

## Solid electrolyte interphase (SEI) modifying coatings for enhanced lithium-ion battery stability

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### ABSTRACT

This review explores solid electrolyte interphase (SEI) modifying coatings, which play a crucial role in enhancing the stability and safety of lithium-ion batteries (LIBs). The SEI forms on anodes during battery cycling, providing a protective layer that mitigates electrolyte degradation. However, its degradation over time leads to capacity loss, necessitating innovative coating solutions. Various materials, including polymeric, ceramic, and metal oxide coatings, are discussed for their unique properties that improve SEI stability. Techniques such as atomic layer deposition (ALD), chemical vapor deposition (CVD), and scalable spray coating methods are highlighted for their effectiveness in applying these coatings. Performance evaluations reveal significant enhancements in capacity retention, thermal stability, and cycling longevity attributed to these coatings. Nonetheless, challenges related to material compatibility, manufacturing scalability, and sustainability remain. The review emphasizes the importance of ongoing research into eco-friendly and hybrid materials to further improve battery performance and align with environmental goals. Overall, SEI-modifying coatings are identified as a promising avenue for advancing LIB technology, ensuring enhanced safety and longevity for various applications in energy storage.

### KEYWORDS

Solid electrolyte interphase (SEI); Polymeric coatings; Atomic layer deposition (ALD); Chemical vapor deposition (CVD)

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### Introduction

Lithium-ion batteries (LIBs) have transformed energy storage, powering everything from smartphones to electric vehicles and serving as crucial components in renewable energy systems. Their high energy density, relatively long life, and rechargeability make them preferred over other technologies, especially as industries aim for clean and efficient power sources. However, LIBs face challenges regarding durability, environmental impact, and safety, particularly concerning degradation processes that affect their lifespan. These issues highlight the need for innovative solutions to improve LIB stability and reliability as demand continues to grow globally [1].

The solid electrolyte interphase (SEI) is vital to LIB stability, as it forms a protective layer on the anode, mitigating direct electrolyte degradation and safeguarding electrodes from dissolution. The SEI layer prevents unwanted reactions during charging and discharging, maintaining cell integrity and prolonging battery life. Despite its protective role, SEI degrades over time, leading to capacity loss and a heightened need for technologies that reinforce its stability. SEI degradation remains a significant challenge, especially in applications requiring prolonged cycling, such as electric vehicles. This degradation compromises battery capacity, stability, and safety, creating a pressing need for research into coatings that can modify SEI to enhance its durability. Effective SEI-modifying coatings could drastically improve LIB longevity and reliability [2].

This review delves into SEI-modifying coatings as a promising solution to mitigate SEI degradation in LIBs. We explore the coating materials, mechanisms, and recent advances aimed at improving LIB stability, providing insights for

researchers and industry stakeholders in energy storage solutions [2].

### Solid Electrolyte Interphase (SEI) in Lithium-Ion Batteries

The SEI layer forms on the surface of lithium-ion battery electrodes, primarily the anode, during initial battery cycling. This process is triggered when electrolyte components decompose at electrode interfaces due to high reactivity, leading to the deposition of various chemical species [3]. These species, often organic and inorganic compounds, accumulate to form a protective film on the anode, known as the SEI layer. The SEI minimizes direct contact between the electrode and electrolyte, reducing the risk of further reactions that would otherwise cause rapid degradation and capacity loss. This initial formation, however, is only partially self-limiting, as the SEI continues to evolve over the battery's life [4].

The SEI typically exhibits a multi-layered structure, with a complex mix of inorganic (e.g., LiF, Li<sub>2</sub>CO<sub>3</sub>) and organic compounds, formed from electrolyte reduction products. The inner SEI layer, closest to the electrode, consists of inorganic species that confer high stability, while the outer layer contains organic species and tends to be more reactive. This heterogeneous composition allows the SEI to act as both an electronic insulator and an ionic conductor, essential for maintaining battery functionality. However, SEI structure and composition can vary depending on electrolyte formulation, electrode material, and cycling conditions, impacting the layer's stability and effectiveness in different applications [1,6].

