

Exploring the Impact of Key Assembling Parameters on the Electrochemical Performance of Lithium Metal Symmetry Cell

To cite this article: Zhipeng Wen et al 2020 J. Electrochem. Soc. 167 020532

View the article online for updates and enhancements.





Exploring the Impact of Key Assembling Parameters on the Electrochemical Performance of Lithium Metal Symmetry Cell

Zhipeng Wen,¹ Yinxin Lin,² Yueying Peng,³ Jing Zeng,^{1,z} and Jinbao Zhao^{1,z}

¹State Key Lab of Physical Chemistry of Solid Surfaces, Collaborative Innovation Centre of Chemistry for Energy Materials, State-Province Joint Engineering Laboratory of Power Source Technology for New Energy Vehicle, Engineering Research Center of Electrochemical Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China ²College of Energy & School of Energy Research, Xiamen University, Xiamen 361102, People's Republic of China

²College of Energy & School of Energy Research, Xiamen University, Xiamen 361102, People's Republic of China ³Materials science, Japan Advanced Institute of Science and Technology, Japan

With the urgent demand for higher energy density storage system, much attention has been focused on the Li metal based batteries. During the exploration of new strategy for the Li metal protection, numerous researches are based on Li/Li symmetry cell for galvanostatic cycling tests. Here, we systematically explored the relationship between some experimental parameters (size of Li foil, thickness of separator and electrolyte amount) and Li/Li symmetry cell cycling performance. And we find that the cycling stability of Li/Li symmetry cell has been significantly improved when the size of Li foil decreases or the thickness of separator increases. In the designed experiments, it can be seen that the failure of most of cells is attributed to the decrease in ions transport ability due to continuous consumption of the electrolyte and continuous increase of dead Li. At last, the investigation of electrolyte amounts reveals that Li/Li symmetry cell exhibits lower Li deposition overpotential and longer cycling life as adding more electrolytes. Therefore, our work suggests that research on the protection of electrolyte is very important issue in promoting the commercialization of Li metal batteries. And standardizing experimental parameters during the experiment can make more efficient comparison of different literature results achieved.

© 2020 The Electrochemical Society ("ECS"). Published on behalf of ECS by IOP Publishing Limited. [DOI: 10.1149/1945-7111/ ab6b11]

Manuscript submitted November 13, 2019; revised manuscript received January 2, 2020. Published January 29, 2020.

Supplementary material for this article is available online

Among the development of rechargeable energy storage systems, metallic lithium has been found to be the most ideal anode material because it has huge specific capacity (3860 mAh cm^{-2}) and the lowest reduction voltage (-3.04 V vs standard hydrogen electrode).¹⁻³ So far, Li metal based energy storage systems (e.g. Li-S cell,⁴ Li-O₂ cell⁵) have obtained enormous developments. Unfortunately, practical application of Li metal anode still is impeded by the unstable Li metal/electrolyte interface and the formation of Li dendrite.^{6,7} During charge/discharge process, a solid electrolyte interface (SEI) film is formed on Li metal owing to the reactions between the high reactive Li metal and the organic solvents and Li salts. However, the Li metal anode exhibits infinite relative volume change due to the non-host deposition and dissolution, which results in the fracture of native SEI film and the exposure of fresh Li metal to organic electrolyte, thus leads to continuous consumption of the electrolyte and the Li metal. In addition, uneven Li deposition is more likely to occur in the crack of SEI film, contributing to the formation of Li dendrite. Uncontrollable Li dendrite is easy to detach from the conductive skeleton to form dead Li, which further results in uneven Li deposition and sustained consumption of Li metal. These issues are influenced and related to each other, leading to the vicious circle. As a result, the Li metal based batteries have suffered from low coulombic efficiency, limited cycling span and even safety risk.8,9

