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Thermodynamic Understanding of Formation and Evolution of Solid Electrolyte Interface in Li-Ion Batteries

Yitao He,[a, b] Jinkun Wang,[b] Li Wang,[b] and Xiangming He*[b]

Formation is an essential process in the manufacturing of lithium-ion batteries and determines the performance of batteries, including life time, rate capability and so forth. The core of formation is to form a stable solid electrolyte interphase (SEI), which profoundly influences interfacial reactions and ion transport within Li-ion batteries, on the surface of electrode. It is crucial to fully and deeply understand the intricate structure and evolution of SEI, which remains largely uncharted. This paper aims to systematically analyze SEI thermodynamics, encompassing energy distribution, entropy dynamics during SEI formation, and enthalpy changes. SEI evolves towards an equilibrium state, maximizing entropy. The intricate relationship between SEI thermodynamics and battery performance is established by dissecting the impacts of temperature and current density on SEI thermodynamic parameters and battery characteristics. Elevated temperatures and higher current densities foster the development of a more porous and high-entropy outer SEI layer, rendering organic SEI constituents prone to decompose into high-energy gases and low-energy inorganic compounds. Notably, a fast formation strategy within a high state-of-charge range offers a potential solution to high quality SEI. This review strives to bridge the divide between fundamental thermodynamics and practical battery performance, ultimately contributing to the advancement of battery manufacturing.

1. Introduction

The interface between the electrode and electrolyte is pivotal in governing redox reactions, adsorption phenomena, ion intercalation/de-intercalation processes, corrosion mechanisms, passivation phenomena, and ultimately further device performance, including capacity and stability, in various energy storage devices, such as lithium-ion batteries (LIBs).[1] The electrode/electrolyte interface in LIBs is called as solid electrolyte interphase (SEI).[2] An excellent SEI has many important functions:

1) Ensuring electrode surface stability and structural integrity.[3]
2) Desolvation and adsorption of intercalable ion.[4]
3) Acting as a thermally stable interface to prevent gas production.[5]
4) Expanding the electrochemical stability window of the electrolyte by enhancing the lowest unoccupied molecular orbital (LUMO) and decreasing the highest occupied molecular orbital (HOMO) at the anode and cathode surfaces, respectively.[6]

Therefore, the critical step in battery manufacturing is to establish a high-quality SEI before introducing the batteries to the market. Nonetheless, delving into the intricate properties of the SEI is a lengthy endeavor. While the dual-layer structure of

the SEI has been unveiled through materials characterization,[7] attaining a precise understanding of its fine structure throughout remains a challenge. Consequently, numerous researchers have ventured into employing numerical simulation methods, particularly from a dynamic perspective, to replicate the surfaces of silicon, lithium metal, and graphite anodes.[8] Their goal is to derive characteristic parameters resembling those of the SEI. In 2004, Christensen and Newman[9] initiated their work with the Butler-Volmer equation and the Poisson-Nernst-Planck (PNP) equation. Their aim was to construct a model for SEI growth, which would yield parameters encompassing the physical properties of the SEI film and the characteristics of the electrode/film/electrolyte system. However, due to the complexity of the SEI composition and structure, the simulated parameters occasionally deviated from actual experimental results. It is essential to highlight that the SEI, as a product of the reduction reaction of electrolyte components, possesses a distinct energy profile, which can be released under high-temperature conditions during battery cycling. Consequently, the interface between the electrode and electrolyte experiences energy conversion alongside the deposition or volatilization of reaction products, as well as film formation or loss. Therefore, conducting an in-depth thermodynamic analysis of SEI formation and evolution becomes both necessary and pressing.

In this review, the SEI formation and battery performances were correlated through introducing thermodynamic parameters Gibbs free energy change ($\triangle G$), enthalpy change ($\triangle H$), and entropy change ($\triangle S$), as shown in Figure 1. A thermodynamic model was concluded from thermodynamic analysis on the enthalpy change of the SEI formation reaction and entropy change of SEI components firstly. Then we delved into a meticulous exploration of the influence of temperature and current density on the SEI formation and evolution mechanisms

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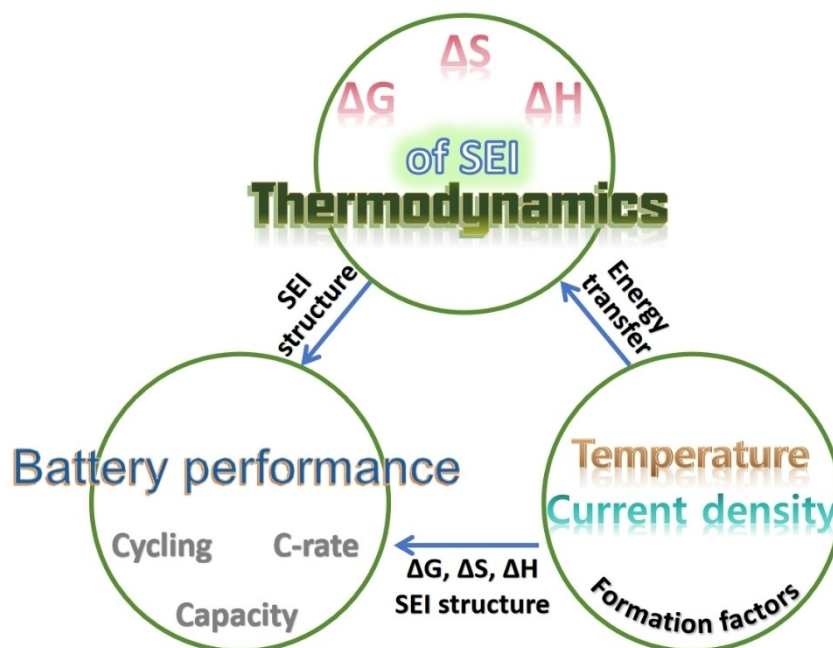E-mail: hexm@tsinghua.edu.cn

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Figure 1. Schematic diagram of strategies to analyze the thermodynamics of SEI. The impacts of temperature and current density on SEI formation and their subsequent effects on battery performance can be elucidated through the lens of SEI thermodynamics. The thermodynamic model of SEI manifests in various aspects, including SEI structure, state of charge, and fast-charging capabilities.

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from a thermodynamic standpoint. This investigation and summarization offer valuable insights into the fundamental thermodynamic factors that determine the quality of the SEI and the conditions under which SEI formation occurs. Finally, the summary encompassed the principles governing entropy changes within the SEI during battery formation, as well as strategies for fast formation, and our intention is to offer theoretical guidance and inspire advancements in the development and commercialization of safer LIBs in the future.

2. Thermodynamic Analysis for SEI

Recently, there has been a surge in interest among researchers in the field of LIBs regarding high-entropy alloy materials[10] and high-entropy electrolytes.[11] For example, high-entropy electrodes, which can include transition metals, refractory metals, and non-metals, are designed to improve the electrochemical performance of energy storage devices. This complex composition can lead to exceptional properties, such as higher energy density, faster charge/discharge rates, and improved cycle life. In fact, the most disordered component within LIBs is the SEI (Figure 2), a complex matter that continues to baffle researchers due to its diverse species. However, despite this, a more comprehensive grasp of SEI thermodynamics remains elusive, which has led to a somewhat conventional approach to understanding the key aspects of SEI formation and evolution. Therefore, in this section, it becomes imperative to establish a valuable thermodynamic model or analysis the thermodynamics by reviewing related references to provide a solid foundation before making connections with the actual battery industry.

2.1. Dynamic Analysis for SEI

Dynamics emphasize parameters directly tied to time, such as reaction rate, growth rate, and ionic diffusion rate. For example, Jha and Krishnamurthy[12] developed a model to simulate SEI formation. They combined equations for current balance, mass conservation, current density in porous electrodes, and the Butler-Volmer equation. While their model successfully established relationships between graphite size, SEI thickness, and discharge rate, it could not precisely predict the intricate structure of SEI. Therefore, integrating dynamic models with other methods becomes essential to gather detailed structural information of SEI. Bryngelsson et al.[13] experimentally probed the dynamic nature of the SEI using X-ray Photoelectron Spectroscopy (XPS). Their research illuminated how the SEI evolves and changes over time during battery cycling, shedding light on the stability of SEI and its influence on battery performance. They unveiled dynamic changes of SEI components like LiF and carbonaceous compounds but could not provide definitive explanations for their origin and distribution. Similarly, other references[14] offered a comprehensive perspective by studying dynamic models of LIBs, incorporating considerations for SEI. Some studies integrated dynamics with theoretical methods like quantum mechanics and molecular force fields. However, these simulations, due to the time constraints (units, μs or ms), could not fully represent real-world matter evolution during charge and discharge. Consequently, there is a continued need to deepen our comprehension of SEI from a thermodynamic perspective, as evidenced by the literature.
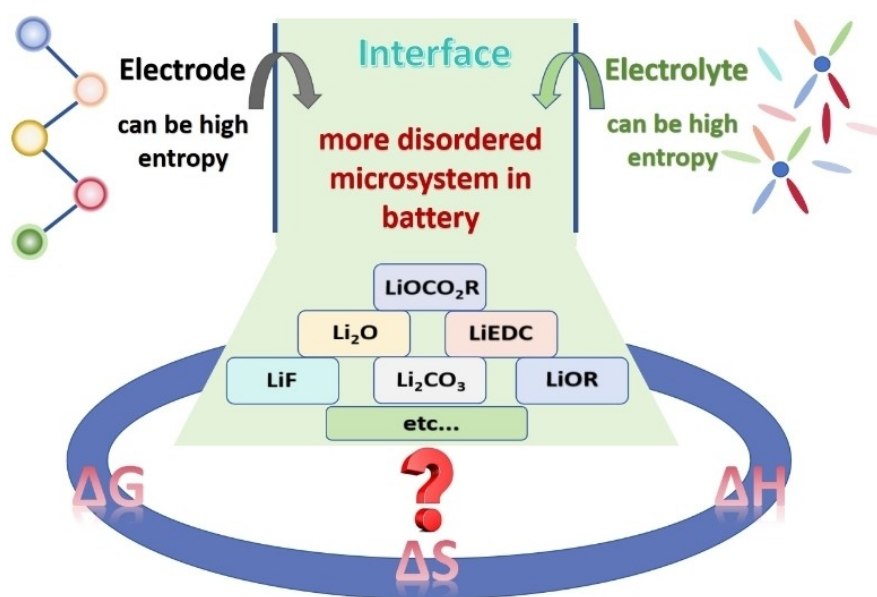

Figure 2. Scheme for disordered microsystem at interface between electrolyte and electrode. When compared to electrodes and electrolytes, which can possess high entropy, it becomes essential to explore the thermodynamic parameters, including entropy, of the SEI. Characterized by its disorder and diverse species, the SEI presents a unique challenge that warrants an in-depth thermodynamic investigation.