Despite its protective role, SEI faces stability challenges, such as growth over repeated cycles, cracking, and reduced ionic conductivity. Continuous electrolyte decomposition can lead to uncontrolled SEI growth, thickening the layer and increasing battery resistance. Mechanical stresses induced by volume changes during cycling can cause SEI cracking, exposing the electrode and allowing further reactions, ultimately reducing battery life. Additionally, the SEI's ionic conductivity can diminish over time, impacting the battery's performance and efficiency. Addressing these issues is critical for advancing LIB technologies, particularly for applications requiring long-term cycling stability and safety [5].

### SEI-Modifying Coating Materials

Polymeric coatings, such as polyethylene oxide (PEO) and polyacrylonitrile (PAN), are valued for their flexibility and elasticity, which help accommodate electrode volume changes during lithium-ion battery cycling. This elastic nature prevents mechanical degradation of the SEI and helps maintain the layer's integrity. Polymeric materials can also facilitate ion transport, enhancing the battery's ionic conductivity while minimizing unwanted side reactions. Polymers further allow for customization with functional additives, which can tailor the SEI's chemical stability and flexibility based on specific battery requirements, making them adaptable solutions in SEI engineering [6].

Ceramic coatings, such as lithium phosphorus oxynitride (LiPON) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ), provide excellent thermal and chemical stability, essential for high-performance lithium-ion batteries. These coatings protect the SEI from electrolyte decomposition, especially under high-temperature conditions, and enhance battery longevity. Ceramic materials offer high ionic conductivity while preventing electron transfer, which mitigates undesired reactions at the electrode-electrolyte interface. However, ceramic coatings can be brittle, which makes them less adaptable to the volume changes of the electrodes, a limitation that is mitigated by careful engineering of ceramic thickness and application techniques [7,8].

Metal oxides, including titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide (ZnO), have gained traction due to their high chemical stability and potential to improve SEI durability. Hybrid coatings, which combine polymers and ceramics, leverage the advantages of both flexibility and stability, offering a more balanced solution for SEI protection. Recent research highlights advances in these hybrid materials, which exhibit enhanced tolerance to mechanical stress, superior ionic conductivity, and increased cycling stability. These properties make hybrid coatings a promising avenue for addressing the inherent limitations of individual coating types [8,9]. Coatings excel in flexibility and are effective in handling electrode volume changes, they may fall short in providing the high thermal stability seen in ceramics. Conversely, ceramic coatings offer exceptional thermal and chemical stability but lack the mechanical adaptability of polymers. Metal oxides provide strong chemical stability but may need hybridization for enhanced mechanical resilience. Hybrid coatings, combining elements of both polymeric and ceramic properties, show promise for achieving an optimal balance, offering robust SEI protection, extended cycle life, and improved overall battery stability [10].

### Mechanisms of SEI-Modifying Coatings

One of the primary mechanisms through which SEI-modifying coatings enhance LIB stability is by controlling SEI growth. During cycling, SEI tends to thicken due to continuous reactions between the electrolyte and electrode surface, increasing internal resistance and reducing battery efficiency. Coatings act as a protective layer, limiting SEI expansion by forming a stable barrier that prevents excessive electrolyte decomposition on the electrode. For instance, ceramic coatings like LiPON and  $\text{Al}_2\text{O}_3$  are known to inhibit SEI thickening by restricting lithium-ion interfacial reactions, reducing resistance build-up, and improving the long-term performance of the battery [11].

SEI-modifying coatings play a critical role in minimizing side reactions at the electrode-electrolyte interface, which otherwise lead to electrolyte decomposition and capacity fade. Coatings, especially those with high chemical stability, can suppress these reactions by preventing direct contact between reactive electrolyte species and the electrode. For example, polymeric and hybrid coatings often incorporate additives to enhance stability and reduce the formation of harmful byproducts. By creating a stable interface, coatings reduce the continuous formation of SEI, which is driven by side reactions, thereby preserving the electrode's active material and improving cycling efficiency [12,13].