To tackle these serious issues, enormous useful strategies have been applied to improve the cycling stability of Li metal, such as electrolyte addictive,^{10–12} construction of artificial SEI film,^{13,14} modification of conductive substrate^{15,16} and structure design of Li metal anode.¹⁷ Among these studies, most researchers are prone to use the Li foil as working electrode and counter electrode to assemble Li/Li symmetry cell for galvanostatic cycling tests in order to evaluate the electrochemical performance.^{18–20} The cycling stability of the Li metal anode is measured by the overpotential and the cycle life. However, during the process of cell assembling, each experimental parameter selected has great influence on the cycling performance of the Li/Li symmetry cell, such as the Li foil size, thickness of separator and electrolyte amounts. A recent report of Dahn's group has revealed the impact of mechanical pressure on the cycling performance of anode-free Li metal cell.²¹ The increase in the average mechanical pressure is found to improve the cycling span generally. In fact, some seemingly useless parameters play a vital role in the stability of Li metal cell. Understanding the impact of common parameters on the cycling performance of Li metal cell can verity the advantages of proposed strategies more intuitively, which promotes the progress in the investigation. In addition, it also can contribute to find the most critical parameters affecting the electrochemical performance of Li metal cell, thus improving the efficiency of Li metal cell for practical application. At last, it can effectively regulate the assembly experiment of Li/Li symmetry cell, which is beneficial to achieve horizontal comparison of similar experiment results in different literatures. However, the comprehensive study on how experimental parameters affect the performance of Li/Li symmetry cells is rarely reported. Therefore, a systematic research on the impact of common parameters on performance of Li/ Li symmetry cell is urgently needed.²

Bare these in mind, we systematically explored the relationship between some experimental parameters (size of Li foil, thickness of separator and electrolyte amounts) and Li/Li symmetry cell cycling performance. And the results show that the cycling stability of Li/Li symmetry cell has been significantly improved when the size of Li foil decreases or the thickness of separator increases. Reducing the size of the Li foil can significantly reduce the contact area between the electrolyte and the Li metal, thereby the consumption of the electrolyte is reduced. Increasing the thickness of the separator not only provides a stronger barrier to Li dendrite, but also absorbs more electrolytes. In the designed experiments, the failure of most of cells is attributed to the decrease in ions transport ability due to continuous consumption of the electrolyte and continuous increase of dead Li. As the electrolyte amount increases, the cell exhibits more stable cycling performance and lower overpotential. When the electrolyte amount is sufficient, more stable electrolyte/electrode interface has formed, contributing to better cycling stability and the suppression in Li dendrite. In summary, our work rigorously investigates the relationship between the cycling performance and experimental parameters of Li/Li symmetry cell, contributing to evaluate the new strategy of Li metal protection more accurately and promoting the practical process of Li metal-based batteries.

Experimental

Material characterization.—For the accuracy of experimental results, when the cells failed, the Li foils were characterized at once after disassembling the failed cells. The scanning electron microscope (SEM) images were carried out by using the HITACHI S4800 at the acceleration voltage of 10 kV and the probe current of 10 μ A.

Electrochemical measurements.—For the electrochemical measurements, the coin-type cells (CR2032) were assembled in the argon-filled glove box. The commercial 301 carbonate electrolyte (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.) was used as the electrolyte which was composed of 1 M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1, in volume) with 2 wt.% vinylene carbonate (VC) as an additive, the celgard 2400 was used as the separator, and the Li foil of same size were used as the working electrode and counter electrode, respectively.

During the investigation of the impact of Li foil size, the Li foils with different size of 1.0 cm^2 and 2.0 cm^2 were tested. In order to eliminate the interference of other parameters, $60 \ \mu$ l commercial 301 carbonate electrolyte and one layer of celgard 2400 separator were applied in the investigation. When investigating the impact of separator thickness, different separators with thickness of 25 μ m, 50 μ m and 75 μ m were tested, while keeping the size of Li foil (1.0 cm^2) and electrolyte amounts ($60 \ \mu$ l) unchanged. In the last investigation, the different electrolyte amounts of $10 \ \mu$ l, $20 \ \mu$ l, $30 \ \mu$ l, $40 \ \mu$ l and $60 \ \mu$ l were consumed to study the impact of the amount of electrolyte, testing with Li foil in the size of 1.0 cm^2 and one layer of celgard 2400 separator.