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2.2. What is Entropy?

In classical thermodynamics, entropy is a measure of the amount of thermal energy in a closed system that is unavailable to do work. It quantifies the level of disorder or randomness in a system. Entropy tends to increase over time in isolated systems, a concept known as the second law of thermodynamics. This principle implies that systems naturally tend toward states of higher disorder or randomness. As for the SEI in LIBs, entropy relates to the disorder or randomness of SEI components and their arrangements. As a LIB undergoes charge and discharge cycles, the SEI is subject to dynamic/thermodynamic changes. These changes can impact the entropy of the SEI layer.

However, a comprehensive thermodynamic investigation of SEI formation and evolution remains incomplete. On one hand, entropy arises from the lattice structure of compounds, and research may commence by examining the entropy changes in Li-ion intercalated compounds (LICs), a topic that has been studied for many years. Some findings indicate a relationship between the configuration entropy of LICs and the disorder of Li^+ vacancies within or outside the plane.[15] Simultaneously, vibrational entropy is associated with the disorder arising from the vibrational motion of Li atoms near their equilibrium positions between two adjacent carbon hexagons in graphite. Consequently, lattice disorder contributes to the entropy of LICs. On the other hand, entropy arises from chemical reactions, and many references utilized an equation to calculate the entropy change in reversible reactions:[16]

$$\Delta S = nF\frac{dE_{eq}}{dT} \tag{1}$$

where ΔS represents entropy change; n, mole of electrons; F, Faradic constant; E_{eq}, equilibrium voltage; T, temperature. However, SEI formation represents an irreversible reaction that consumes Li ions, leading to permanent capacity loss in LIBs. Consequently, there is a pressing need for the development of a dedicated thermodynamic model tailored to irreversible SEI formation reactions. It is our expectation that through such a model, we can establish a robust correlation between entropy changes and the structural characteristics of SEI, thereby facilitating a deeper exploration of the SEI formation mechanism.

2.3. Is SEI High-Entropy?

Given the intricate nature of the SEI structure, the question arises: does the SEI inherently possess a high level of entropy? To address this inquiry effectively, it is crucial to establish a meaningful link between the structural complexity of SEI and the principles of thermodynamics. In this section, we undertake an in-depth analysis of both enthalpy and entropy, drawing insights from the findings gleaned from the referenced sources.

2.3.1. Enthalpy Change and Heat Transfer of SEI Formation Reaction

In 2005, Huang et al.[16b] conducted a preliminary analysis of the ΔS and ΔH using the potentiometric and electrochemical-calorimetric methods to gain insights into the thermal behavior of $Li_{1-x}CoO_2||$mesocarbon microbeads (MCMB) and $Li_{1-x}CoO_2||$Li batteries. Their findings indicated that the conversion of Li to Li^+ should be an endothermic process, absorbing heat. They calculated the ΔS as 112.9 J K^{-1}mol^{-1}, indicating that this reaction generates entropy. However, if we consider this reaction as the primary process during SEI formation on the anodes, given that Li^+ is the predominant species within the SEI film, it contradicts the conventional expectation that the transition from a liquid to a solid state should involve an exothermic reaction with a reduction in enthalpy. In reality, during the initial charging and battery formation, reactions involved Li(ion) occur on the anode: $Li^{+,electrolyte}+e^-\rightarrow Li$ on the Li anode, or $xLi^{+,electrolyte}+xe^-+6\,C\rightarrow Li_xC_6$ on the graphite anode. These reactions proceed in the opposite direction to the earlier one and are inherently exothermic. Therefore, it is plausible to consider that SEI formation involving $Li^{+,electrolyte}$ as the reactant might indeed be an exothermic process. If this hypothesis holds true, the heat released during SEI formation can be quantified using the irreversible heat equation, which is related to the resistance:[17]

$$Q_{irr} = -i^2R \tag{2}$$

where Q_{irr} correspond to the irreversible heat; i, current at anode. R represents the SEI resistance after formation, or solid/liquid interface resistance before formation. The minus sign refers to heat release. Following this, it is reasonable to make a secondary, important speculation. In line with the principle of energy conservation, the conversion process involves the transformation of input electrical work into stored ions and irreversible heat. The partial irreversible heat induces and promotes the formation of the SEI film. This implies that the SEI inherently harbors a certain amount of energy. One component of SEI energy is the film adhesion energy, which can be quantified as follows:[18]

$$E_{adhesion} = \frac{1}{A}[E_{interface} - (E_{anode,slab} + E_{SEI,slab})] \tag{3}$$

where $E_{adhesion}$ is the adhesion energy per unit area; A, the interfacial area; $E_{interface}$, the energy of the interfacial structure; $E_{anode,slab}$ and $E_{SEI,slab}$ are the energies of isolated strained anode materials and SEI slabs, respectively. Another facet of SEI energy stems from internal energy, originating from both irreversible heat and the chemical energy of electrolyte components. The heat generated within LIBs comprises reversible heat (Q_{rev}) and irreversible heat (Q_{irr}). By combining this concept with Eq.(2) and the second law of thermodynamics, the equation can be formulated for calculating the total heat quantity as follows:[17]

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$$Q = Q_{rev} + Q_{irr} = T\Delta S_{rev} - i^2 R \qquad (4)$$

where T refers to temperature; ΔS_{rev}, the entropy change derived from the reversible reaction, such as intercalation/de-intercalation reaction. The Q_{rev} of charge and discharge have the same absolute value with opposite symbols, and they are proportional to the ΔS_{rev} associated with the lithiation and de-lithiation. The Q_{irr} generated during charge and discharge is always exothermic ($Q_{irr} < 0$), and its absolute value $|Q_{irr}|$ increases with the charge/discharge rate and is the square of the current i. When the battery returns to its initial state, the ΔS_{rev} reaches zero, leading to $Q_{rev} = 0$.[17]

Of the two types of energy, internal energy can be accurately quantified using the differential scanning calorimetry (DSC) method. Oh et al.[19] employed this method to examine the heat generated during the exothermic reaction of fully discharged anode materials with SEIs formed at various current densities. Their findings revealed that the released heats of the materials at 0.1, 0.5, and 1.0 C were 131, 146, and 212 $J g^{-1}$, respectively. Notably, higher current densities were associated with greater released heat, indicating the presence of a larger quantity of SEI components on the anode. Additionally, Son et al.[20] also employed DSC to investigate the thermal properties of electrode materials. Similarly, their results demonstrated that the thermal decomposition of the SEI contributed to exothermic heat flows. These collective findings provide strong evidence for the existence of internal energy within the SEI.

Another significant conclusion drawn from the analysis is that the formation of the SEI is an exothermic reaction, a fact substantiated by the formation enthalpies of SEI species. Li et al.[21] reported that the formation enthalpies of species such as Li_2O, Li_3N, Li_3P, and Li_3PO_4 are all below zero. Similarly, Mukai et al.[22] found that the formation of LiF within the SEI is an exothermic process, with exothermic heat increasing as the crystallinity of LiF rises. Furthermore, Yang et al.[23] observed that the formation of Li-ion intercalated compounds (Li_xC_y) due to the intercalation of Li ions into the graphite anode is also an exothermic reaction. In light of these findings, in conjunction with Yang et al.'s discoveries, it can be inferred that the heat generating within the battery comes from three exothermic reactions when Li^+ contacts the charged graphite anode: 1) heat released from Li^+ intercalation; 2) heat released from SEI formation; 3) irreversible heat stemming from liquid/solid interface resistance. It would be inappropriate to view low temperatures as solely disadvantageous for SEI formation, as lower temperatures are conducive to some exothermic reactions. Simultaneously, a lower internal environmental temperature can reduce ion mobility, resulting in a slower reaction rate for SEI formation and Li^+ intercalation. This hypothesis aligns with the findings of Attia et al.,[24] who noted that lower temperatures can decrease irreversible capacity loss, primarily caused by the reduction of ethylene carbonate (EC) from the electrolyte. Hence, based on the considerations mentioned above, it becomes evident that SEI enthalpy, the heat released during SEI formation, temperature, and SEI energy are intricately interconnected. As the SEI grows, heat is released at the electrode/electrolyte interface, contributing to a decrease in the overall enthalpy of substances involved in the reaction. Ultimately, a SEI layer possessing a certain amount of energy is formed.

2.3.2. Entropy Change of SEI Formation Reaction and its Essence

As previously mentioned by Huang et al.,[16b] Li^+ formation represents a reaction associated with an increase in entropy. Therefore, in this section, it is imperative to continue the analysis of entropy changes during SEI formation. The precise experimental standard entropy values of SEI components can be readily obtained from established databases and other reputable references.[25] The standard formation entropies for key constituents of electrodes or SEI, namely lithium, carbon, LiF, Li_2O, Li_3N, and Li_2CO_3, are as follows: 29.12, 5.74, 35.66, 37.89, 62.61, and 90.17 $J K^{-1} mol^{-1}$, respectively. These values affirm that SEI formation indeed leads to an increase in entropy of the interface of solid electrode-electrolyte. In thermodynamics, entropy is often defined as the change in heat (ΔQ) divided by the absolute temperature (T) at which the heat transfer occurs. Additionally, in the realm of statistical mechanics, entropy can be defined in terms of microstates (W):

$$S = k \ln W \qquad (5)$$

Entropy is rigorously defined as Boltzmann constant (k) multiplied by the natural logarithm of the number of microstates available to a system within a specific macrostate. The variable "W" signifies the potential number of arrangements of atoms and molecules. Tolman and Fine[26] have elaborated vividly on this statistical definition. They proposed an illustrative scenario where initially, all N atoms are situated at a single, designated point. In this scenario, there is only one way to achieve this distribution, resulting in $W = 1$ and $S = 0$, indicating minimal entropy. However, due to thermal motion, this orderly distribution is rapidly disrupted, leading to various distributions with a higher number of realizations, resulting in positive entropies. Eventually, it evolves into an equilibrium distribution with the most realizations, signifying maximal entropy. This natural progression toward higher entropy is inherently probabilistic and not necessarily irreversible. Hence, the reverse process, which entails transitioning from more probable distributions to the less probable ones, becomes increasingly improbable, particularly as more atoms are involved. This concept can be applied to the context of the SEI in LIBs. The entropy of SEI plays a role in promoting the structural evolution of SEI. If the initial SEI entropy has not yet reached its maximum, its structure must continue to evolve in order to attain a state of structural equilibrium. This state with maximum entropy is often associated with stability. Therefore, reduced maximal entropy within the SEI holds the promise of accelerating the process of structural equilibrium attainment. The expedited attainment of equilibrium has the potential to

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enhance the protective properties of SEI, ensuring more robust and longer-lasting battery performance.

