Electronic Supplementary Material (ESI) for Chemical Society Reviews.

TUTORIAL REVIEW PROPOSAL

CHEMICAL SOCIETY REVIEWS

Please upload your completed form at https://mc.manuscriptcentral.com/csr

Please read the following information carefully before completing the form. Forms which are incomplete or do not follow the guidance provided may be returned to the authors for editing prior to consideration. Please do not submit your full review at this stage.

Tutorial Reviews are concise, authoritative overviews of important contemporary topics in the chemical sciences. They should appeal to advanced undergraduates, the general research chemist who is new to the field, as well as the expert. They provide a solid introduction to the development of a subject, the latest breakthrough results and their implications for the wider scientific community.

Tutorial Reviews must be:

- **Accessible**: Appeal to advanced undergraduate students and beyond. Tutorial reviews are often used in advanced undergraduate and Master's studies.
- **Authoritative**: Provide an essential introduction to the field which will lay the foundation of knowledge in the area, followed by the most important recent advances. Authors should include throughout the article their own insights into the development of the field and its future potential.
- **Exciting**: In particular highlight areas where there has been a significant recent advance.
- **Concise**: There is no strict reference limit; however please include only the most important historical and recent research, referencing the major contributions. Tutorial Reviews are typically up to 15 journal pages in length.
- **Jargon free**: Specialist terms and symbols should be defined and fundamental ideas simply explained.

Tutorial reviews should include a 'key learning points' box, containing up to five key learning points that a reader should expect to gain from reading the review. These should be provided on submission, either at the beginning of the review or as a separate document.

All articles should focus on key developments in a field, with the author providing their own analysis and insight throughout on developments, trends, future directions and significance for the wider scientific community. **Articles which simply summarise research in the topic with minimal or no analysis or insight from the author are not suitable for publication in *Chem Soc Rev*.** To achieve this goal, we ask authors to use new graphics where possible (e.g., by redrawing schemes), and to aim for no more than 20% of graphics in their article to be reused from previously published work. We understand that in some cases it is necessary to include more previously published graphics (for example, where graphs or microscope images are shown), and in these cases we ask authors to provide a very brief justification at full manuscript submission.

PROPOSED TITLE:
3D hosted lithium metal anodes

AUTHOR(S):
Xin He, Kai Zhang, Zhiqiang Zhu, Zhangfa Tong and Xiao Liang*

ADDRESS:
Dr. X. He, Prof. Z. Zhu, Prof. X. Liang
State Key Laboratory of Chem/Bio-Sensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082 China;
Prof. K. Zhang
Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China
Prof. Z. Tong,
Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

EMAIL:
xliang@hnu.edu.cn;

ORCID ID:

RESEARCH WEBPAGE:

PROPOSED SUBMISSION DATE:

PROPOSAL QUESTIONS:

Please complete all sections, ensuring your answers are succinct and within the word limit.

1) Please comment on why the proposed topic is currently important

In recent years, lithium metal has gained considerable attention as a highly desirable anode material for rechargeable batteries, owing to its remarkable theoretical capacity than that of graphite. Nevertheless, the uneven plating and stripping of lithium metal anodes have resulted in the formation of dendrites and reduced coulombic efficiency, thereby impeding its potential in real-world applications. In order to address these challenges, the implementation of the 3D scaffold/host strategy has emerged as a compelling approach to concurrently mitigate volume fluctuations and dendrite growth in lithium metal anodes. However, the identification and development of suitable scaffold/host materials that satisfy the requirements of practical applications remain a formidable obstacle. In light of this, a comprehensive discussion and summary of potential design criteria and developmental trends for scaffold/host materials is of utmost significance, as it can provide invaluable guidance for future researchers engaged in the advancement of lithium metal anodes.

2) What are the implications for the wider scientific community?

Through the progressive advancement of Li composite anodes utilizing scaffold/host strategies, there exists the potential to substantially augment the energy density of existing batteries, leading to a transformative impact on the energy market. An exemplary outcome of such advancements can be observed in the integration of Li metal anodes, which has the capacity to significantly enhance the driving range of electric vehicles, consequently revolutionizing the trillion-dollar automotive industry. Furthermore, the development of these aforementioned Li composite anodes holds the promise of facilitating the practical implementation of other battery systems based on alkali metals.