To test the cycling performance of Li/Li symmetry cells, the cells were tested after a rest time of 10 h to wet the separator. The Li deposition and dissolution process were investigated with the current density of 1 mA cm^{-2} and the Li amounts of 1 mAh cm^{-2} .

The electrochemical impedance spectra (EIS) of the Li/Li symmetry cell with different electrolyte amounts, which have cycled 2 cycles with the current density of 1 mA cm^{-2} and the Li capacity of 1 mAh cm^{-2} , were measured in the frequency range of 10 mHz-100 kHz via an Autolab PGSTAT 101 cell test instrument.

Exploration of the impact of key parameters.-To further investigate the impact of pivotal parameters on cell cycling performance, the following experiments were designed. (i) After the cell failed, the cycled separators were taken to pair with fresh Li foils and the same amounts of electrolyte to assemble new Li/Li symmetry cell to check the failure of the separator. If the cycled separator had been pierced by Li dendrite, the new cell with cycled separator cannot operate normally. Therefore, the experiment result can reflect whether the cell failure is caused by Li dendrites. The experiment result is marked with "Cycled Separator" in the following discussion. (ii) To investigate the impact of electrolyte amounts, the failed cells were added the same amounts of electrolyte as before. If the failed cell restarts cycling due to refilled electrolyte. the test can prove that the consumption of the electrolyte is a major factor for the cell failure process. All the reassembled cells were tested with the current density of 1 mA cm^{-2} and the Li amounts of 1 mAh cm^{-2} . The experiment result is marked with "Re_Electrolyte" in the following discussion.

Results and Discussion

The impact of the size of Li foil.—At the beginning of investigation on the impact of experimental parameters, the size of



Figure 1. (a) Cycling performances of Li/Li symmetry cells with different sizes of Li foil. Optical photos of cycled cells after failure with different size of Li foil, (b) 1.0 cm², (c) 2.0 cm².

Li foil was selected. Two kinds of Li foil were chosen to study the issues of Li metal degradation during long-term cycling performance. Although reaction surface areas of the Li foils were different, current density and capacity density were ensured to be the same for comparison (Table SI is available online at stacks.iop.org/JES/167/ 020532/mmedia). For the purpose of cycling performance, the cells with different sizes of Li foil were cycled with a current density of 1 mA cm⁻² and a capacity density of 1 mAh cm⁻² until short circuit happened (Fig. 1a). The cell with Li foil of 1.0 cm² can cycle for nearly 400 h with the stable overpotential of 60 mV. However, the cell with Li foil of 2.0 cm² exhibits a high overpotential of 200 mV, and the overpotential continuously increases after 150 h due to the continuous formation of dead Li. This result indicates the cycling performance rapidly decays with the increase in the size of Li foil. For the purpose of observing the degradation of Li metal anode more intuitively, the optical photographs were collected in Figs. 1b and 1c. It can be easily seen that the cell of Li foil (2.0 cm^2) accompanies with more serious formation of dead Li. And from the high magnification optical photograph of cycled separator (Fig. S1), the result reveals that the separators are dry after long-term cycles, which indicates the complete consumption of electrolyte. In a word, the increase in the size of Li foil will bring the more serious Li metal anode degradation and shorter cycling span, simultaneously.

The corresponding experiments were designed to explore the reasons why the size of Li foil affects the performance of Li metal anode. The cycled separators are taken to pair with new Li foil to assemble new Li/Li symmetry cells (Figs. 2a, 2d). The Li/Li symmetry cells with long-term cycled separator have no failure and still achieves the normal Li stripping/plating, indicating the separator are not pierced by Li dendrite. In addition, the electrolyte are refilled to the failed symmetry cells with different sizes of Li foil, and all the failed cells resumes to normal cycle (Figs. 2a, 2d). This result suggests that the failure of cell is related to the amount of electrolyte. SEM was used to observe the morphology of cycled Li