It should be noted that a SEI with extremely low entropy could potentially lead to certain drawbacks. A highly ordered or inflexible SEI structure with significantly reduced entropy may restrict its adaptability to changing operating conditions, such as high current densities.[27] And it needs a high economic cost and much more time to promote battery formation. Moreover, batteries, particularly those employed in portable devices, often undergo mechanical stresses during their operational lifespan. An excessively ordered SEI may exhibit increased susceptibility to mechanical strain, potentially leading to the development of cracks or delamination within the SEI layer. Such structural issues have the potential to deteriorate the battery integrity and long-term reliability. Furthermore, it is important to acknowledge that battery performance requirements can vary significantly based on their intended applications and usage scenarios. A SEI characterized by very low entropy may demonstrate optimal performance exclusively under specific conditions, rendering it less versatile and adaptable to diverse operational environments. In fact, in the context of external limiting factors, such as specific environmental conditions or constraints, in-situ SEI components like LiF can take on a disordered and amorphous form, as opposed to the ordered crystalline structure typically expected under normal ambient conditions.[28] Hence, it is evident that the SEI, like any other constituent of a Li-ion battery, necessitates a delicate equilibrium between order and disorder within its structure. Achieving the appropriate balance of entropy levels within the SEI is indispensable for ensuring not only the rapid attainment of structural equilibrium but also the compatibility of the SEI with a wide range of operational conditions. Based on the comprehensive review and analysis conducted above, it is evident that the formation of the SEI is indeed an exothermic reaction associated with an increase in entropy. Importantly, this reaction type usually exhibits spontaneous behavior thermodynamically, implying that the SEI can begin to form promptly upon immersing the graphite anode in the electrolyte solution. Nevertheless, it is noteworthy that in the absence of an applied current, the rate of SEI formation becomes exceedingly slow, making it hardly form a complete film.

2.4. Thermodynamic Model of SEI Formation

Eq.(3) encompasses various crucial components, including the internal energy of SEI, the internal energy of the electrode, interface energy, and adhesion energy, all of which contribute to our understanding of the exothermic and entropy-increasing nature of SEI formation reaction. Sharafi et al.[29] have discussed the significance of adhesion energy, highlighting that a higher adhesion energy signifies a stronger interaction between the substrate and the membrane. In addition, a low interface energy can encourage the formation of cracks in the SEI and the growth of dendrites.[30] However, excessive interface energy may also raise diffusion barriers for Li atoms and encourage dendrite growth.[31] To achieve a high-quality SEI, it is imperative

to have both an appropriate interface energy and a high adhesion energy. In this equation, when the internal energy of the SEI on the anode remains at a lower level, it results in higher adhesion energy within the film. Hence, this leads to the creation of a more substantial surface film on the material and a denser electrode/electrolyte interface. While it is essential to acknowledge the complexity of the relationship between the internal energy of SEI and interface energy, considering factors like surface groups, species, coverage, thickness, among others, the general trend suggests that lower internal energy of SEI near the surface, combined with appropriate interface energy, is advantageous for achieving increased adhesion energy and a more energetically stable SEI. Consequently, the minimum energy state emerges at the SEI/electrode interface, creating an energy gradient across the SEI. It is important to note that the SEI exhibits a double-layer structure, consisting of an outer organic layer and an inner inorganic layer.[32] This dual-layer structure contributes to an inherent entropy gradient within the SEI due to the higher entropy of the organic components and lower entropy of the inorganic components. The interplay between entropy and energy gradients adds complexity to the thermodynamics of the SEI. Research on the SEI extends beyond the realm of materials science alone. Initially, the SEI, composed of a mixture of organic and inorganic components, possesses lower entropy and energy. However, external factors such as current density and temperature can drive the SEI to evolve further toward a state of maximal entropy.

Moreover, the underlying cause of the observed double-layer structure in the SEI cannot be fully elucidated through a purely dynamic perspective, as highlighted in reference.[33] Dynamic analyses primarily serve to simulate the growth rate of the SEI. In the literature, the assumption of a double-layer SEI structure often derives from direct experimental observations.[34] However, it is feasible to delve into the internal mechanisms responsible for the distinctions between the outer and inner components within the SEI. Several factors can be integrated with thermodynamics to shed light on this phenomenon. Maibach et al.[35] were among the first to consider the role of the electric double layer (EDL) at the SEI/electrode interface. Due to the substantial differences in the material composition between the SEI and the electrode, such as graphite, a discrepancy in work functions arises, leading to the presence of an ordered dipole moment at the interface. Consequently, potential gradients emerge within the SEI, resulting in varying formation enthalpies, released heats, and Gibbs free energies. Another contributing factor is the surface tension between the solid/liquid phases and the associated surface entropy or enthalpy, which can be influenced by factors such as concentration,[36] chemical groups,[37] and morphology.[38] As a result, the thermodynamic properties, especially the Gibbs free energy, can undergo alterations as the initial surface film forms due to changes in surface tension. These changes give rise to energy gradients, the diversity of matter within the SEI, and the subsequent evolution of the SEI structure. Therefore, by considering the path to structural equilibrium and the associated entropy/energy gradients (as depicted in Figure 3), we can construct a comprehensive thermodynamic model of SEI
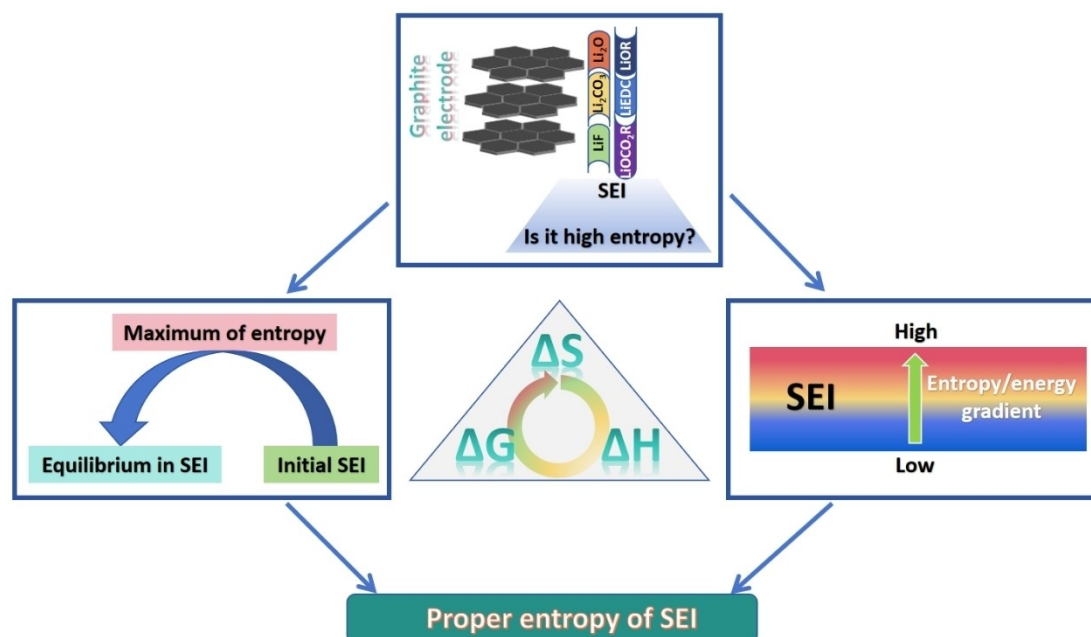
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Figure 3. Illustrative diagram depicting the approach to addressing the question of whether high entropy must exist within the SEI. While the SEI in LIBs is characterized by greater disorder than other components, it eventually reaches an equilibrium state as it evolves towards maximum entropy. Consequently, it is important to establish suitable initial/maximum entropy values for the SEI.

formation. This model can be instrumental in analyzing the impact of various factors on the actual performance of batteries.

3. Correlations between SEI Thermodynamics and Battery Performance

In our thermodynamic model, the direction of entropy increase is dictated by the maximum entropy at the equilibrium state inside the SEI. The evolution of SEI induces the formation of entropy/energy gradients within the interface, consequently influencing the distribution of specular structures on the electrode surface. To establish a connection between this model and real-world battery performances, identifying the key parameters that influence the quality and thermal properties of the SEI is imperative. Recently, Lee et al.[39] highlighted the ongoing ambiguity surrounding the fundamental mechanism and thermal degradation process of the SEI. In response, they investigated the impact of surface electronic conductivity, temperature, and current density on alterations in the SEI's chemical composition and its solubility in the solvent. Their findings revealed the development of Q_{irr} during the formation process, attributed to the energy barrier for electrons leaving the electrode surface, indicative of the presence of surface electronic conductivity. Elevated temperatures prompted the dissolution of organic components, while the dissolving of inorganic components, such as LiF and Li_2CO_3, occurred due to their high binding energy with Li ions. This underscores the significance of temperature variations during battery operation

in influencing SEI formation and thermal stability. Concurrently, current density influences temperature due to irreversible heat generation at the interface. Chang et al.[40] analyzed heat generation in LIBs by employing a combined pseudo-two-dimensional (P2D) electrochemical model and thermal model. They observed a strong correlation between the entropic coefficient and heat generation in LIB being influenced by current densities (C-rates) during SEI formation. Similarly, Gervillié-Mouravieff et al.[41] obtained comparable results. They investigated the relationship between heat generation rate and voltage in a pouch cell using NMC cathodes, carbon anodes and 1 M $LiPF_6$ EC:DMC electrolyte. The heat generation rate peaked during the initial charge stage, followed by a subsequent decrease during the rest charge time and a relatively constant rate during the second cycle. This phenomenon was attributed to irreversible activity in the first cycle and SEI formation on the carbon anode in the low-voltage range. Additionally, the heat generation rate exhibited high sensitivity to changes in C-rate and current pulse speed, underscoring the crucial relationship between heat generation, temperature, and C-rate, particularly for the initially formed interface at the electrode/electrolyte interface in LIBs. These studies collectively demonstrate that temperature and current density play pivotal roles in shaping the thermal properties of the SEI.

