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This is the peer reviewed (post-print) version of the following article:

Original

Lithium dendrite inhibition via 3D porous lithium metal anode accompanied by inherent SEI layer / Yang, T., Sun, Y., Qian, T., Liu, J., Liu, X., Rosei, F., Yan, C. - In: ENERGY STORAGE MATERIALS. - ISSN 2405-8297. - 26:(2020), pp. 385-390. [10.1016/j.ensm.2019.11.009]

Availability:

This version is available at: 11368/3086782 since: 2024-08-29T20:52:01Z

Publisher:

Published

DOI:10.1016/j.ensm.2019.11.009

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Lithium dendrite inhibition via 3D porous lithium metal anode accompanied by inherent SEI layer

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ARTICLE INFO

Keywords:

Lithium metal anode
3D porous
Inherent SEI layer
Dendrite-free structure

ABSTRACT

Lithium (Li) metal anodes have been considered as the ultimate anode materials for the next-generation rechargeable batteries. However, uneven dendrite formation and anode volume expansion still can put a brake on the development of Li metal anode. Here, freestanding three-dimensional Li metal foam accompanied by inherent solid electrolyte interphase (SEI) capsulation formed by template-free chemical etching is constructed to promote the uniform lithium deposition and suppress dendritic Li growth. Contrary to planar Li metal foil, the 3D porous Li matrix can buffer the volume change and guide Li deposition inside its porous structure. Moreover, the encapsulated artificial SEI layer, which efficiently uniform the diffusion of Li ions on the interface, enables deeply deposited Li metal. Benefiting from the unique deposition kinetics, the Li plating/stripping process based on our strategy can be deeply cycled at various current densities with low overpotential between 1.0 and 20.0 mA cm⁻² and achieve long lifetime up to 350 h. Moreover, Li metal batteries with LiNiCoMnO₂ (Ni:Co:Mn=1:1:1) cathode exhibit excellent electrochemical performance at high current density and active material loading for more than 20.4 mg cm⁻². In terms of both porous Li matrix and inherent dense SEI layer, our cell greatly suppresses the gassing process and reduces heat generation, further demonstrating the reliability and security of the batteries.

1. Introduction

The ever-increasing energy demands require a development in Li-ion battery techniques that provide with long-term cycling stability, high energy density, and high rate capability [1]. However, current commercialized Li-ion battery composed of Li-ion host and graphite electrode with the limited theoretical capacity cannot keep up with the increasing demand for modern electric vehicles and smart grids. Among all the possibilities, metallic Li is strongly considered as the alternatives of graphite anode due to its extremely low redox potential (−3.04 V vs SHE) and ten times theoretical specific capacity (3860 mAh g⁻¹) higher than that of graphite [2–8]. The applications of Li metal-based batteries are restrained by several serious challenges that have puzzled researchers

for half a century [7–10]. As a ‘hostless’ electrode, Li plating/stripping process will facilitate the huge volume expansion that can easily crack the SEI, which results in an increased local ion flux and uneven dendritic Li deposition. The Li dendrites not only electronically connect the anode and cathode resulting in safety hazards such as internal short circuit, but also facilitate side reactions after exposing to the electrolyte. The products of side reactions will isolate the Li metal anode from the conductive matrix, breeding “dead Li” with fast capacity decay, and resulting in a large polarization, poor lifespan, and low Coulombic efficiency [2–14].

To address the challenging issue, various modification means have been proposed to exercise for dendrite-free Li metal anode. One method is to control the morphology of Li metal anode by three-dimensional (3D) intermediate layer such as porous Cu foam, 3D nickel foam, and modified