metal. As shown in Figs. 2b and 2c, the Li foil of 1.0 cm^2 shows Li deposition with a relatively dense morphology. Instead, the Li foil of 2.0 cm^2 exhibits extremely rough surface with many cracks on Li metal (Figs. 2e and 2f). Based on the above experimental results, it can be summarized that consumption of the electrolyte is the main reason for the failure of cell. The increase of the size of used Li foil increases the contact area between Li metal and the electrolyte, which results in an increase in the consumption of electrolyte under the same test conditions. During cycling process, a larger-sized Li foil accelerates the consumption of electrolyte and leads to a decrease in ions transport ability, resulting in the failure of cell happens earlier.

The impact of the thickness of separator.--Separator, as an important part of the battery, plays a role in the prevention of short circuit. In addition, the separator also has the function of blocking Li dendrite in Li metal-based batteries. As shown in the previous reports, high mechanical strength separator, such as ceramic separator, can block Li dendrite and effectively improve the cycle life of Li metal-based batteries.^{25–27} Here, under a current density of 1 mA cm⁻² and a deposition capacity of 1 mAh cm⁻², Li/Li symmetry cells with different layers of separator were assembled and tested to study the effect of the thickness of the separator on the performance of the Li/Li symmetry cell (Detailed operations are shown in Experimental Methods). As illustrated in Fig. 3a, the cell with 25 μ m separator has cycled for 300 h with a stable overpotential of 94 mV and fails due to the micro short circuit after 392 h. When the thickness of separator increases to 50 μ m, the cell has cycled for more than 500 h. This is because an increase in separator thickness can greatly improve the mechanical strength and electrolyte retain. However, compared with the cell using 50 μ m separator, the cell with 75 μ m separator exhibits a larger overpotential and no obvious improvement in the cycling performance. The reason is that excessive thickness of separator increases the pathway and



Figure 2. Li/Li symmetry cell performance with cycled separator and refilling the electrolyte with the Li foil of (a) 1.0 cm^2 and (d) 2.0 cm^2 . SEM images of cycled Li metal of (b, c) 1.0 cm^2 and (e, f) 2.0 cm^2 .



Figure 3. (a) Cycling performances of Li/Li symmetry cells with different thickness of separator. Optical photographs of cycled cell after failure with different thickness of separator, (b) 25 μ m, (c) 50 μ m, (d) 75 μ m.

resistance of Li⁺ conduction. Therefore, it can be concluded that a proper increase of thickness of separator is beneficial to slow down the growth of Li dendrite and effectively improve the cycling performance, while excessive thickness of separator leads to an increase in the impedance and decrease in ion transport ability. Optical photographs of disassembled cells are shown in Figs. 3b–3d. The cell with separator of 25 μ m exhibits less dead Li in the surface of Li foil due to the limited cycling span. Additionally, the quite obvious puncture phenomenon cannot be found in the different thickness of separator, which indicates that the cycling failure cannot happen due to the huge Li dendrite.

For the purpose of exploring the possibility of cell short circuit due to the separator piercing, the similar explorations were also designed. From the overall cycling performance experimental results, it can be easily seen that the cycling overpotential increases quickly when the cycled separator assembled with new Li foil. Additionally, during the experiment of refilling the electrolyte, the cycled cell can obtain normal Li plating/deposition process. When the thickness of separator is limited to 25 μ m, the cell fails after cycling for 390 h. However, the cell can cycle normally with new Li foil, which indicates that the guilt of cell failure is not on the separator. With refilled same amounts of electrolyte, the cell of separator (25 μ m) shows very unstable cycle curve, and the overpotential is often reduced in cliff type (Fig. 4a), resulting from the dead Li formed in previous cycles. This judgment can also be confirmed by SEM photographs. As shown in Fig. 4c, there is Li dendrite formatted on the surface of Li foil. When the thickness of separator increases to 50 μ m, the electrochemical performance has changed differently. Whether matched with new Li foil or re-added the electrolyte, the cells guarantee normal cycle process (Fig. 4d). On the one hand, after the cycled Li foil is replaced, the cell can keep the stable deposition potential of 100 mV cycled for 150 h. On the other hand, after the electrolyte is re-added, a stable overpotential of 70 mV can be maintained. Such excellent electrochemical properties also confirm the inhibition of Li dendrite by thicker separator, which