3.1. Influences of temperature on the Relationships between Thermodynamics and SEI Properties

In 2009, Yan et al.[42] initiated foundational research into the thermodynamics of SEI formation on graphite, clearly establish-

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ing that SEI particles spontaneously appear when the Gibbs free energy falls below zero. They put forth quantitative relationships between geometric parameters and Gibbs free energy. Nevertheless, their studies imposed constraints on temperature and pressure, overlooking the potential influences of temperature fluctuations, gas generation, current, and applied voltage on both actual battery performance and SEI formation. Consequently, it becomes imperative to establish a correlation between the thermodynamic model and the real-world battery formation and SEI evolution during cycling to gain a comprehensive understanding of these intricate processes. Therefore, this section presents a comprehensive review of the impact of temperature on SEI formation, with the aim of elucidating its thermodynamic implications for actual battery lifespan and capacity.

3.1.1. Temperature Effects on Structure of SEI and Battery Performances

Wang et al.[43] pioneered an analysis of SEI film impedance and capacitance using electrochemical impedance spectroscopy (EIS) at both 25 °C and 65 °C. The study divided the SEI into two distinct regions: an inner layer with a dense structure and an outer layer with a porous structure. These regions were further subdivided into three impedance regions and a capacitance region. To simulate the SEI microphase, the authors applied an equivalent circuit based on Peled's work.[7a] The findings revealed that the resistances of the three SEI layers were nearly identical, but their capacitances exhibited significant differences. Specifically, the dense inner layer had a small capacitance, while the porous outer layer possessed a larger specific surface area, providing more capacitance. During the initial charge at 25 °C, SEI formation occurred between the open-circuit potential (OCP) and 0.8 V, and the SEI continued to grow during subsequent charging. As a result, the resistance of the inner layer increased, while the resistance of the outer layer decreased. This decrease in resistance was attributed to volume expansion caused by the co-intercalation of solvents. However, at 65 °C, the first charging process generated an unstable porous SEI film that could co-intercalate into the graphite lattice along with the solvents, preventing the graphite particles from coming into contact with each other. Consequently, the significant charge-transfer resistance at the affected graphite anode reduced its inherent cycling life. The study also revealed that allowing the passivated SEI film to form initially on the electrode at 25 °C could slow down the co-intercalation of solvents and SEI components, extending the battery lifespan during subsequent cycling at 65 °C. Results also indicated that the SEI film prepared at room temperature could enhance the capacity stability of graphite at high temperatures. After pre-cycling at 25 °C, the capacity of the graphite electrode remained close to 300 mAh g^{-1}. However, during the subsequent cycle at 65 °C, the capacity dropped to 100 mAh g^{-1}. In contrast, without room temperature pre-cycling, the capacity of battery during cycling at 65 °C was only below 40 mAh g^{-1}. These results

suggest that the porous outer layer of SEI formed at high temperatures exhibits poor stability and increased porosity.

In 2004, Zhang et al.[44] not only reaffirmed this conclusion but also delved deeper into the topic. The researchers posited that SEI formation involves two opposing processes: accelerated growth and reduced dissolution. The growth of SEI was linked to the electrochemically induced electrolytic reduction process of the solvent, which was relatively insensitive to temperature variations. Conversely, higher temperatures significantly hastened the dissolution of the initially formed SEI in the electrolyte. The findings of the study revealed that the resistance of SEI decreased as the formation temperature increased. This phenomenon could be attributed to the SEI formed at elevated temperatures being more porous and more susceptible to the increased dissolution of initially formed SEI. Consequently, the ionic conductivity of the SEI was primarily due to the absorbed liquid electrolyte. However, it became evident that a highly conductive SEI did not necessarily translate to better battery performance. To further investigate this, the authors measured the OCP of Li∣∣graphite cells and compared their self-discharge behavior at 60 °C after formation at different temperatures. The results indicated that the order of lithium storage stability at different formation temperatures was as follows: 60 < 45 < 20 < 35 °C. Interestingly, even though batteries formed at 60 °C exhibited the SEI with the highest ionic conductivity, they had the fastest self-discharge rate. This suggested a trade-off between the stability of SEI and its ionic conductivity. Therefore, the optimal SEI formation temperature was determined to be 35 °C, as it struck a balance between structural stability and electrical conductivity. However, it is worth noting that this difference in performance was most pronounced after 150 cycles when assessing the long-term cycle stability of the battery, with batteries formed at 35 °C displaying optimal stability.

Similar conclusions can be drawn from full cells using graphite as the anode. He et al.[45] conducted a comparative analysis of LiCoO$_2$∣∣graphite cells at 25 °C and 50 °C, employing techniques such as EIS, cyclic voltammetry (CV), and cycle life testing. The findings indicated that the initial Coulombic efficiency during the first cycle at 25 °C was higher than that at 50 °C, with both cells exhibiting similar cycling performance in subsequent cycles. However, at 50 °C, there was a more pronounced reduction peak in the electrolyte, and the reduction potential increased. This observation suggested that the reduction reaction of the electrolyte was more favorable at higher temperatures, and SEI formation was triggered by temperature variations.[46] The EIS analysis revealed that at 50 °C, a single high-frequency arc was observed, whereas at 25 °C, two arcs were present in the mid-high frequency range. This indicated that the SEI resistance at 50 °C was significantly lower than that at 25 °C and overlapped with the charge-transfer resistance arc. The elevated SEI formation temperature led to an increase in defects within the SEI layer, resulting in reduced resistance for lithium ions traversing the SEI. These defects are likely associated with the pores in the outer layer of SEI, and the higher temperature contributed to an increase in defect or porosity. Additionally, the authors conducted galvano-

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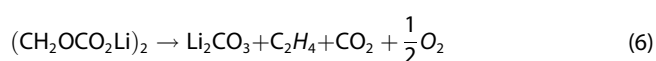European Chemical
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static charge and discharge tests at different temperatures. The results showed that at 50 °C, the initial voltage rise was slower, which implied a higher rate of electrolyte reduction occurring on the surface of the graphite anode. This observation aligns with Wang *et al.*'s earlier explanation that the higher rate of electrolyte reduction at elevated temperatures may be attributed to solvent co-intercalation.[43] Consequently, He *et al.* attributed the higher Coulombic efficiency observed during the first cycle at 25 °C, compared to 50 °C, to two factors:

1) The dissolution of the initially formed SEI. Higher temperatures increased the solubility of SEI components, resulting in decreased efficiency.

2) The low-effective desolvation of Li-ions. The solvation of Li-ions passed through defect sites within the SEI layer and entered the surface region of the graphite anode. At 50 °C, solvent reduction and decomposition occurred in the graphite lattice, leading to lower Coulombic efficiency.

Collectively, the experimental evidence suggests that a higher SEI formation temperature is unfavorable for the development of a highly inert SEI film, particularly with regard to the stability of the outer porous layer of SEI. Larger porosity weakens the desolvation effect of SEI, which can lead to solvent co-intercalation. Based on the analysis above, we can continue to analyze the influence of temperature on the thermal stability of SEI from thermodynamic perspective.

3.1.2. Temperature Effects on Thermal Sability and Entropy Increase of SEI

Indeed, as early as 1999, Richard and Dahn conducted a series of influential studies[47] that yielded crucial insights into the influence of temperature on the SEI. Their research directly indicated that the inner inorganic layer of the SEI is relatively stable, whereas the outer organic layer exists in a metastable state. Using an accelerating rate calorimeter to examine the temperature at which the first exothermic peak related to SEI formation occurs, they observed that the metastable SEI components can decompose and transform into stable inorganic constituents. The reaction is shown as follow:

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + \frac{1}{2}O_2 \qquad (6)$$

Consequently, as outlined in our prior thermodynamic model, the inorganic layer situated near the surface of the graphite anode possesses lower energy due to it needing higher adhesion energy, contributing to the overall stability of the SEI film. Another significant insight can be drawn from the reaction. The metastable outer layer not only brings entropy gradient in the SEI but also induces a potential unstable exothermic source. In the field of fluid mechanics, extensive research has demonstrated that the entropy of porous materials filled with liquids or gases rises as porosity increases.[48] Consequently, the outer SEI layer formed at elevated temperatures, characterized by higher porosity, exhibits greater entropy. As a result, based on the thermodynamic model, the

route for the SEI to reach internal equilibrium becomes more protracted, posing challenges to the SEI ability to achieve a stable state. Hence, the instability of the SEI formed under high temperatures is associated with the increased porosity of the outer layer, leading to diminished desolvation ability, co-intercalation, dissolution of organic constituents, low Coulombic efficiency, and a limited long-term lifespan. However, opting for a lower formation temperature does not necessarily yield better results. Since SEI formation is driven by temperature, extremely low ambient temperatures can prevent the formation of the protective SEI layer. Furthermore, substantial interface polarization can lead to the direct deposition of Li metal.[44,49] Zhang *et al.*[50] delved into this issue extensively. They conducted initial investigations into how SEI films change at low temperatures and their impact on battery performance using galvanostatic discharge curves and EIS. Their findings indicated that batteries operating in cold temperatures experienced a decrease in both operation voltage and capacity. This reduction in operation voltage can be ascribed to reduced ionic conductivity in both the electrolyte and SEI, leading to a slower electrochemical reaction and an ensuing increase in polarization. Greater polarization, under the same current conditions, causes the battery voltage to reach the charging cutoff threshold more quickly and results in a larger voltage drop (IR drop) during discharge. The mid-frequency Faradic charge-transfer resistance began to noticeably increase at −10 °C, whereas the SEI impedance and the internal resistance of the battery itself only started to significantly rise at −40 °C. Hence, the authors proposed that in low-temperature environments, it is primarily the charge-transfer resistance that has a pronounced adverse effect on battery performance, with the influence of SEI film impedance being comparatively insignificant.

Recently, Chang *et al.*[51] employed an ultrasonic pulser-receiver to analyze ultrasonic signals emanating from a Li-ion pouch cell utilizing $LiPF_6$ EC:DMC electrolyte while varying the temperature from low (< 20 °C) to 60 °C. Their investigation revealed that signal attenuation was linked to the high acoustic impedance resulting from gas generation. Exploiting this discovery and integrating it with XPS and Raman test results, the researchers ascertained that following cycling at 0 °C, products containing C−F bonds originating from the main salt $LiPF_6$, as well as Li_2CO_3 product, formed at the graphite interface. Simultaneously, Li metal deposited on the SEI. As the temperature gradually rose to 60 °C, the initial SEI began to decompose, generating gas. Additionally, the Li metal reacted with the electrolyte, dissolving into it. These combined factors resulted in the battery failure at elevated temperatures. It is worth noting that this conclusion appears to diverge slightly from that of Richard *et al.*, who posited that the decomposition of the metastable organic layer gave rise to Li_2CO_3 and gas. In contrast, Chang *et al.*, employing XPS, identified the presence of Li_2CO_3 from the outset.