3) To which communities will your article appeal?

1. Academic researchers from universities who specialize in high-energy batteries would be interested in the development of new technologies and materials that can enhance energy density.
2. Automobile and electric vehicle enterprises are keenly interested in exploring new high-energy-density power cells.
3. Government staff responsible for industrial management have a vested interest in the development of high-energy batteries.
4. Financial managers of venture capital firms are interested in investing in cutting-edge technologies with high growth potential.

4) Please comment on any other reviews published on a similar topic, justifying why there is room for another review. Why would a Tutorial-style article be the best format?

While there have been numerous reviews discussing strategies to inhibit Li dendrites in Li metal anodes, there is a scarcity of reviews specifically focusing on the scaffold/host strategy for Li metal anodes. Only three related reviews have been published to date which are mostly focused on materials (Adv. Mater. 2020, 32, e2002193; Energy Storage Mater. 2021, 38, 276-298; Mater. Today Nano 2021, 13, 100103). These reviews lack crucial aspects such as the developmental stage and trends of scaffold/host materials, detailed working mechanisms of scaffold/host for dendrite suppression, and the prospect of potential design criteria. These missing components are pivotal in providing guidance for future advancements in scaffold/host design.

This Tutorial-style review aims to address these gaps by firstly highlighting the significance of scaffold/host strategies and summarizing the regulatory mechanisms of dendrite-free scaffold/host materials. The review also covers the historical background and recent key progress in this field. Furthermore, scaffold/host materials are categorized based on their material texture, and the advantages and disadvantages of each type are analysed. Then, we briefly outline the challenges and difficulties faced in using scaffold/host strategies. Lastly, the physicochemical characteristics of scaffold/host materials and their impact on electrochemical performance are discussed, along with the possible design criteria and developmental tendencies. This systematic introduction of the scaffold/host strategy caters not only to advanced undergraduate and Master's studies but also to scientific researchers with a specific interest in high-energy batteries.

5) Tutorial reviews are expected to teach the reader about a topic which is not familiar to them. Please list up to five key points that a reader will learn from your review

1. The Benefits and Challenges of Lithium Metal-Based Batteries
2. Regulatory Mechanisms of Scaffold/Host Strategy for Dendrite-Free Lithium Metal Anodes
3. Developmental History, Classifications, and Physicochemical Characteristics of Scaffold/Host Materials
4. Advantages and Disadvantages of Different Types of Scaffold/Host Materials and Composite Li Anode Preparation Methods
5. Design Criteria and Development Trends for Scaffold/Host Materials

6) Please provide section headings along with a brief discussion of each section and associated key references. This should:

- **Clearly outline the intended content of the review**
- **Include at least 10 of the core references used to support your review**
- **Ensure that the title and DOI of each reference is included**

1. Introduction

The introduction provides an overview of the advantages and challenges associated with Li metal-based batteries. The importance and impact of scaffold/host strategies are briefly introduced, highlighting the limited coverage in existing reviews on Li scaffold/host materials. The significance and advantages of the present review are emphasized. Lastly, a brief overview of the subsequent sections is provided.

2. Working Mechanisms of Scaffold/Host

The section begins with a concise introduction to the possible formation mechanisms and influencing factors of Li metal dendrite growth. Subsequently, a comprehensive summary of the working mechanisms of scaffold/host materials for dendrite suppression is presented, based on a systematic analysis of relevant literature. The four identified working mechanisms will be included: (1) decreasing local current density and increasing Sand's time through porous structure, (2) modifying the deposition matrix to induce uniform deposition, (3) modifying the solid-electrolyte interphase (SEI) film to alter Li^+ transportation, and (4) designing the structure to influence deposition location.

3. Development of Scaffold/Host

The section starts with a brief overview of the historical development and recent progress in scaffold/host materials. The development history of scaffold/host materials is categorized into five stages, namely texture selection, lithiophilic modification, structure designing, multi-strategy combination, and practicality. Each stage will be outlined, highlighting the key focus and achievements during that period.