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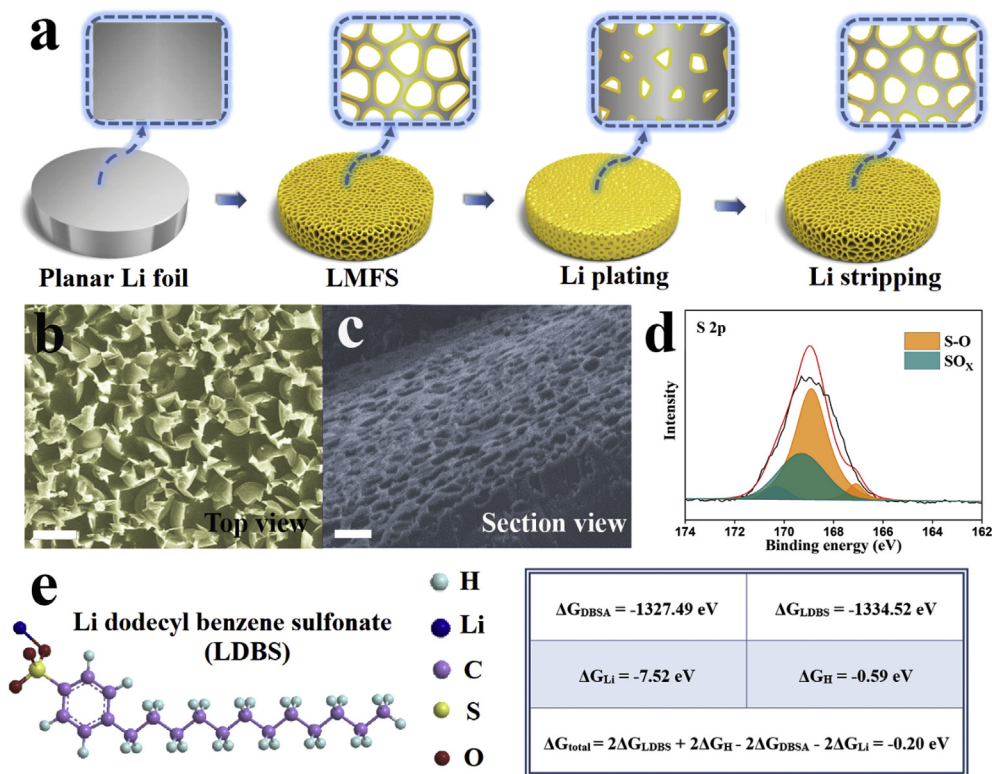


Fig. 1. Scheme, theoretical consideration of LMFS anode. (a) Schematic configuration of the structure and functions of LMFS anode before and after cycles. (b) The top view and (c) section view SEM images of LMFS. Scale bars in **b** and **c** equal to 10 μm. (d) XPS spectra of S 2p performed on the surface of LMFS. (e) Theoretical calculation of Gibbs free energy for LDBS.

carbon paper, which can provide enough sites for the electrodeposition of metal ions and minimize Li volume expansion [15–22]. Nevertheless, this approach will result in an inescapable loss of energy density, and deleterious additional side reactions are still unavoidable, ultimately shortening the battery’s lifespan. Therefore, artificial SEI layers between electrolytes and Li foil are introduced to inhibit the side reactions, improve the defects of traditional 3D host, and decrease the direct contact between Li metal and electrolyte [23–26]. Ideally, the encapsulation of artificial SEI layers on the surface of 3D host can be expected to obtain a deeply cyclable Li metal anode, serving as a protective layer for homogenous Li-ion flux as well as mechanically robust to suppress dendritic Li growth. Unfortunately, the recently reported artificial SEI layers based on surface coating or electrolyte additives are usually unstable and show poor affinity with metal anodes, which have been limited to shallow cycling with the very low depth of only 0.5–1.0 mAh cm⁻² [27–32].

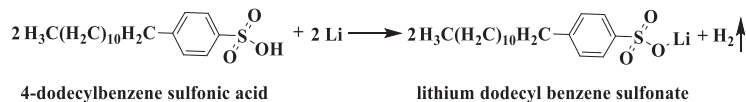
In this study, as an alternative to planar Li foil, freestanding porous

reactions between electrolyte and Li metal, and reducing the gas evolution and heat generation. Taken these advantages, our strategy of inherent SEI Layer encapsulated 3D Li matrix can be deeply cycled at high current densities from 1.0 to 20.0 mA cm⁻² and exhibits stable cycling performance up to 350 h with low overpotential. In addition, LMFS||LiNiCoMnO₂ Li metal batteries also show the excellent cycling performance with high active material loading up to 20.4 mg cm⁻².