The research conducted by Parimalam *et al.*[52] appears to offer a reconciling perspective on both of these conclusions. The authors put forth the idea that the initial SEI comprises a combination of Li_2CO_3 and organic lithium components. They conducted a comprehensive investigation into the decomposi-

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tion reactions of SEI constituents using techniques such as nuclear magnetic resonance (NMR) spectroscopy, infrared spectroscopy with attenuated total reflectance (IR-ATR), XPS, and gas chromatography with mass selective detection (GC-MS), with a focus on a LiPF$_6$ in DMC electrolyte. Furthermore, they explored the thermal stability of common SEI components, including Li$_2$CO$_3$, lithium ethylene dicarbonate (LEDC), and lithium methyl carbonate (LMC), in the presence of LiPF$_6$. The experimental findings revealed that the inclusion of the main salt LiPF$_6$ reduced the stability of these components. As the temperature increased to 55 °C, these SEI components underwent reactions leading to the generation of gas, inorganic lithium fluoride salts like LiF, and partially soluble substances. The reactions also produced certain low-polymeric species containing phosphorus and organic compounds with oxygen, collectively contributing to the formation of a new SEI. When combining these insights with previous research findings, it becomes apparent that at low or room temperatures, the nascent SEI comprises both Li$_2$CO$_3$ and organic lithium salts. However, as the battery undergoes cycling and temperatures rise, the SEI components, particularly the organic constituents, begin to decompose, as shown in Figure 4. This decomposition results in the formation of gases and lithium salts containing both fluorine and oxygen. The subsequent loss of some SEI exacerbates interfacial reactions, ultimately leading to battery failure.

As previously discussed, the SEI itself possesses inherent energy, and the SEI decomposition reaction induced by high temperatures results in an exothermic peak. This exothermic reaction involves the conversion of the porous and metastable solid/liquid mixture of the outer SEI layer into an inorganic solid state and gas. The former has lower energy, whereas the latter

clearly has higher energy. A thermodynamic analysis alone suggests that, in accordance with the principle of energy conservation, when a substance with moderate energy transforms into a lower-energy state, higher-energy substances or heat must inevitably be generated to preserve energy. Consequently, it is reasonable to observe the simultaneous generation of lower-energy inorganic solids, higher-energy gases, and heat. Throughout this process, the SEI structure undergoes disruption, causing the high-entropy outer layer to vanish. This, in turn, necessitates continued electrolyte reactions to introduce fresh entropy in the non-adiabatic system, thereby exacerbating the occurrence of unfavorable interface reactions. To prevent such scenarios from leading to a continual rise in electrode interface resistance and rapid battery failure, it is imperative for the battery to operate at an appropriate temperature. For batteries designed for extended continuous cycling, cooling mechanisms should be incorporated to forestall interface failure and the subsequent release of substantial heat. Thermodynamic models can further elucidate the influence of temperature on SEI entropy. According to the formula for irreversible entropy change:[53]

$$\Delta S_{irr} = \int_{T_1}^{T_2} \frac{C}{T} dT \tag{7}$$

where C is the heat capacity of the body in which the energy is dissipated; $\triangle S_{irr}$ represents the entropy change of irreversible reaction. The entropy change depends on the heat capacity of the SEI, the initial equilibrium temperature (T_1), and the final equilibrium temperature (T_2). In general, organic substances exhibit higher heat capacity compared to inorganic solids, while liquids have significantly greater heat capacity than solids.
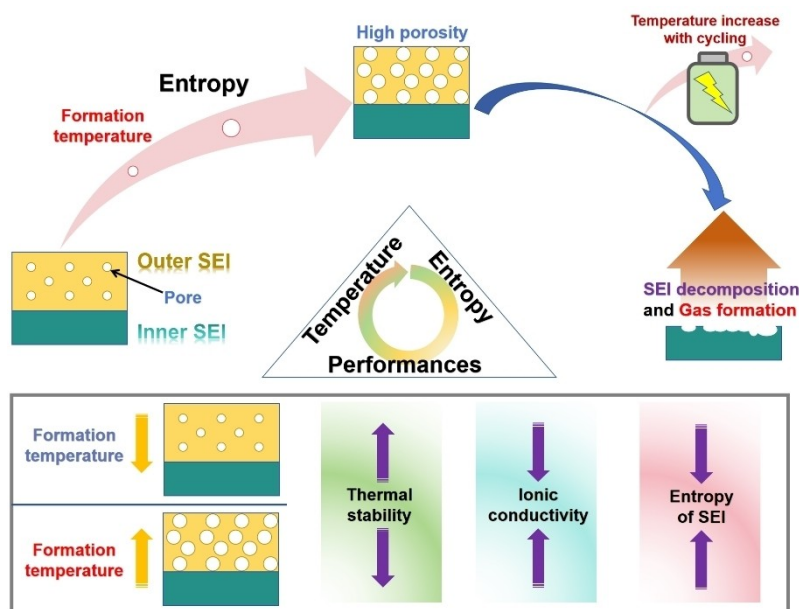

Figure 4. Diagram illustrating the interplay between temperature, entropy, and battery performance, alongside a comparison of SEI formation under high and low temperature conditions. Elevated temperatures during SEI formation result in a more porous and high-entropy outer layer of the SEI. Subsequently, continued elevated temperatures during subsequent cycling can lead to the decomposition of this outer layer and the formation of gas. Nevertheless, this porous SEI exhibits higher ionic conductivity.

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Therefore, at the same temperature, the porous organic outer layer of the SEI, filled with liquid in its pores, possesses a greater heat capacity, resulting in maximal entropy change. This maximal entropy change renders it challenging for various physical and chemical processes within the outer SEI layer to reach equilibrium due to its large maximum entropy, ultimately destabilizing the outer layer. Additionally, as per the formula for the rate of irreversible entropy change:[53]

$$\left(\frac{dS}{dt}\right)_{irr} = \frac{1}{T}\frac{dE}{dt} \tag{8}$$

It is evident that, at a specific temperature, the rate of energy dissipation within the SEI is directly proportional to the rate of entropy change. During battery cycling, when the temperature reaches the SEI decomposition temperature, the outer porous organic layer undergoes decomposition. The rate of energy dissipation in the outer organic layer significantly surpasses that in the inner inorganic layer. Consequently, entropy gradients and entropy change gradients coexist within the SEI. When the outer layer experiences a notable entropy increase, it tends to produce high-entropy gases, low-entropy inorganic solids, or directly dissolve into the electrolyte, resulting in the formation of a new SEI (Figure 5). Therefore, to enhance SEI stability at elevated temperatures, it is crucial to establish an initially formed SEI with an appropriate entropy value at a suitable temperature (e.g., 35 °C proposed by Zhang[44]). This facilitates the rapid attainment of an equilibrium state within the SEI structure.

There are undoubtedly numerous factors that impact entropy, enthalpy, and Gibbs free energy, particularly within electrochemical systems. Temperature is just one of these factors. Factors like current density, cut-off voltage, and state-of-charge (SOC) also play significant roles and cannot be overlooked. Therefore, it is essential for us to delve deeper into the influence of current density, often expressed as the C-rate, on the formation of the SEI.

3.2. Influences of Current Density/SOC on the Relationships between Thermodynamics, SEI Properties and Battery Performances

Batteries must begin charging or discharging immediately upon applying a current. Therefore, we must take into account the combined influence of current density and SOC or SOL (state-of-lithiation) on battery performance. The exploration of current density effects should be prioritized.

3.2.1. Current Density/SOC Effects on Physico-Chemical Properties of SEI and Battery Performances

In their study, Zhang et al. delved into the impact of current density on the structure and characteristics of SEI, in conjunction with the influence of temperature.[44] Initially, the researchers explored the lithiation behavior of Li||graphite cells created at varying current densities and then stored at a consistent SOL, all under a temperature of 60 °C. While the OCP changes for each cell exhibited considerable similarity, a slower initiation of the second-stage lithiation plateau was noticeable at a lower current density of 7 mA g⁻¹. However, it was observed that the SEI formed at lower current density had only a marginal advantage in terms of stability, albeit it possessed a greater lithiation capacity. Moreover, EIS findings suggested that the SEI developed on the graphite surface under higher current densities demonstrated enhanced conductivity. The authors reasoned that the inherent conductivity of the SEI itself was relatively low, with the majority of its conductivity arising from electrolyte infiltration. Consequently, higher current density resulted in a more porous and loosely structured SEI film, enriched with a higher amount of liquid electrolyte, thereby amplifying the SEI conductivity. Conversely, lower current density favored the creation of a high-resistance passivation film, subsequently reducing electrode self-discharge rates. In summary, the authors recommended that the selection of
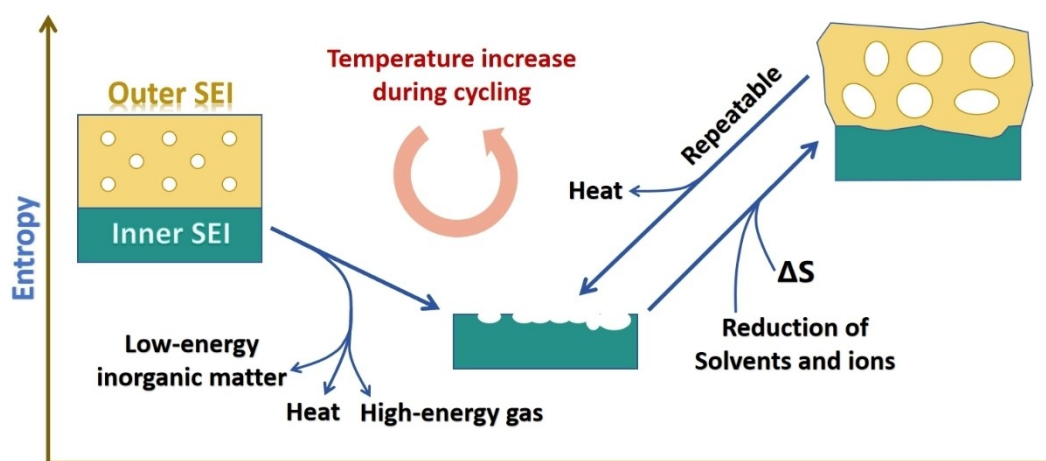

Figure 5. Diagram illustrating the structure change of SEI and its energy evolution under elevated temperature during battery cycling. When the SEI, particularly its organic outer layer, decomposes into high-energy gas and low-energy inorganic matter at elevated temperatures, a part of the internal energy of SEI is released in the form of heat. The loss of the high-entropy structure leads to the regeneration of entropy through electrolyte reduction and the formation of new SEI. This repetitive process can trigger thermal runaway.

current density should aim to strike a balance between achieving high conductivity and promoting passivation effects. They proposed a recommended current density range of 10–20 mA g^{-1} for battery formation. He *et al.*[54] observed similar trends when investigating how current density affects the formation of LiCoO$_2$||graphite and Li||graphite cells. The resistance of the SEI on the graphite anode decreased as the formation current density increased. Higher formation currents led to an improvement in the first-cycle Coulombic efficiency but a decline in the second-cycle Coulombic efficiency. Moreover, elevated current density caused increased polarization, resulting in a rapid voltage rise during the formation of LiCoO$_2$||graphite cells. Conversely, lower formation current densities led to a more gradual increase in battery voltage, allowing sufficient time for the development of a high-quality and dense SEI. During full-cell cycling tests, LiCoO$_2$||graphite cells formed at lower current densities exhibited superior cycling stability at both room temperature and high-temperature conditions (50 °C). In this context, it became evident that the SEI formed at lower current densities exerted a more pronounced influence on the full-cell cycling performance compared to its impact on half-cell cycling performance, as observed in Zhang's study.