(1) At the first stage (in 2015 to 2016), scientists explored the possibility and electrochemical performance of different materials for inhibiting dendrite, such as Cu-based, carbon-based, silicon-based, Ni-based and other metal-based materials. This phase can be summarized as texture selecting stage.

(2) At the second stage (in 2017 to 2018), scientists studied the lithiophilic modification methods for decreasing nucleation barrier and inducing uniform deposition. The common methods are elements doping (such as N, O, F and so on) and alloying. This phase can be called as lithiophilic modification stage.

(3) At the third stage (in 2017 to 2019), researchers explored the ion-conductive design of scaffold/host to fit in all-solid-state battery, and the structure design for changing the deposition location for inhibiting dendrites growth, such as gradient structure for preferentially deposition at the bottom and egg roll structure for horizontal direction. This phase can be deemed as structure designing stage.

(4) At the fourth stage (in 2020 to 2021), researchers explored the multi-strategy combination for inhibiting dendrite, such as host combined SEI strategy and host combined solvent modification. This may be the trend of further development and design due to the complexity of Li deposition.

(5) At the last stage (in 2022 to 2023), researchers explored the practical applications of scaffold/host through the combination of Cu foil current collector and scaffold materials for improving anti-pulverization, high-continuity and mechanical strength and energy density. This marks the scaffold/host step into commercialization exploration phase.

4. Classification of Scaffold/Host

The scaffold/host materials are categorized into three main groups: carbon materials, metal materials, and polymer materials. To determine the development trends of scaffold/host strategies, a quantitative analysis is conducted based on physicochemical properties (stiffness/modulus, density/capacity, and ionic/electronic conductivity), preparation cost, and industrialization feature. Carbon-based materials are identified as having the highest score, indicating their potential for future development. Polymer-based materials show a higher development potential than metal-based materials for dendrite-free anodes. The preparation methods of composite lithium anodes based on scaffolds/hosts will also be discussed, including mechanical (rolling and pressing), melting-diffusion, and electrodeposition methods, with a quantitative analysis of their respective advantages and disadvantages.

5. Challenges and difficulties

While 3D scaffold structures offer promising advantages in enhancing lithium metal battery performance, several technical difficulties and practical issues need to be addressed. For instance, the minimum amount of inactive scaffold/host in the composite Li anode for LMBs changes with the thick of anode and energy density, which the quantitative relationships are essential to explore. Besides, the challenges of translating composite lithium metal anodes (LMAs) prepared using scaffold/host strategies to pouch cells are significant, which is closer to actual level. Furthermore, one significant technical challenge is achieving uniform and stable scaffold/host structures at large-scale production.

6. Criteria and Prospects

This section discusses the physicochemical characteristics of scaffold/host materials and their impact on electrochemical performance. Design principles and development trends are proposed, including material texture selection based on application requirements and the potential of carbon-based scaffold/host materials. The importance of multi-strategy combination, such as structure design and optimization of electrolyte or artificial protection layers, will be emphasized. Simplifying the preparation process and reducing costs are crucial for practical applications, which will also be discussed. Additionally, future research directions, such as investigating Li dendrite growth mechanisms, exploring the structural/morphological evolution of scaffolds/hosts during battery failure, and assessing the feasibility of scaffold/host-based anodes in pouch cells, are suggested.

7. Conclusion

A brief summary and review of the manuscript are provided in the conclusion section.

Core References:

[1] D.C. Lin, Y.Y. Liu, Y. Cui, Reviving the lithium metal anode for high-energy batteries, *Nat. Nanotechnol.* **2017**, *12*, 194-206. DOI: 10.1038/nnano.2017.16.

[2] X.Y. Zhang, A.X. Wang, X.J. Liu, J. Y. Luo, Dendrites in Lithium Metal Anodes: Suppression, Regulation, and Elimination, *Acc. Chem. Res.* **2019**, *52*, 3223-3232. DOI: 10.1021/acs.accounts.9b00437.