2. Results and discussion

2.1. Design of porous Li metal foam accompanied by inherent SEI layer

LMFS was prepared directly using planar Li foil via chemical etching of DBSA. Freestanding porous Li metal foam was obtained by fully submerging lithium foil into DBSA, as described in the following reaction:



lithium metal foam accompanied by inherent SEI layer (LMFS) has been constructed via chemical etching of Li foil using 4-dodecylbenzene sulfonic acid (DBSA) for high-performance Li metal battery (Fig. 1a). The freestanding 3D Li matrix shows abilities to accommodate Li to deposit inside its porous structure, and provides enough space to remit the huge volumetric expansion during Li deposition. Meanwhile, the Li dodecyl benzene sulfonate (LDBS) layers as the protective SEI layers can strongly anchor on the whole surface of 3D matrix during the etching, effectively inducing a uniform electric field for Li-ion diffusion, suppressing the side

3D porous spongy structure (Fig. 1b) with the thickness of 42.5 μm was appeared in the cross section view of LMFS (Fig. 1c) by the scanning electron microscopy (SEM) images. During the chemical etching, the uniform LDBS layer (artificial SEI layer) was anchored on the porous Li matrix. The combination of 3D porous Li matrix and protective artificial SEI layer was further characterized by the EDS mapping (Fig. S1) and X-ray photoelectron spectroscopy (XPS, Fig. S2). As shown in Fig. 1d, the S 2p signal exhibits the main peaks at 169.5 eV and 168.2 eV, which is attributed to R-SO₃ in the LDBS. No signal corresponding to element S

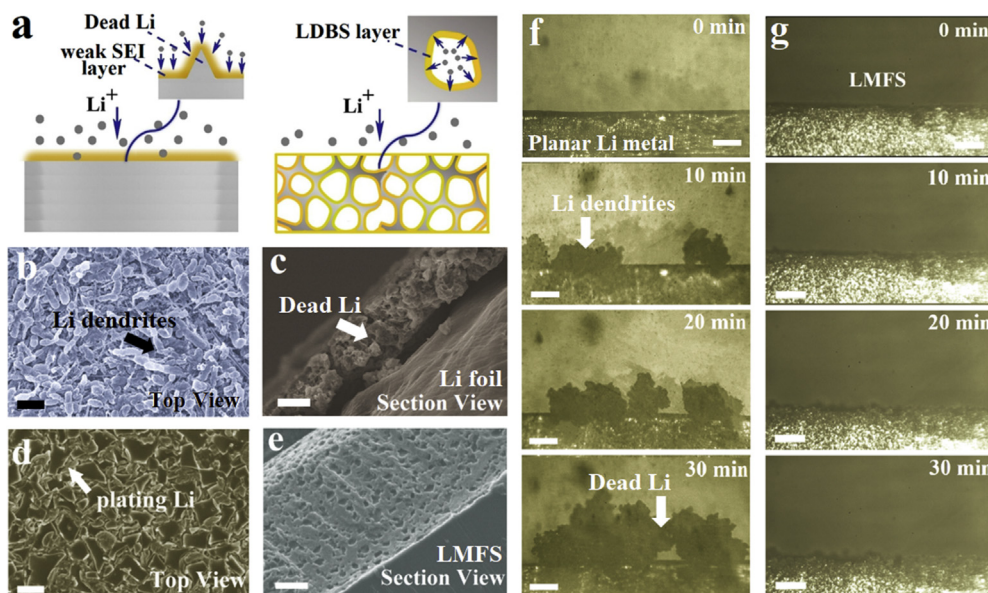


Fig. 2. SEM images and *in-situ* optical microscopy. (a) A schematic of the structural changes in different Li metal anodes. For planar Li metal, the Li^+ flux is concentrated at the tips of small Li dendrites, which will finally lead to the formation of dendritic and mossy Li. In the cycling process of LMFS anode, Li is likely to nucleate and grow at the porous foam matrix on the inner surface of the pores. (b) The top view and (c) section view SEM images of planar Li metal foil after Li plating. (d) The top view and (e) section view SEM images of LMFS after Li plating, which is filled with plating Li. *In-situ* optical microscopy observations of Li deposition process of (f) planar Li metal and (g) LMFS. The scale bars in b, c and e equal 10 μm , d equal 5 μm , f and g equal 100 μm .