In the realm of the research concentrating on influence of SOC on SEI, An *et al.*[55] conducted a practical study. Building upon Kim *et al.*'s prior research[14b] (Figure 6a, large Li density is beneficial to the formation of dense matter), the authors postulated that the SEI formed on the anode at higher SOC levels (formation protocol is shown in Figure 6b) is denser and more stable than that obtained at lower SOC levels. This phenomenon stemmed from the inherent instability of the electrolyte at higher SOC and the increased availability of lithium ions for electrode reactions (Figure 6c). Consequently, the authors opted to depart from the conventional approach of employing full charge-discharge cycles for formation. Instead, they devised an alternative protocol, involving repetitive cycling within a high SOC range (following the initial charge) until the end of the cycle culminating in full discharge. Between the initial charge and discharge, the authors introduced four short cycles within the voltage range of 3.9 to 4.4 V as part of their modified formation procedure. They compared the impedance of cells produced using this enhanced protocol against those created through a typical formation protocol, all conducted at a low current density of C/20. The findings unveiled that during impedance testing at elevated potentials (>3.4 V) within the high SOC region, the SEI film formed by the high SOC region formation strategy exhibited lower impedance, which is favorable for ion intercalation/de-intercalation. Notably, even when subjecting these cells to high current density, they exhibited a slight edge in terms of capacity retention during cycling assessments. This suggested the potential for substantial reductions in battery production time. The experimental observation of achieving lower impedance, indicative of SEI films with enhanced conductivity, aligns harmoniously with earlier reports in the literature.

We still need to employ thermodynamic models to analyze such phenomena and provide guidance for SEI design. While
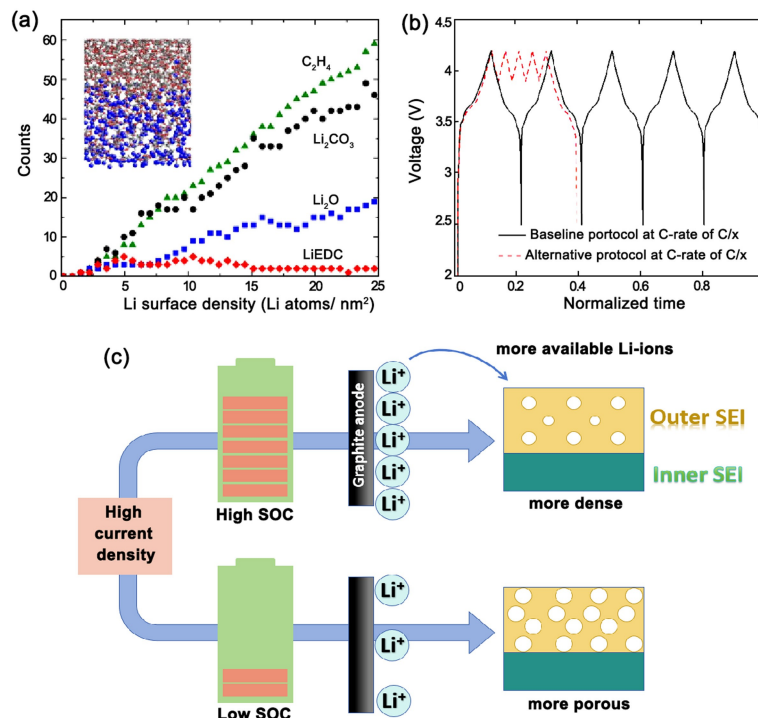

Figure 6. (a) The evolutions of EC based SEI components with increasing Li density;[14b] (Copyright © 2011 Published by Elsevier B.V.) (b) The voltage profiles from a baseline and alternative (rapid strategy) SEI formation protocol;[55] (Copyright © 2017 Published by Elsevier B.V.) (c) Diagram illustrating the influence of SOC on the SEI structure at high current density. The SEI formed on the anode at higher SOC levels exhibits a denser and more stable nature in contrast to that formed at lower SOC levels, which can be attributed to an increased abundance of Li ions becomes readily available for electrode reactions. As a result, the SEI structure formed under these conditions gains greater cohesion and robustness, contributing to its enhanced stability.

Eq.(7) can be used to calculate irreversible entropy change, it is essential to consider the entropy change caused by the current during battery formation. When calculating the entropy change for the entire battery, Viswanathan *et al.*,[56] attributed all irreversible heat generation to Joule heating, represented by Eq.(2). Therefore, for the graphite interface, knowing the current and the irreversible heat generated by SEI impedance, along with the temperature of SEI, enables us to determine the entropy change value, i.e., the ratio of heat to temperature. The smaller the SEI resistance obtained at high current density, the less irreversible heat it generates. Consequently, the rate at which the SEI reaches its maximum entropy slows down, and the SEI film takes longer to achieve its stable equilibrium state. Moreover, according to the battery power calculation $P = iU$ (with units $J\,t^{-1}$), the voltage determined by SOC directly contributes to the energy. Thus, entropy change should also be related to the SOC. Therefore, the authors employed an electrochemical thermodynamic measurement system (ETMS) to measure the relationship curves between SOC-ΔS and SOC-released heat amount for LIBs with different combinations of cathodes and anodes. The results revealed that the high current formation strategy within high SOC region would lead to an increase in ΔS, but it would also cause a decrease in irreversible heat generation. In summary, the high SOC region formation strategy leads to a greater increase in SEI entropy.

3.2.2. Current Density/SOC Effects on Fast Charging Performance and Entropy Increase of SEI

It can be seen that the conclusion that high current density promotes the formation of high conductivity SEI is crucial for the rapid formation of batteries. The series of conclusions obtained from previous analyses can be used to further optimize and develop strategies for rapid formation in the high SOC region. Recently, Weng *et al.*,[57] building on the work of An *et al.*, further explored methods for rapid formation in the high SOC region of batteries and battery life prediction. The authors inserted a rapid formation step between the initial charge and discharge, involving four cycles at a 1 C current density within the high SOC range of 3.9 to 4.2 V. Subsequent capacity and cycling test results showed that compared to the baseline formation, rapid formation led to a 0.3% decrease in capacity and a 0.8% decrease in Coulombic efficiency. However, it notably bolstered cycling stability. This enhancement was primarily attributed to the higher SOC, which allowed for the accumulation of more Li$^+$ ions, rendering the SEI generated during rapid formation more passivating. Furthermore, Rangom *et al.*[58] advanced their research to leverage the high conductivity of SEI formed under high current densities to improve the fast-charging capability of the battery. They conducted their experiments on a graphite electrode with a particle size of 23 μm and found that the SEI formed at a current density of 100 C exhibited superior conductivity compared to that formed at 0.1 C current density. The authors also evaluated the impact of SEI formation at 0.1 C and 100 C current densities on the delithiation capacity in rate performance tests. Interestingly, the

results showed that Li||graphite cells formed at 100 C exhibited a higher capacity when cycled at the same current density. Moreover, the SEI formed under high current densities proved to be more conducive to enhancing the rate performance of the graphite electrode. These experimental findings present a challenge in terms of a comprehensive explanation, particularly when considering the influence of a porous SEI film saturated with electrolyte alone.

The work by Ishii *et al.*[59] might offer some insights. The authors prepared composite anode materials using mesoporous carbon and TiO$_2$, aiming to achieve improved rate performance. They observed that the SEI would block the diffusion of Li-ions, preventing them from reaching the inner TiO$_2$ crystals, resulting in poor charge-discharge capacity at high current densities. However, after formation at a high current density of 50 mA g^{-1}, the cells could maintain a significant reversible capacity even under an extremely high current density of 1000 mA g^{-1}. This high-rate performance was attributed to the small particle size of the electrode material and its large specific surface area. Although this material is not a pure graphite electrode, it can still be combined with previous analyses: formation at high current densities leads to the creation of a porous and loose SEI, accommodating more electrolyte. This not only enhances the conductivity of the film itself but also allows more Li-ions to reach the graphite grains deep within the electrode, significantly boosting the rate performance of electrode.

Another factor that may contribute to the high-rate performance of SEI formed at high current densities could be associated with the inorganic layer. In their research, Oh *et al.*[19] employed XPS analysis to investigate the influence of current density on SEI formation. They observed that when using an electrolyte comprising 1 M LiPF$_6$ EC:DEC:EMC, the SEI formed at a low current density of 0.1 C exhibited lower oxygen content. This suggests that only a small portion of the SEI originated from the decomposition of carbonate solvents at this point. Conversely, the SEI formed at a high current density of 1.0 C was thicker and contained a notable quantity of carbonate groups. When considering the findings related to the temperature effect, it can be deduced that Li$_2$CO$_3$ primarily stems from solvent decomposition at high current densities. Li$_2$CO$_3$ also tends to decompose and release gas, which diminishes the SEI stability at elevated temperatures. Moreover, of greater significance, SEIs formed at both high and low current density contained LiF, but Li$_x$PO$_y$F$_z$ was exclusively identified in the inner layer of the SEI formed at high current densities. The authors posit that this phenomenon is due to PF$_6^-$ being able to penetrate the SEI layer more effectively with the assistance of high current during the discharge step. These observations align with prior conclusions, indicating that the electrolyte can infiltrate the interior of the SEI under conditions of high current density.