[3] X. Liang, Q. Pang, I. Kochetkov, M.S. Sempere, H. Huang, X. Sun, L.F. Nazar. A Facile Surface Chemistry Route to a Stabilised Lithium Metal Anode, *Nature Energy, **2017***, 2, 17119 DOI: 10.1038/nenergy.2017.119

[4] K. Yan, Z.D. Lu, H.W. Lee, F. Xiong, P.C. Hsu, Y.Z. Li, J. Zhao, S. Chu, Y. Cui, Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth, *Nat. Energy* **2016**, *1*, 16010. DOI: 10.1038/nenergy.2016.10.

[6] X.B. Cheng, R. Zhang, C.Z. Zhao, Q. Zhang, Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review, *Chem. Rev.* **2017**, *117*, 10403−10473. DOI: 10.1021/acs.chemrev.7b00115.

[7] C.P. Yang, Y.X. Yin, S.F. Zhang, N.W. Li, Y.G. Guo, Accommodating lithium into 3D current collectors

with a submicron skeleton towards long-life lithium metal anodes, *Nat. Commun.* **2015**, *6*, 8058. DOI: 10.1038/ncomms9058.
[8] D.C. Lin, Y.Y. Liu, Z. Liang, H.W. Lee, J. Sun, H.T. Wang, K. Yan, J. Xie, Y. Cui, Layered reduced graphene oxide with nanoscale interlayer gaps as a stable host for lithium metal anodes, *Nat. Nanotechnol.* **2016**, *11*, 626-632. DOI: 10.1038/nnano.2016.32.
[9] Z. Liang, K. Yan, G.M. Zhou, A. Pei, J. Zhao, Y.M. Sun, J. Xie, Y.B. Li, F.F. Shi, Y.Y. Liu, D.C. Lin, K. Liu, H. Wang, H.X. Wang, Y.Y. Lu, Y. Cui, Composite lithium electrode with mesoscale skeleton via simple mechanical deformation, *Sci. Adv.* **2019**, *5*, eaau5655. DOI: 10.1126/sciadv.aau5655.
[10] S.H. Wang, J.P. Yue, W. Dong, T.T. Zuo, J.Y. Li, X.L. Liu, X.D. Zhang, L. Liu, J.L. Shi, Y.X. Yin, Y.G. Guo, Tuning wettability of molten lithium via a chemical strategy for lithium metal anodes, *Nat. Commun.* **2019**, *10*, 4930. DOI: 10.1038/s41467-019-12938-4.
[11] Y.Y. Liu, D.C. Lin, Y. Jin, K. Liu, X.Y. Tao, Q.H. Zhang, X.K. Zhang, Y. Cui, Transforming from planar to three-dimensional lithium with flowable interphase for solid lithium metal batteries, *Sci. Adv.* **2017**, *3*, eaao0713. DOI: 10.1126/sciadv.aao071.
[12] C. Jin, O. Sheng, M. Chen, Z. Ju, G. Lu, T. Liu, J. Nai, Y. Liu, Y. Wang, X. Tao, Armed lithium metal anodes with functional skeletons, *Mater. Today Nano* **2021**, *13*, 100103. DOI: 10.1016/j.mtnano.2020.100103.
[13] Y.F. Cheng, J.B. Chen, Y.M. Chen, X. Ke, J. Li, Y. Yang, Z.C. Shi, Lithium Host: Advanced architecture components for lithium metal anode, *Energy Storage Mater.* **2021**, *38*, 276-298. DOI: 10.1016/j.ensm.2021.03.008.
[14] X. Shen, X.B. Cheng, P. Shi, J.Q. Huang, X.Q. Zhang, C. Yan, T. Li, Q. Zhang, Lithium–matrix composite anode protected by a solid electrolyte layer for stable lithium metal batteries, *J. Energy Chem.* **2019**, *37*, 29-34. DOI: 10.1016/j.jechem.2018.11.016.
[15] S. Park, H.J. Jin, Y.S. Yun, Advances in the Design of 3D-Structured Electrode Materials for Lithium-Metal Anodes, *Adv. Mater.* **2020**, *32*, 2002193. DOI: 10.1002/adma.202002193.