can be observed in the S 2p spectrum of bare planar Li metal (Fig. S3). C 1s spectrum can be fitted with an obvious peak at 284.7 eV and a weak peak at 285.4 eV, on behalf of the C-C and C-S bonds (Fig. S4). To examine the reaction mechanism from the theoretical point of view, DFT calculations were employed and shown in Fig. 1e, illustrating the spontaneity of the reactions and the satisfactory chemical stability of LDBS layer.

2.2. Nucleation behavior and *in-situ* optical microscopy observation

As the anode in most common Li metal batteries, the planar Li metal foil is an unstable Li host (Fig. S5), providing minimal reaction sites for Li deposition. The unstable surface and concentrated ion-flux could lead to a heterogeneous charge distribution and expedite the uneven deposition of Li, which induces the growth of Li dendrites (Fig. 2a). Furthermore, the plating/stripping process of planar Li metal foil also accompanied by the repeated crack/repair of weak SEI layer and virtually relative infinite volume change, leading to the internal pressure change and interface fluctuation. From Fig. S6, the nucleation overpotential of planar Li metal anode is about 33.6 mV, which is too high for Li ions to conquer nucleation barriers. As shown in Fig. 2b, after a high Li plating capacity of 5.0 mAh cm^{-2} , the obvious Li dendrites are observed covering the entire surface of planar Li metal foil, indicating the uneven Li deposition. Notably, the sectional view of Li metal (Fig. 2c) shows a loose structure, corresponding to the dead and mossy Li. In a sharp contrast, the free-standing 3D Li metal foam with protective LDBS layer achieves homogeneous charge distribution and smooth Li deposition. The Li metal nucleation overpotential on the LMFS is essentially 3.2 mV, enabling deeply deposited Li metal. As shown in Fig. 2d, the porous matrix with deep perforated tunnel is able to divide the smooth surface of 2D planar surface into various confinements, so that Li ions are expected to move along porous structure, deposit on the surface of tunnel inside LMFS. Li metal will fill the 3D porous matrix rather than directly deposit on the surface of Li metal anode, efficiently accommodating the volumetric change of the Li metal. The encapsulated artificial SEI layer, which efficiently uniform the diffusion of Li ion on the interface and inhibit the side reactions, enables deeply deposited Li metal. Furthermore, no raised Li dendrites are found from the sectional view SEM image of LMFS after plating 5.0 mAh cm^{-2} Li metal (Fig. 2e), which further implies that short-circuiting in the LMFS based Li metal battery is scarcely possible.

In order to illustrate the efficient suppression of Li dendrites growth, *in-situ* optical microscopy observation was used to record the growth

process of Li deposition on planar Li metal and LMFS. Originally, the surfaces of both electrodes are smooth and lack any protuberance. As time goes on, dendrites and protrusions start to appear along the edge of the planar Li metal (Fig. 2f and Video), and become more and more obvious. This process shows the formation and preferential growth of Li dendrites during the plating process, which may cause a notorious internal short circuit of the Li metal batteries and lead to extra safety concerns. In contrast, the edge of LMFS remains smooth, free from Li dendrites or dead Li (Fig. 2g), which is consistent with the results shown in the SEM images.

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.ensm.2019.11.009>.