Lithium-ion batteries experience volumetric changes during charge-discharge cycles, particularly with high-capacity electrodes such as silicon. These expansions can crack the SEI, exposing the electrode surface to the electrolyte and causing additional degradation. Flexible coatings, like polymer-based or hybrid coatings, alleviate this issue by offering elasticity, allowing the SEI to expand and contract without cracking. This flexibility is crucial in preventing mechanical degradation and maintaining the electrode's structural integrity. Studies indicate that flexible polymeric coatings, such as polyacrylonitrile (PAN), help retain SEI stability even under high-stress cycling conditions, effectively prolonging battery life by reducing wear and tear on the electrode [14].

Maintaining thermal and chemical stability in LIBs is essential for high-temperature and high-voltage applications. Coatings such as ceramic and metal oxides are particularly effective here, providing robust protection against thermal degradation. For instance,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  coatings maintain chemical integrity at elevated temperatures and high voltage ranges, which prevents rapid SEI breakdown and minimizes performance losses. These coatings can tolerate high thermal stress without deteriorating, ensuring the stability of the SEI and reducing the risks of thermal runaway or short-circuiting, thereby enhancing both safety and operational lifespan for high-energy-density batteries [15].

### Advances in SEI Coating Techniques

Atomic Layer Deposition (ALD) is a cutting-edge technique that excels in producing highly uniform and conformal coatings at the nanoscale. This method involves sequentially depositing monolayers of material, allowing precise control over the thickness and composition of the coating. For lithium-ion batteries, ALD is particularly advantageous for applying thin layers of materials such as aluminum oxide ( $\text{Al}_2\text{O}_3$ ) or lithium

phosphorous oxynitride (LiPON) on electrode surfaces [16]. These coatings effectively enhance the stability of the solid electrolyte interphase (SEI) by providing a uniform barrier that mitigates side reactions and improves ionic conductivity. Studies indicate that ALD-coated electrodes demonstrate significant improvements in cycling performance due to the effective passivation of active materials. [17].

Chemical Vapor Deposition (CVD) is another powerful technique used to create robust SEI-modifying coatings. This method allows for the deposition of strong, chemically bonded materials that enhance the structural integrity of the SEI. CVD can be employed to fabricate coatings from materials like silicon carbide (SiC) or titanium dioxide (TiO<sub>2</sub>), which exhibit excellent thermal and chemical stability. The strong bonding of CVD coatings not only prevents delamination during battery cycling but also enhances the electrochemical performance by creating a stable interface that reduces interfacial resistance. Recent advancements in CVD techniques have demonstrated their effectiveness in commercial battery applications, contributing to improved safety and performance [18]. Spray and dip coating methods are emerging as cost-effective and scalable techniques for applying SEI-modifying coatings in industrial lithium-ion battery production. These techniques involve immersing electrodes in solutions containing coating materials or spraying a mist onto the surfaces, resulting in uniform coverage. For example, polymeric coatings can be applied via spray methods, providing an elastic and flexible SEI that enhances battery life by accommodating mechanical stresses. These methods have been successfully implemented in large-scale battery production, demonstrating their practicality and efficiency [19].

Electrochemical and Surface Emerging techniques, including electrochemical and surface treatment methods, offer innovative ways to modify the SEI in situ. These techniques involve applying external voltages or currents to alter the composition and properties of the SEI during battery operation. For instance, electrochemical treatments can enhance the formation of protective layers by promoting favorable reactions at the electrode surface. This real-time modification of the SEI can lead to enhanced long-term stability, making these methods promising for future research and development [20].

### Performance Evaluation of SEI-Modifying Coatings

Electrochemical stability is crucial for assessing the effectiveness of SEI-modifying coatings in lithium-ion batteries. Common methods for testing include Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV is used to analyze the electrochemical behavior of electrodes by measuring current as a function of applied voltage, providing insights into redox processes and SEI formation. EIS complements this by offering information on interfacial resistance and charge transfer kinetics, enabling a deeper understanding of how coatings affect battery performance under operational conditions. These techniques help identify the stability window of coatings and their influence on the overall electrochemical performance of Cycle Life [21].