Besides enabling easy liquid permeation due to its porous structure, the SEI formation at high current densities benefits from abundant grain boundaries (GB) in the subsequent generated inorganic layer, acting as efficient pathways for rapid ion transport.[60] The scheme is shown in Figure 7a. Consequently, the resulting SEI at high current densities manifests as
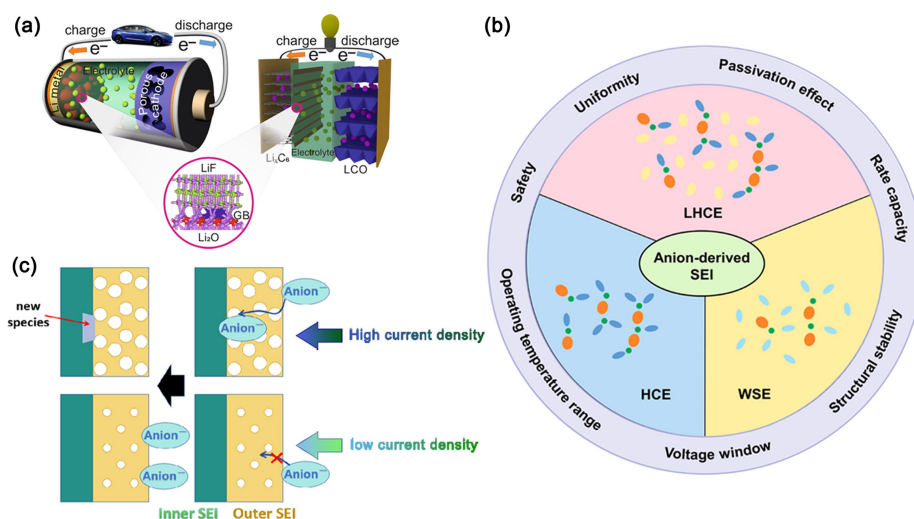
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Figure 7. (a) Schematic illustration of the SEI on the Li metal surface or graphite anode in batteries; lower picture shows the atomic structure of a representative GB which provides rapid ion transport channels;[60] (Copyright © 2019, American Chemical Society) (b) Schematic diagram of the design strategy for anion-derived SEIs by solvation structure regulation. LHCE: localized highly concentrated electrolyte; HCE: highly concentrated electrolyte; WSE: weakly solvating electrolyte;[62] (Copyright © 2021 OAE Publishing Inc.) (c) Schematic of evolution of inner inorganic layer under low or high current density conditions. A high formation current density facilitates the permeation of anions into the SEI, enabling them to reach its inner layer. Subsequently, the decomposition of these anions enriches the composition of the inner layer of SEI.

an interface layer with a porous and thicker structure, encompassing an inner inorganic layer with a polycrystalline configuration, collectively contributing to enhanced conductivity. While literature on the developmental stages of SEI through anion modulation during formation is currently scarce, researchers have already established that anion-regulated (Figure 7b), enriched inorganic SEI displays accelerated charging capabilities.[61] This phenomenon stands as a pivotal approach for regulating SEI composition through anions. Specifically, it entails utilizing high current density during the discharge phase of formation to drive anions to infiltrate the internal graphite SEI, culminating in the formation of an internally rich inorganic layer abundant in anion decomposition (Figure 7c).

In the battery industry, while high current density can indeed reduce formation time and manage production costs, it is essential to note that more is not necessarily better. The increased entropy generated by high currents leads to a higher structural entropy within the SEI, resulting in a logically more porous structure that can accommodate a greater amount of electrolyte. This raises the question of whether this increased porosity might heighten contact between the electrolyte and the electrode, potentially leading to undesirable side reactions. Attia *et al.*[24] introduced the concept of striking a balance between formation time and irreversible capacity loss. Through a comparison of various formation protocols, the researchers observed that in a 1 M LiPF$_6$ in EC:DEC electrolyte, reduction of EC on the carbon electrode predominantly contributed to irreversible capacity. Notably, with prolonged formation times at lower current densities, SEI growth resulted in a substantial irreversible capacity loss in the initial cycle but led to an improvement in Coulombic efficiency in subsequent cycles. Conversely, shorter formation periods at higher current densities led to the rapid depletion of solvated ions participating in

SEI formation, making surface transport the rate-limiting step and approaching the diffusion limit. In such cases, the irreversible capacity loss in the first cycle was reduced, but it increased in the second cycle. Particularly, at current densities exceeding 10 C, EC was not reduced on the carbon electrode surface during the first cycle but contributed significantly to irreversible capacity loss in the second cycle. Therefore, the authors proposed that employing a 1 C formation current density could effectively balance reaction rates and the time required to reach the diffusion limit, consequently reducing irreversible capacity loss and formation time. Another important factor that requires attention in the real-world battery industry is the manufacturer-set limit of current density, which is capped at 4 C to prevent overcharging.[63] An excessively high C-rate can lead to ultrahigh irreversible heat production, directly linked to the degradation of LIBs.[64] Consequently, an authentic setting for the current density value cannot surpass a safe criterion, triggering an inevitable SEI evolution process aimed at achieving maximum entropy and an equilibrium state.

In summary, as depicted in Figure 8, the current density employed during battery formation has the most straightforward connection with the subsequent cycling stability and reversible capacity of the battery. SEI formed at lower current densities, which is associated with lower entropy, promotes higher reversible specific capacity and enhanced thermal stability. Conversely, SEI formed at higher current densities, with higher entropy characteristics, shows reduced reversible specific capacity and thermal stability but provides rapid charging capabilities and improved long-term cycling stability. Opting for a speedy formation strategy within the high SOC region proves more beneficial for boosting the rate performance of the battery.
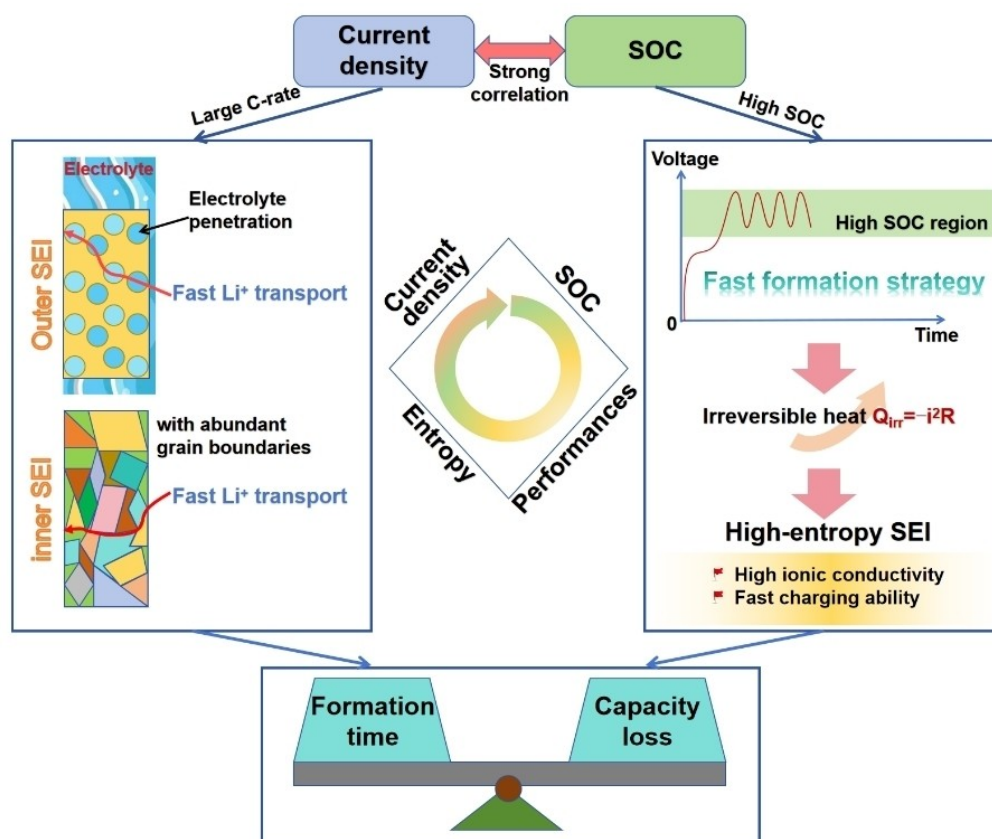
Figure 8. Diagram illustrating the influence of current density or SOC on SEI structure and properties. A high current density promotes the formation of a porous outer layer and enriches the composition of the inner layer of SEI. Fast formation within the high SOC region allows the high-entropy SEI to exhibit enhanced ionic conductivity and rapid charging capabilities.

4. Additional Key Characteristics of SEI Linked to the Thermodynamic Model

The stresses in the electrode materials primarily arise from ion intercalation/de-intercalation reactions, accompanied by changes in lattice dimensions, crystal structures, and phase transformations involving both crystalline and amorphous phases.[65] It is imperative to consider the mechanical properties of materials and interfaces, such as hydrostatic pressure and elastic behavior, due to their impact on lithium intercalation and diffusion.[66] During battery operation, the mechanical mismatch between active particles and the SEI layer promotes cracking at the particle surface. This results in the exposure of more active material to electrochemical reactions at the fresh crack surface, leading to the formation of new SEI and, consequently, a loss in capacity fade and an increase in resistivity.[67] Researchers have, therefore, developed coupled electrochemical-mechanical or electrochemical-thermal-mechanical models of LIBs to investigate the mechanisms of SEI evolution and degradation. The application of the previously discussed thermodynamic model offers valuable insights into the examination of the confluence of electrochemical and mechanical properties of SEI, contributing to an enhanced understanding of battery degradation.