2.3. Polarization performance of deeply cyclable Li metal anode

The electrochemical behaviors of different Li metal anodes were investigated by a deeply galvanostatic cycling test of the Li||Li and LMFS||LMFS symmetrical cells with LiPF₆/EC/DEC electrolyte. Specifically, Fig. 3a and Fig. S7 show the voltage profiles of different Li metal anodes at a current density of 1.0 mA cm^{-2} and an area capacity of 1.0 mAh cm^{-2} . Due to the high ionic conductivity of the porous structure and dense SEI protection, the overpotential of LMFS electrode is stable at 25 mV. The overpotential can be retained even after cycling for more than 350 h, which is superior to the previously reported results. The cell with the planar Li metal also shows a high and fluctuant overpotential from 100 to 462 mV, which is due to the continuous break/reform of weak SEI layer and the growth of Li dendrites. Moreover, the LMFS anode shows relatively flat and stable voltage plateaus at steady-state while the planar Li metal electrode reports fluctuant voltage response, which is also apparent in the voltage-time profiles of the symmetric cells at higher current densities of 3.0 mA cm^{-2} (Fig. S8) and 5.0 mA cm^{-2} (Fig. 3b) with a larger area capacity of 2.0 mAh cm^{-2} . The results further manifest that the combination of 3D porous Li matrix and protective artificial SEI layer could effectively lower overpotential, elongate the cell lifetime, and stabilize cycling behavior.

Many obsolete strategies show that an electrode containing superfluous Li is only plating and stripping to the very low depth of only 0.5–2.0 mAh cm^{-2} , which are far from commercial applications. It is critical to develop deeply cyclable Li metal anodes and further improve fast-charging capability of the batteries. The symmetrical cells based on LMFS anodes exhibit excellent cycling stability and extra-high rate capability at different current density, mainly arising from the high ionic