The performance of SEI-modifying coatings is often evaluated in terms of capacity retention and cycle life. Effective coatings can significantly reduce capacity degradation during cycling, thereby enhancing the longevity of lithium-ion

batteries. For instance, studies have shown that electrodes with optimized SEI-modifying coatings exhibit less than 5% capacity loss after 500 cycles, compared to uncoated electrodes, which may experience up to 30% loss under similar conditions. This improvement is attributed to the coatings' ability to stabilize the SEI, mitigating detrimental side reactions that lead to capacity fade [22,23].

Thermal and evaluating thermal stability and safety performance under extreme conditions is critical. Coatings that enhance thermal stability can help reduce heat generation during battery operation and prevent flammability risks. For example, ceramic-based SEI-modifying coatings have demonstrated improved thermal stability, allowing batteries to withstand higher temperatures without significant degradation. This is essential for ensuring the safety and reliability of lithium-ion batteries in various applications [24].

Case Studies of Effective SEI Real-world examples highlight the impact of SEI-modifying coatings on battery performance. A case study of aluminum oxide-coated electrodes showed a 20% increase in cycle life and improved thermal stability, validating the effectiveness of such coatings in commercial applications. Another study focused on polymeric coatings, which exhibited exceptional flexibility and contributed to enhanced performance even under mechanical stress [25].

### Challenges and Future Directions

One of the significant challenges in developing SEI-modifying coatings is ensuring compatibility with various electrode materials, such as graphite, silicon, and lithium metal. Different materials exhibit unique electrochemical behaviors and structural characteristics, which can lead to adverse interactions when coatings are applied. For instance, certain polymeric coatings may not adhere well to silicon anodes, resulting in delamination during battery cycling. Ongoing research aims to identify and engineer coatings that can provide robust protection across a range of electrode materials, thereby enhancing the overall performance of lithium-ion batteries [26].

Translating laboratory-scale coating techniques to industrial production presents another challenge. While methods like atomic layer deposition (ALD) and chemical vapor deposition (CVD) demonstrate high precision and uniformity in controlled settings, scaling these processes to meet commercial demand is complex and costly. Innovations in manufacturing processes, such as spray coating and roll-to-roll techniques, are being explored to improve scalability without compromising coating quality. Bridging this gap is essential for the widespread adoption of SEI-modifying coatings in commercial lithium-ion batteries [27].

The future of SEI modification lies in the exploration of novel materials, particularly nanomaterials and hybrid structures that combine the benefits of different material classes. For example, integrating carbon-based nanomaterials with inorganic compounds could yield coatings that offer both flexibility and thermal stability. This approach may lead to breakthroughs in battery performance and longevity [28,29]. Sustainability is increasingly becoming a focal point in battery technology. Research into eco-friendly materials for SEI modification is gaining traction, with a focus on using biodegradable polymers and naturally occurring compounds.



Such sustainable approaches not only enhance battery stability but also align with global efforts to reduce the environmental impact of energy storage technologies [29,30].

## Conclusions

SEI-modifying coatings represent a pivotal advancement in enhancing the stability and safety of lithium-ion batteries (LIBs). Key findings indicate that these coatings effectively inhibit undesirable SEI growth, suppress side reactions, and mitigate electrode degradation, leading to improved electrochemical performance and cycle life. However, challenges remain, particularly concerning material compatibility, manufacturing scalability, and the development of sustainable coatings.

The implications for LIB safety are significant; enhanced SEI stability can reduce risks associated with thermal runaway and increase the longevity of battery systems. As the demand for high-performance, reliable batteries grows in sectors like electric vehicles and renewable energy storage, the importance of such innovations cannot be overstated. Looking ahead, there is a critical need for further research into scalable, cost-effective, and environmentally friendly SEI-modifying materials. Exploring hybrid and nanomaterial-based coatings could unlock new potentials for battery technology, contributing to a more sustainable energy future. Continued interdisciplinary collaboration will be essential in overcoming current limitations and realizing the full benefits of SEI-modifying coatings in lithium-ion batteries.

## Disclosure statement

No potential conflict of interest was reported by the authors.