can be seen in Fig. 4f. The thicker separator not only inhibits the formation of Li dendrite, but also protects the electrolyte certainly, reducing the endless loss of electrolyte during the cycle. However, the cycling performance of the cell has not been further improved as expected, when the thickness of separator increases. When the cycled Li foil has been replaced, the cell exhibited larger deposition overpotential at the beginning, meaning that Li⁺ encountered greater impedance during the deposition process. When the electrolyte is readded, the cell can maintain stable overpotential of 70 mV for 200 h. The thicker separator guarantees more stable cycling performance, compared with the cycling performance of separator (50 μ m). Since the re-addition of the electrolyte is equivalent to ensuring that the electrolyte required for the Li foil is sufficient, therefore, it can be concluded that the thicker separator can provide more effective protection for the limited electrolyte, and thus can greatly reduce the unnecessary electrolyte loss, thereby improving the electrochemical performance. By comparing the SEM images of separator (50 μ m), the surface of the Li foil in the cell with 75 μ m separator is more severe, which may be due to the uneven electric field on the surface of the Li foil. In general, it can be seen that the thicker separator can lead to more stable electrochemical performance. This is not only because the thicker separators has more effective inhibition of the formation of Li dendrite, but also because the thicker separator possesses better liquid retention ability and can effectively reduce the loss of electrolyte, so it can effectively improve cycling performance. However, too thick separator will have a greater hindrance to the transport of Li+, thus promoting more uneven electric field on the surface of the Li foil and will result in an increase in the deposition overpotential.

The impact of electrolyte amounts.—The above analyses show that the amount of electrolyte has a great effect on the long cycling performance of Li/Li symmetry cell, which is agree with previous report.²⁸ Thus Li/Li symmetry cells with different amounts of electrolyte (10 μ l, 20 μ l, 30 μ l, 40 μ l, 60 μ l) were assembled to



Figure 4. Li/Li symmetry cell performances with cycled separator and refilling the electrolyte with the separator thickness of (a) 25 μ m, (d) 50 μ m and (g) 75 μ m. SEM images of cycled Li metal with the separator thickness of (b, c) 25 μ m, (e, f) 50 μ m and (h, i) 75 μ m.

investigate the effect of the amount of electrolyte on the cycling performance. According to the calculation in Supporting Information, it can be found that one layer of celgard 2400 can storage 2.9 μ l electrolyte at most. Therefore the separator can be wet by added even 10 μ l electrolyte. As shown in Fig. 5a, it can be easily found that the cell with larger amount of electrolyte exhibits better cycling performance. When only 10 μ l electrolyte is added, the cell shows a large deposition overpotential because the stable electrolyte/ anode interface cannot be formed at the beginning, and the cell fails after cycling for 100 h. When the electrolyte increases to 20 μ l, the cell can be cycled for 200 h, which is obviously higher than the cell with 10 μ l electrolyte. When the amount of electrolyte continues to increase, the cells can also be cycled for a longer period of time. Specially, when the amount of electrolyte is $60 \mu l$, that is, the electrolyte is excessive, the Li/Li symmetry cell can maintain the long-term cycling lifespan of 500 h. As shown in Fig. 5b, the cells with larger amount of electrolyte exhibit excellent cycling stability

with lower overpotential. This is because the increase in electrolyte repeatedly repairs the unstable electrolyte/electrode interface. Figures 5b–5c shows that the cell with small amount of electrolyte exhibits the sudden increase of the overpotential as the cycling goes on, whereas the cell with large amount of electrolyte has cycled with stable overpotential. This is due to a fact that the sufficient electrolyte can ensure the ion transport during the long cycling, which mitigates the increase in impedance. In short, when using more electrolytes, the cell can achieve more stable long cycle life.