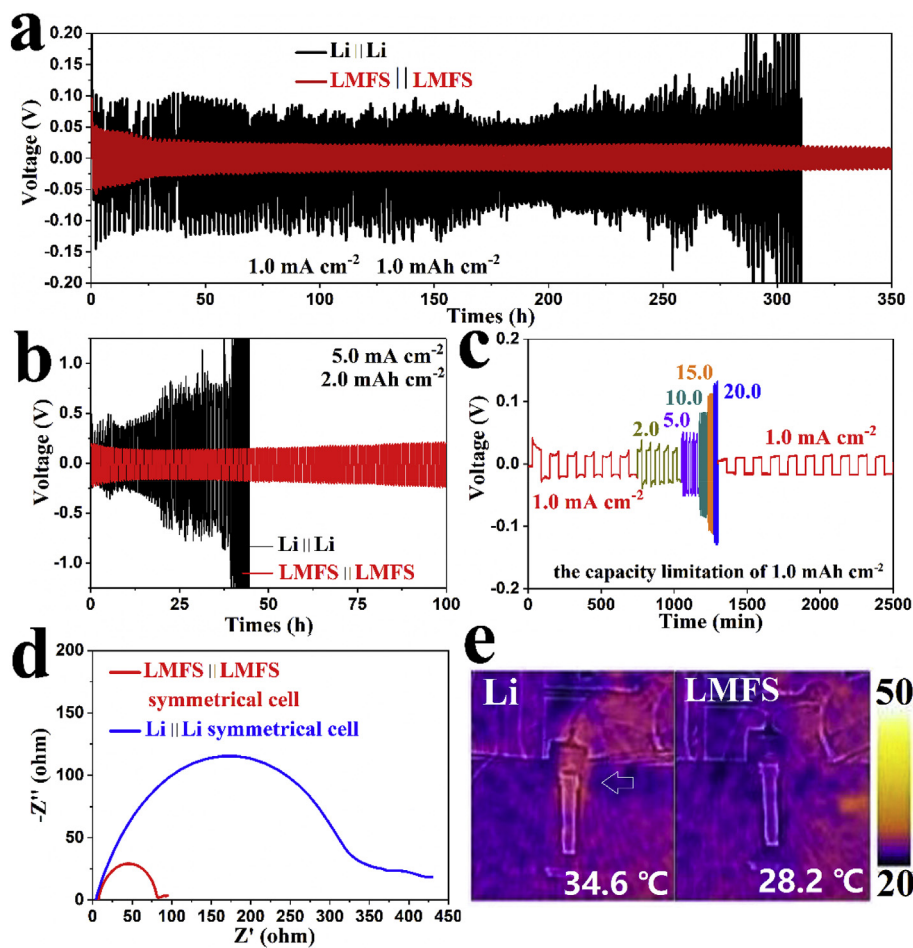


Fig. 3. Electrochemical behavior of Li metal anodes. Voltage-time profiles of the symmetric cells using planar Li metal anode and LMFS anode (a) at a current density of 1.0 mA cm^{-2} with a plating/stripping capacity of 1.0 mAh cm^{-2} , and (b) 5.0 mA cm^{-2} with a plating/stripping capacity of 2.0 mAh cm^{-2} . (c) Voltage profile of LMFS symmetric cell at different rate various from 1.0 to 20.0 mA cm^{-2} with the capacity limitation of 1.0 mAh cm^{-2} . (d) Nyquist plots showing the impedance evolution of symmetric cells with LMFS (red) and Li foil (blue) electrodes. (e) the IR thermal images of different cells after 30 min plating at a current density of 20.0 mA cm^{-2} . (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article).

conductivity and protective effect of LDBS layer. Fig. 3c shows the fast-charging capability of LMFS||LMFS symmetric cell at increasing current densities of 1.0 , 2.0 , 5.0 , 10.0 , 15.0 , and 20.0 mA cm^{-2} with the constant capacity limitation of 1.0 mAh cm^{-2} . The ultra-low overpotential of 84 mV (10 mA cm^{-2}), 114 mV (15 mA cm^{-2}), and 136 mV (20 mA cm^{-2}) can be obtained for LMFS anodes. Furthermore, electrochemical impedance measurement was carried out to study the interfacial stability of fresh symmetrical cells at the open circuit condition. (Fig. 3d). The resistance of LMFS anode (79.6Ω) is far smaller than that of the planar Li metal (365.3Ω), indicating excellent Li ion mobility through the combination of 3D porous Li matrix and protective artificial SEI layer. This can be further demonstrated by the IR thermal test in Fig. 3e. During Li plating/stripping process, the heat generations took place, which is caused by the joule heating and entropy change, and the larger resistance corresponds to more heat generation. The surface temperature of LMFS anode is only 28.2°C after 30 min plating with a high current density of 20.0 mA cm^{-2} , which is smaller than that of planar Li metal anode (34.6°C). The difference of SEI layers between LMFS and planar Li metal after cycles were determined by XPS and AFM analysis. Compared with the traditional compositions of SEI layer for planar Li metal foil, the extra compositions are introduced by artificial SEI layer (LDBS layer) on the whole surface of 3D matrix, which are further confirmed by the C-S and S-O species in XPS spectra of artificial SEI layer (Fig. S9). The LDBS layer endows the SEI layer with enhanced rigidity (high Young's modulus of 11.74 GPa , Fig. S10), which far exceeds that of traditional SEI (low Young's modulus of 0.97 GPa). All of these promote the formation of dense SEI layers with the excellent rigidity, which can suppress the growth of Li dendrites.

2.4. Electrochemical performance of Li metal batteries

Li metal batteries with LiNiCoMnO_2 (Ni:Co:Mn=1:1:1, $\sim 3.0 \text{ mg cm}^{-2}$) cathode and LMFS anode were tested at 0.5 C ($1 \text{ C} = 280 \text{ mA g}^{-1}$) to further demonstrate the advantages and feasibility of LMFS electrode. As shown in Fig. 4a and Fig. S11, the Li metal batteries exhibit high initial discharge capacities of 136.6 mAh g^{-1} . Moreover, the Li metal battery was evaluated by the deeply galvanostatic charge-discharge test at various current rates. From Fig. 4b, it can be seen that a high average discharge capacity was obtained at various rates of 0.2 C – 15.0 C . The capacity can be largely restored for repeated cycles when abruptly switching current rate returns to 0.2 C after deep cycling at 15.0 C . Long-term cyclability is crucial but challenging for rechargeable Li metal batteries, due to its huge volume changes, side reactions and dendritic growth. In this regard, we have evaluated the long-term cycling performance of Li metal batteries based on LMFS anode. Obviously, the LMFS based battery exhibits excellent cycling performance (capacity retention of 84% for 500 cycles) and high Coulombic efficiency (nearly 100%), indicating that the LDBS SEI layer has a great endurance capacity to high voltage and contributes greatly to the excellent reversibility of the battery (Fig. 4c). Even after cycled at a high current rate over 500 cycles, it is still capable of delivering a reversible capacity of about 112.0 mAh g^{-1} . For comparison, the cycling performance of planar Li metal-based battery is also investigated under the identical testing conditions. As a contrast, the battery shows low capacity with fast capacity decay in 140 cycles. Furthermore, a stable cycling performance of LMFS based Li metal batteries with the active material loading of 11.2 mg cm^{-2} and 20.4 mg cm^{-2} at 0.5 C are revealed in Figs. S12–14 with high capacities of 122.6 mAh g^{-1} (82.54 Wh L^{-1}) and 118.3 mAh g^{-1}