## References

1. Meda US, Lal L, Sushantha M, Garg P. Solid Electrolyte Interphase (SEI), a boon or a bane for lithium batteries: A review on the recent advances. *J Energy Storage*. 2022;47:103564. <https://doi.org/10.1016/j.est.2021.103564>
2. Shen Z, Huang J, Xie Y, Wei D, Chen J, Shi Z. Solid Electrolyte Interphase on Lithium Metal Anodes. *ChemSusChem*. 2024; e202301777. <https://doi.org/10.1002/cssc.202301777>
3. Rufino Júnior CA, Sanseverino ER, Gallo P, Amaral MM, Koch D, Kotak Y, et al. Unraveling the Degradation Mechanisms of Lithium-Ion Batteries. *Energies*. 2024;17(14). <https://doi.org/10.3390/en17143372>
4. Adenusi H, Chass GA, Passerini S, Tian KV, Chen G. Lithium batteries and the solid electrolyte interphase (SEI)—progress and outlook. *Adv Energy Mater*. 2023;13(10):2203307. <https://doi.org/10.1002/aenm.202203307>
5. Fedorov RG, Maletti S, Heubner C, Michaelis A, Ein-Eli Y. Molecular engineering approaches to fabricate artificial solid-electrolyte interphases on anodes for Li-ion batteries: a critical review. *Adv Energy Mater*. 2021;11(26):2101173. <https://doi.org/10.1002/aenm.202101173>
6. Heiskanen SK, Kim J, Lucht BL. Generation and evolution of the solid electrolyte interphase of lithium-ion batteries. *Joule*. 2019;3(10):2322-2333. <https://doi.org/10.1016/j.joule.2019.08.018>
7. Wu J, Ihsan-Ul-Haq M, Chen Y, Kim JK. Understanding solid electrolyte interphases: Advanced characterization techniques and theoretical simulations. *Nano Energy*. 2021;89:106489. <https://doi.org/10.1016/j.nanoen.2021.106489>
8. Wang A, Kadam S, Li H, Shi S, Qi Y. Review on modeling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries. *npj Comput Mater*. 2018;4(1):15. <https://doi.org/10.1038/s41524-018-0064-0>
9. Horstmann B, Single F, Latz A. Review on multi-scale models of solid-electrolyte interphase formation. *Curr Opin Electrochem*. 2019;13:61-69. <https://doi.org/10.1016/j.coelec.2018.10.013>
10. Owejan JE, Owejan JP, DeCaluwe SC, Dura JA. Solid electrolyte interphase in Li-ion batteries: evolving structures measured in situ by neutron reflectometry. *Chem Mater*. 2012;24(11):2133-2140. <https://doi.org/10.1021/cm3006887>
11. Zhang Q, Han L, Pan J, Chen Z, Cheng YT. Chemically stable artificial SEI for Li-ion battery electrodes. *Appl Phys Lett*. 2017;110(13). <https://doi.org/10.1063/1.4979108>
12. Zhang Y, Du N, Yang D. Designing superior solid electrolyte interfaces on silicon anodes for high-performance lithium-ion batteries. *Nanoscale*. 2019;11(41):19086-19104. <https://doi.org/10.1039/C9NR05748J>
13. Rao Rikha V, Ranjan Sahu S, Chatterjee A, Gopalan R, Sundarajan G, Prakash R. Composition-dependent long-term stability of mosaic solid-electrolyte interface for long-life lithium-ion battery. *Batter Supercaps*. 2021;4(11):1720-1730. <https://doi.org/10.1002/batt.202100127>
14. Maske VA, More AP. Conformal coatings for lithium-ion batteries: A comprehensive review. *Prog Org Coat*. 2024;188:108252. <https://doi.org/10.1016/j.porgcoat.2024.108252>
15. Cabana J, Kwon BJ, Hu L. Mechanisms of degradation and strategies for the stabilization of cathode-electrolyte interfaces in Li-ion batteries. *Acc Chem Res*. 2018;51(2):299-308. <https://doi.org/10.1021/acs.accounts.7b00482>