The optical photographs of cycled cells and the SEM images of cycled Li metal were observed to investigate the impact of electrolyte amounts on the morphology of the Li metal anode (Fig. 6). Firstly, it can be seen from the optical pictures that as the amount of electrolyte increases, the Li metal undergoes longer cycling time, so the amount of dead Li generated by parasitic reactions also increases. When the amount of the electrolyte is $10 \ \mu$ l, the shape of the Li foil is broken, and only the part of surface has



Figure 5. (a) Comparison of the cycling performances of Li/Li symmetry cells with different amounts of electrolyte. (b) Comparison of the voltage hysteresis of the Li stripping/plating with different amounts of electrolyte. (c) Detailed voltage profiles of the Li/Li symmetry cells at 1st, 100th, 200th, and 300th cycle, respectively.

dead Li. However, when the electrolyte amount is $60 \mu l$, the symmetry cell has already undergone about 500 h, and the dead Li completely covers above the fresh Li metal. Not only that, although only 10 μ l of electrolyte is added, it can be seen that all the surface of the Li foil has participated in the Li metal stripping/plating process. Therefore, it can be inferred that there is no state in which only the electrode is partially involved in the electrochemical reaction due to insufficient electrolyte. However, more electrolyte amounts is beneficial to form more even and stable electrode/ electrolyte interface, as shown in SEM images of cycled Li metal anode with different electrolyte amounts. The heterogeneous electric field environment increases the polarization of Li deposition and easily promotes the formation and growth of Li dendrite. By contrast, the interface formed is stable when the amount of electrolyte is sufficient, which can effectively promote electric field homogenization and block further contact between the electrolyte and the Li metal. Therefore, not only the long cycle life can be achieved, but also the formation of Li dendrite can be delayed with the sufficient electrolyte. In short, more electrolyte amount not only help to form a more stable electrode/electrolyte interface and suppress the formation and growth of Li dendrite, but also promote the cycling performance of Li metal symmetry cell.

To further explore the role of electrolyte in Li/Li symmetry cell, the cycling performances with cycled separator and refilling electrolyte have been collected in Fig. 7a. It is obviously shown that the cell resumes normal operation when the electrolyte has been refilling. Nevertheless, when the cycled Li foil is replaced, the cycle time of the sample with more electrolytes added decreases. It is mainly because the sample with more electrolyte addition undergoes more cycles during the first test, resulting in more dead Li on the surface of Li metal, which hinders further operation of the cell. In addition, from the EIS spectra of the Li/Li symmetry cell with different electrolyte amounts (Fig. 7b), it can be seen that he impedance of cell increases due to the consumption of the electrolyte, and the sufficient electrolyte can promote the formation of lower impedance SEI film. Combined with the above mentioned, we find that electrolyte plays an important even decisive role in Li metal batteries. Both the size of the Li foil and the thickness of separator affect the electrolyte environment to a certain extent and the performance of the Li metal battery. The amount of electrolyte affects the stability of the electrode/electrolyte interface, and has significant impact on the cycling life and safety performance of Li/Li symmetry batteries. Therefore, the protection of the electrolyte during cycling can be vital issue in the preparation of high cycling performance and high safety performance Li metal battery.

Conclusions

In this work, we systematically investigate the impact of key parameters (size of Li foil, thickness of separator and electrolyte amount) on the cycling performance of Li/Li symmetry cell. The results show that these experimental parameters have a significant impact on the experimental results. As the size of Li foil increases, the cycling life span of Li/Li symmetry cell drops rapidly, from 460 h to 225 h. However, the Li/Li symmetry cell holds more stable long-term cycling performance when the thickness of separator increases, due to better protection from the separator. At last, the investigation of electrolyte amounts reveals that the Li/Li symmetry cell exhibits lower Li deposition overpotential and longer cycling life as adding more electrolytes. In addition, the electrode/electrolyte interface formed is more stable when the amount of electrolyte is sufficient. Therefore, it can contribute to more stable Li deposition