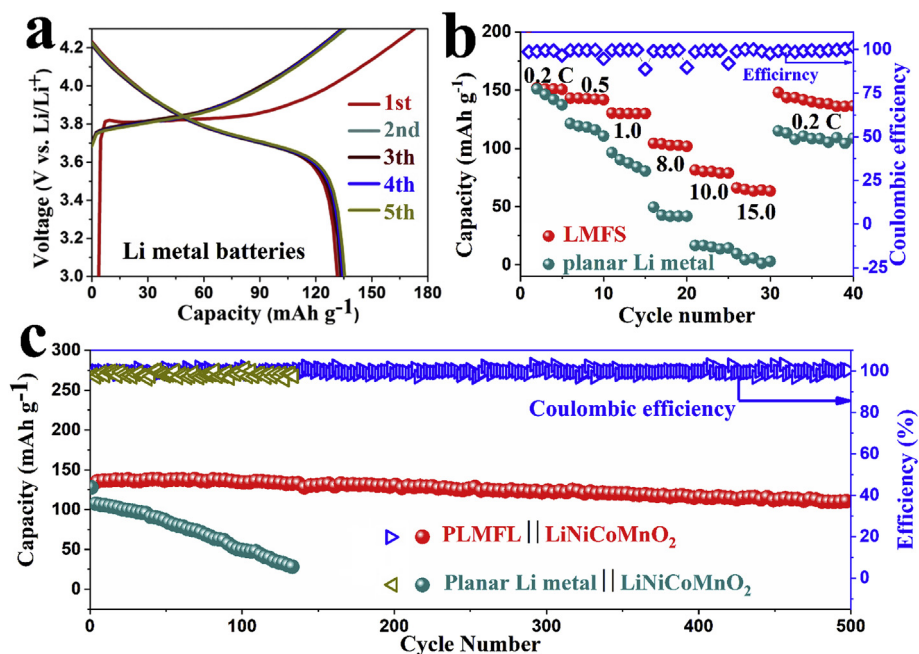


Fig. 4. The electrochemical performance of Li metal batteries. (a) The charge/discharge voltage profiles of first five cycles of LMFS anode for Li metal battery with LiNiCoMnO_2 cathodes at 0.5 C ($1\text{ C} = 280\text{ mA g}^{-1}$). (b) The capacities retention between LMFS and planar Li metal at current densities from 0.2 C to 15.0 C. (c) Long cycling stability and Coulombic efficiency at 0.5 C for more than 500 cycles.

(145.07 Wh L^{-1}) after 100 cycles, respectively.

2.5. In-situ monitoring gas pressure evolution for Li metal batteries

The consumption of active masses and electrolytes in Li metal batteries are caused by the side reactions during the charge and discharge process, accompanied with gas evolution, which results in safety hazards of cell explosion and loss of irreversible capacities (Fig. 5a,b). Gas evolution, which must be limited, is critical to their successful application in

Li metal batteries. The electrolyte decomposition and formation of SEI on Li metal were detected, involving gas evolution and an increase of pressure due to the formation of CH_4 and H_2 [33,34]. For Li metal batteries with planar Li metal in Fig. 5c, the gas pressure increases significantly to 4.6 pounds per square inch (PSI) during the initial 50 h cycles. By contrast, the battery assembled with LMFS anode shows a low and controlled gas pressure with 2.4 PSI after 50 h, due to the covering of LDBS layer. The stable protective layer and Li deposition process can effectively reduce excess side reactions, and suppress the gas evolution.

