without no external pressure. Furthermore, the generality of sustainable SEI was also verified by the rational design of FS-SEI in practical Li metal batteries. This work develops fresh design principles of SEI for high-energy-density Li metal batteries and other types of batteries, especially under practical conditions.

Experimental Section

Experimetal details are available from supporting information, including the fabrication of the sustained-release membrane, the prepartion of electrolyte, electrochemical measurements, and characterizations.

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A design principle of solid electrolyte interphase (SEI) was proposed for practically high-energy-density Li batteries. The intrinsically uniform SEI with specific spatial distribution and abundant heterogeneous grain boundaries, and the constant supplements of building blocks jointly afford to sustainable SEI. A pouch cell with a specific energy of 340 Wh kg⁻¹ demonstrated 60 stable cycles with a retention of 90% based on sustainable SEI.



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Page No. – Page No.

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