Figure 6. The optical photographs of cycled cells and the SEM images of cycled Li metal anode after failure with electrolyte amounts of (a)–(c) 10 μ l, (d)–(f) 20 μ l, (g)–(i) 30 μ l, (j)–(l) 40 μ l, and (m)–(o) 60 μ l.

environment and suppression in Li dendrite. In general, these experimental parameters can significantly affect battery properties. Among them, the electrolyte is a decisive factor in battery cycling performance. Therefore, this work suggests that research on the protection of electrolyte is a very important issue in promoting the commercialization of Li metal batteries. And standardizing experimental parameters during the experiment can make more efficient comparison of different literature results achieved.



Figure 7. (a) Comparison of the Li/Li symmetry cells cycling performances with cycled separator and refilling the electrolyte. (b) EIS spectra of the Li/Li symmetry cell with different electrolyte amounts.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Nos. 21875198 and 21875195), the National Key Research and Development Program of China (No. 2017YFB0102000), and the Fundamental Research Funds for the Central Universities (No. 20720190040).

References

- W. Xu, J. L. Wang, F. Ding, X. L. Chen, E. Nasybutin, Y. H. Zhang, and J. G. Zhang, "Lithium metal anodes for rechargeable batteries." *Energ. Environ. Sci.*, 7, 513 (2014).
- X. B. Cheng, R. Zhang, C. Z. Zhao, and Q. Zhang, "Toward safe lithium metal anode in rechargeable batteries: a review." *Chem. Rev.*, **117**, 10403 (2017).
- H. Kim, G. Jeong, Y. U. Kim, J. H. Kim, C. M. Park, and H. J. Sohn, "Metallic anodes for next generation secondary batteries." *Chem. Soc. Rev.*, 42, 9011 (2013).
- Y. Y. Peng, Z. P. Wen, C. Y. Liu, J. Zeng, Y. H. Wang, and J. B. Zhao, "Refining interfaces between electrolyte and both electrodes with carbon nanotube paper for high-loading lithium-sulfur batteries." ACS Appl. Mater. Interfaces, 11, 6986 (2019).
- J. L. Ma, F. L. Meng, Y. Yu, D. P. Liu, J. M. Yan, Y. Zhang, X. B. Zhang, and Q. Jiang, "Prevention of dendrite growth and volume expansion to give highperformance aprotic bimetallic Li-Na alloy-O2 batteries." *Nat. Chem.*, 11, 64 (2019).
- J. Yamaki, S. Tobishima, K. Hayashi, K. Saito, Y. Nemoto, and M. Arakawa, "A consideration of the morphology of electrochemically deposited lithium in an organic electrolyte." J. Power Sources, 74, 219 (1998).
- F. Shi, A. Pei, D. T. Boyle, J. Xie, X. Yu, X. Zhang, and Y. Cui, "Lithium metal stripping beneath the solid electrolyte interphase." *Proc. Natl. Acad. Sci. USA*, 115, 8529 (2018).
- J. M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries." *Nature*, **414**, 359 (2001).
- H. Li, C. Y. Liu, X. B. Kong, J. Cheng, and J. B. Zhao, "Prediction of the heavy charging current effect on nickel-rich/silicon-graphite power batteries based on adiabatic rate calorimetry measurement." *J. Power Sources*, 438, 226971 (2019).
- Y. Yang, J. Xiong, S. B. Lai, R. Zhou, M. Zhao, H. B. Geng, Y. F. Zhang, Y. X. Fang, C. C. Li, and J. B. Zhao, "Vinyl ethylene carbonate as an effective SEI-forming additive in carbonate-based electrolyte for lithium-metal anodes." ACS Appl. Mater. Interfaces, 11, 6118 (2019).
- F. Ding et al., "Dendrite-free lithium deposition via self-healing electrostatic shield mechanism." J. Am. Chem. Soc., 135, 4450 (2013).
- 12. E. Markevich, G. Salitra, and D. Aurbach, "Fluoroethylene carbonate as an important component for the formation of an effective solid electrolyte interphase

on anodes and cathodes for advanced Li-Ion batteries." ACS Energy Lett., 2, 1337 (2017).