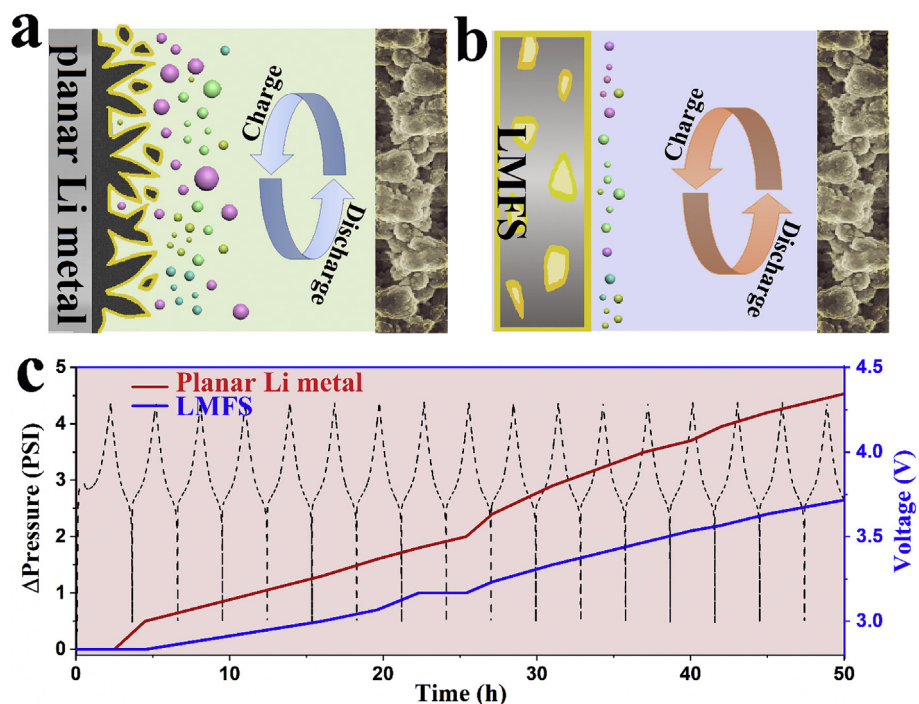


Fig. 5. The gas evolution of Li metal batteries. Overview of the reactions producing gases in Li metal batteries with (a) planar Li metal and (b) LMFS electrode. (c) Pressure trends with dependence on the different charge and discharge time for Li metal batteries.

The results are helpful to better understand the failure mechanisms and thus, developing a new Li metal anode to enhance the safety and performance of Li metal batteries.

3. Conclusion

In summary, we have demonstrated a novel freestanding 3D porous lithium metal foam accompanied by inherent LDBS layer (artificial SEI layer) serves as an alternative to planar Li metal anode. The freestanding 3D porous Li matrix can guide Li deposition inside its porous structure and buffer the volume change. Meanwhile, the LDBS layers, as the dense protective SEI layers, are strongly anchored on the surface of whole Li matrix, leading to uniform diffusion of Li ions on the interface and suppressing side reactions and dendritic Li growth. In addition, we achieve stable Li metal anode that can be deeply cycled at high current densities up to 15.0 and 20.0 mA cm⁻² with the low overpotential. Moreover, excellent electrochemical performance can be achieved by assembling Li metal batteries with LiNiCoMnO₂ cathodes at a total active material mass loading up to 20.4 mg cm⁻². Furthermore, *In-situ* pressure measurements are used to present the gassing behavior of Li metal batteries. These results provide further much-needed insight toward porous/micro structures and compatible SEI protection for Li metal anode, especially after further innovation and improvement.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (no. 51622208) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). T.Y. acknowledges the Fonds de Recherche du Québec - Nature et Technologies (FRQNT) for a personal fellowship. XPS analysis is performed on support centers of Thermo Fisher Scientific Inc. in Shanghai.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ensm.2019.11.009>.

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