16. Park JS, Meng X, Elam JW, Hao S, Wolverson C, Kim C, et al. Ultrathin lithium-ion conducting coatings for increased interfacial stability in high voltage lithium-ion batteries. *Chem Mater*. 2014;26(10):3128-3134. <https://doi.org/10.1021/cm500512n>
17. Kaur G, Gates BD. Surface coatings for cathodes in lithium ion batteries: from crystal structures to electrochemical performance. *J Electrochem Soc*. 2022;169(4):043504. <https://doi.org/10.1149/1945-7111/ac60f3>
18. Ma L, Nuwayhid RB, Wu T, Lei Y, Amine K, Lu J. Atomic layer deposition for lithium-based batteries. *Adv Mater Interfaces*. 2016;3(21):1600564. <https://doi.org/10.1002/admi.201600564>
19. Ban C, George SM. Molecular layer deposition for surface modification of lithium-ion battery electrodes. *Adv Mater Interfaces*. 2016;3(21):1600762. <https://doi.org/10.1002/admi.201600762>
20. Carter R, Parker JF, Sassin MB, Klein EJ, Wolak MA, Love CT, et al. Initiated chemical vapor deposition of ultrathin polymer coatings at graphite electrodes for enhanced performance in Li-ion batteries. *J Electrochem Soc*. 2020;167(6):060510. <https://doi.org/10.1149/1945-7111/ab7f22>
21. Feng T, Xu Y, Zhang Z, Du X, Sun X, Xiong L, et al. Low-cost Al<sub>2</sub>O<sub>3</sub> coating layer as a preformed SEI on natural graphite powder to improve coulombic efficiency and high-rate cycling stability of lithium-ion batteries. *ACS Appl Mater Interfaces*. 2016;8(10):6512-6519. <https://doi.org/10.1021/acsami.6b00231>
22. Tripathi AM, Su WN, Hwang BJ. In situ analytical techniques for battery interface analysis. *Chem Soc Rev*. 2018;47(3):736-851. <https://doi.org/10.1039/C7CS00180K>
23. Abdollahifar M, Molaiyan P, Perovic M, Kwade A. Insights into Enhancing Electrochemical Performance of Li-Ion Battery Anodes via Polymer Coating. *Energies*. 2022;15(23):8791. <https://doi.org/10.3390/en15238791>
24. Zu C, Yu H, Li H. Enabling the thermal stability of solid electrolyte interphase in Li-ion battery. *InfoMat*. 2021;3(6):648-661. <https://doi.org/10.1002/inf2.12190>
25. Shen BH, Wang S, Tenhaeff WE. Ultrathin conformal polycyclosiloxane films to improve silicon cycling stability. *Sci Adv*. 2019;5(7):eaaw4856. <https://doi.org/10.1126/sciadv.aaw4856>
26. Khan M, Yan S, Ali M, Mahmood F, Zheng Y, Li G, et al. Innovative Solutions for High-Performance Silicon Anodes in Lithium-Ion Batteries: Overcoming Challenges and Real-World Applications. *Nano-Micro Lett*. 2024;16(1):179. <https://doi.org/10.1007/s40820-024-01388-3>

27. Li J, Cai Y, Wu H, Yu Z, Yan X, Zhang Q, et al. Polymers in lithium-ion and lithium metal batteries. *Adv Energy Mater.* 2021;11(15):2003239. <https://doi.org/10.1002/aenm.202003239>
28. Meyerson ML, Papa PE, Heller A, Mullins CB. Recent developments in dendrite-free lithium-metal deposition through tailoring of micro-and nanoscale artificial coatings. *ACS Nano.* 2020;15(1): 29-46. <https://doi.org/10.1021/acsnano.0c05636>
29. Tubtimkuna S, Danilov DL, Sawangphruk M, Notten PH. Review of the Scalable Core-Shell Synthesis Methods: The Improvements of Li-Ion Battery Electrochemistry and Cycling Stability. *Small Methods.* 2023;7(9):2300345. <https://doi.org/10.1002/smt.202300345>
30. Shin J, Kim TH, Lee Y, Cho E. Key functional groups defining the formation of Si anode solid-electrolyte interphase towards high energy density Li-ion batteries. *Energy Storage Mater.* 2020;25:764-781. <https://doi.org/10.1016/j.ensm.2019.09.009>