- Y. Gu et al., "Designable ultra-smooth ultra-thin solid-electrolyte interphases of three alkali metal anodes." *Nat. Commun.*, 9, 1339 (2018).
- Q. Zhao, Z. Y. Tu, S. Y. Wei, K. H. Zhang, S. Choudhury, X. T. Liu, and L. A. Archer, "Building organic/inorganic hybrid interphases for fast interfacial transport in rechargeable metal batteries." *Angew. Chem., Int. Ed. Engl.*, 57, 992 (2018).
- Z. P. Wen, Y. Y. Peng, J. L. Cong, H. M. Hua, Y. X. Lin, J. Xiong, J. Zeng, and J. B. Zhao, "A stable artificial protective layer for high capacity dendrite-free lithium metal anode." *Nano Res.*, 1 (2019).
- Y. P. Tang, K. Shen, Z. Y. Lv, X. Xu, G. Y. Hou, H. Z. Cao, L. K. Wu, G. Q. Zheng, and Y. D. Deng, "Three-dimensional ordered macroporous Cu current collector for lithium metal anode: uniform nucleation by seed crystal." *J. Power Sources*, 403, 82 (2018).
- Z. Liang et al., "Composite lithium electrode with mesoscale skeleton via simple mechanical deformation." Sci. Adv., 5, eaau5655 (2019).
- H. Zhang et al., "Lithiophilic-lithiophobic gradient interfacial layer for a highly stable lithium metal anode." *Nat. Commun.*, 9, 3729 (2018).
- H. Ye et al., "Guiding uniform Li plating/stripping through lithium-aluminum alloying medium for long-life Li metal batteries." *Angew. Chem., Int. Ed. Engl.*, 58, 1094 (2019).
- W. Tang et al., "Lithium silicide surface enrichment: a solution to lithium metal battery." Adv. Mater., 30, 1801745 (2018).
- A. J. Louli, M. Genovese, R. Weber, S. G. Hames, E. R. Logan, and J. R. Dahn, "Exploring the impact of mechanical pressure on the performance of anode-free lithium metal cells." *J. Electrochem. Soc.*, **166**, A1291 (2019).
- J. W. Xiang, L. Y. Yang, L. X. Yuan, K. Yuan, Y. Zhang, Y. Y. Huang, J. Lin, F. Pan, and Y. H. Huang, "Alkali-metal anodes: from lab to market." *Joule*, 3, 2334 (2019).
- S. H. Jiao, J. M. Zheng, Q. Y. Li, X. Li, M. H. Engelhard, R. G. Cao, J. G. Zhang, and W. Xu, "Behavior of lithium metal anodes under various capacity utilization and high current density in lithium metal batteries." *Joule*, 2, 110 (2018).
- 24. H. Li, "Practical evaluation of Li-Ion batteries." Joule, 3, 911 (2019).
- W. Na, A. S. Lee, J. H. Lee, S. S. Hwang, E. Kim, S. M. Hong, and C. M. Koo, "Lithium dendrite suppression with UV-curable polysilsesquioxane separator binders." ACS Appl. Mater. Interfaces, 8, 12852 (2016).
- W. Luo, L. H. Zhou, K. Fu, Z. Yang, J. Y. Wan, M. Manno, Y. G. Yao, H. L. Zhu, B. Yang, and L. B. Hu, "A thermally conductive separator for stable Li metal anodes." *Nano Lett.*, **15**, 6149 (2015).
- C. Z. Zhao, P. Y. Chen, R. Zhang, X. Chen, B. Q. Li, X. Q. Zhang, X. B. Cheng, and Q. Zhang, "An ion redistributor for dendrite-free lithium metal anodes." *Sci. Adv.*, 4, eaat3446 (2018).
- T. Hirai, I. Yoshimatsu, and J. Yamaki, "Influence of electrolyte on lithium cycling efficiency with pressurized electrode stack." *J. Electrochem. Soc.*, 141, 611 (1994).