Several significant models play a crucial role in the mechanical investigation of SEI in LIBs. Among these, a fundamental model is the coupled model of diffusion-induced stresses and stress-assisted diffusion. For instance, He et al.[68] formulated a stress-assisted diffusion model that considers the concentration-dependent elastic modulus of the active material for multi-layered electrodes in LIBs. The authors incorporated Li-ion diffusion and chemo-mechanical potential using Fick's law and internal stresses/concentration-dependent elastic modulus, respectively. The outcomes revealed that, for both graphite and Si anodes, stress-assisted diffusion enhances Li-ion diffusion, resulting in more uniformly distributed Li-ion concentrations compared to Fick's diffusion. This effect is further amplified in graphite when considering the concentration-dependent modulus. While this model accounts for configurational entropy and temperature in the equations, their significance from a thermodynamic perspective has not been explicitly emphasized. The critical aspect of Li-ion diffusion before intercalation primarily occurs within the SEI, serving a pivotal role in facilitating fast ionic transport and safeguarding battery electrodes from parasitic reactions with solvents. In this context, Hao et al.[69] delved into the mechanical properties of SEI components, LiF and Li_2O, determining the ideal strength of SEI through density functional theory calculations and molecular dynamics simulations. Their findings revealed that while

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tensile strain in SEI, induced by volume changes in the electrode, increases the energy barrier for Li adatom diffusion on Li_2O, the stretching of SEI can promote Li surface diffusion adatoms on the LiF nanofilm. The authors highlighted key parameters, such as temperature and current density, impacting the fundamental mechanical properties of SEI. However, they underscored the challenge of precisely signifying the influences of temperature on the results, particularly in the calculation of diffusion activation energy using the Arrhenius equation. In a related study, Benitez and Seminario[70] specifically investigated ion diffusivity through the SEI and discussed the influence of temperature on diffusion activation energy. The findings indicated that the diffusion coefficients of Li-ions in SEI components (LiF, Li_2O, Li_2CO_3) at elevated temperatures, spanning from 700 K to 1800 K, are at least five orders of magnitude higher than the corresponding low-temperature results. Consequently, certain parameters, with temperature being particularly noteworthy, can establish a connection between the coupled mechanical model of SEI and the aforementioned thermodynamic model.

Primarily, it is crucial to note that, preceding the discussion of our thermodynamic model, combinations of electrochemical-mechanical models and thermal models have conventionally been employed to analyze the evolution and degradation of SEI. Yang et al.[71] investigated the aging behavior of batteries under various C-rates and ambient temperatures in their electrochemical-thermal-mechanical degradation model, aiming to predict the lifetime of LIBs. This model integrated Fick's law, Ohm's law, the Butler-Volmer equation, a lumped thermal model, static mechanical equilibrium equations, and material balance/mass conservation in side reactions. The theoretical model, accounting for C-rate and temperature factors, revealed that high C-rates significantly increased diffusion-induced stress, leading to severe cathode active material loss, heightened local current density, and larger lithium concentration inhomogeneity. Additionally, both lower and higher ambient temperatures accelerated the capacity fade of LIBs. Elevated temperatures facilitated a faster kinetic process of SEI growth reactions and increased the electrolyte solvent diffusion coefficient, while lower temperatures slowed electrochemical processes, resulting in pronounced lithium-ion loss due to lithium-plating. Drawing on these research findings, our thermodynamic model sheds new light on SEI degradation. The integration of various models can be achieved through the correlation established by temperature and current density. As SEI formation is an exothermic reaction associated with an increase in entropy, elevated temperatures enable SEI to acquire a greater amount of entropy. Consequently, heightened entropy induces instability in the SEI structure. Simultaneously, elevated temperature enhances the effect of Li-ion diffusion assisted by stress in active material particles. The combined impact of increased entropy and stress renders particles more prone to cracking, ultimately leading to battery failure after prolonged cycling. Similarly, high C-rates contribute to increased entropy of SEI and stress at the particle interface. Thus, it can be inferred that when the entropy of SEI approaches the maximum toward an equilibrium state, stress also approaches its peak value. In other

words, particle stress at the interface can counterbalance the impact of continuously rising entropy, underscoring the necessity of maintaining a moderate SEI entropy. Excessive initial entropy of SEI results in substantial stress during SEI evolution toward equilibrium, while too small an initial entropy prolongs the time to reach the maximum, leading to excessive consumption of Li-ions due to the overproduction of SEI on particle crack surfaces. Furthermore, from an energy perspective, a low C-rate induces the formation of an intact SEI, facilitating stress-induced Li-ion diffusion. Consequently, it is reasonable to speculate the presence of a stress gradient in SEI with a two-layer structure. Li-ions diffuse in the liquid in the outer loose layer and traverse through stress-assisted pathways and grain boundaries in the inner intact layer.

5. Conclusions and Perspective

Thermodynamics constitutes a cornerstone in battery research, particularly when striving to establish correlations between SEI properties and the actual performance of batteries. Within energy storage devices, especially LIBs, the interplay at the electrode-electrolyte interface profoundly influences their operational characteristics, encompassing capacity and stability. Due to presence of energy transfer and entropy change during interfacial reactions, we endeavor to delve deep into the intricate thermodynamics governing SEI formation and evolution in LIBs. Therefore, our primary objective is to foster a profound understanding of the underlying principles that drive these processes. In this review, we have harnessed key thermodynamic parameters, notably the Gibbs free energy change ($\triangle G$), enthalpy change ($\triangle H$), and entropy change ($\triangle S$), as integral tools to decipher the intricate behavior of SEI formation and its profound influence on battery performance. These parameters provide invaluable insights into the thermodynamic landscape governing the SEI behavior. By doing so, we aspire to bridge the gap between fundamental thermodynamics and practical battery performance following path shown in Figure 9, ultimately contributing to the development of safer and more efficient LIBs in the future.

Firstly, a thermodynamic model was introduced by reviewing many references and analyzed in detail. SEI formation in LIBs is a complex and dynamic process with significant thermodynamic implications. The SEI forms through a series of reactions at the electrode-electrolyte interface, driven by the interaction between Li-ion and the anode material, often graphite. Notably, these reactions are mainly exothermic, releasing heat during the SEI formation, which can be quantified using the irreversible heat equation. This exothermic nature of SEI formation is crucial in understanding its thermodynamics. Additionally, SEI formation leads to an increase in entropy, as confirmed by the standard entropy values of SEI components. This increase in entropy promotes the evolution of the SEI structure toward a state of maximal entropy, which is often associated with equilibrium state, stability and enhanced battery performance. However, achieving the right balance of entropy within the SEI is essential, as excessively low or high
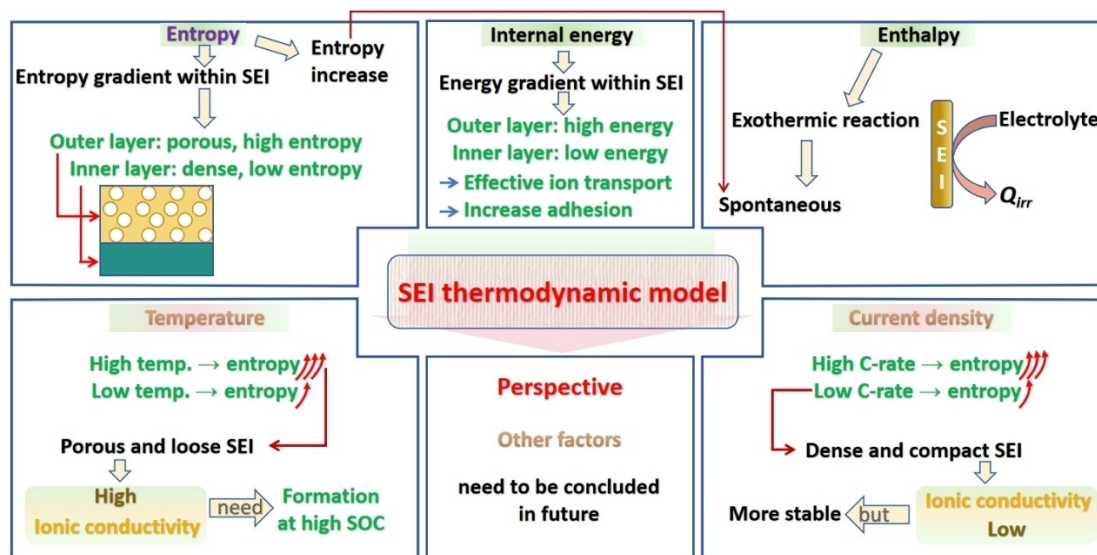
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Figure 9. The flow-process diagram delineates the comprehensive analytical trajectory and logical interconnections underpinning the principal findings within this review. Commencing with the development of a thermodynamic model for SEI, exhaustive investigations into key thermodynamic parameters, with particular emphasis on entropy, have ensued. Subsequently, the intricate relationship between SEI formation variables and battery performance has been established through the integration of the thermodynamic model of SEI.

entropy levels can have drawbacks, affecting the SEI adaptability and structural integrity. The SEI double-layer structure, composed of organic and inorganic components, further complicates its thermodynamics, with factors like the EDL, surface tension, and morphology contributing to energy gradients within the SEI. Understanding these thermodynamic aspects of SEI formation is crucial for optimizing LIB performance and durability under various operating conditions and environmental factors.

Next, the influence of both temperature and current density on SEI formation in LIBs is a multifaceted interplay of factors that impact battery performance. Combining these influences, we can draw the following conclusions:

1) Temperature impact on SEI: Higher temperatures generally accelerate SEI formation kinetics. However, excessively high temperatures can lead to the decomposition of the electrolyte and destabilization of the SEI, especially organic outer layer with high entropy. The decomposition of organic constituents within the SEI due to elevated temperatures results in the generation of new inorganic species characterized by low entropy, while concurrently producing gaseous byproducts with high entropy and irreversibly releasing heat. This process leads to the supplementation of new high-entropy structures within the SEI, followed by their eventual degradation and the potential onset of thermal runaway. Conversely, lower temperatures slow down SEI formation but can result in a more stable and protective SEI. Maintaining an appropriate and carefully controlled temperature is a critical factor in the battery formation process.

2) Current density impact on SEI: Higher current densities tend to promote the formation of a porous and loosely structured SEI. This enhances SEI conductivity but may compromise its

stability. Lower current densities favor the creation of a high-resistance passivation film, which reduces self-discharge rates but might require longer formation times. However, at high current densities, anionic permeation into the inner inorganic layer is facilitated, resulting in an enrichment of its composition and the creation of abundant grain boundaries. When coupled with the presence of a high-entropy, loosely structured outer layer, the SEI demonstrates improved ionic conductivity and a robust ability for enabling rapid charging and discharging.

3) Temperature and current density optimization: Optimizing both temperature and current density during SEI formation is essential for achieving the desired balance between SEI properties and battery performance. It requires careful consideration of specific requirements such as fast charging, capacity retention, and thermal stability.

4) Fast formation at high C-rate: When fast formation is a priority, higher current densities can be beneficial, as they expedite SEI formation with loose structure. The infiltrated liquid electrolyte creates an optimal environment conducive to facilitating rapid ion transport. The fast formation strategy at high SOC regions may enhance rapid charging capabilities and long-term stability at high current densities.[57,72] The intrinsic electrolyte instability and elevated lithium ion abundance at higher SOC offer additional resources for mitigating excessive porosity, thus enhancing the physical and chemical stability of the SEI to some extent.

5) The impacts of coupled mechanical model on SEI degradation: Our thermodynamic model offers new insights into SEI degradation, correlating mechanical models through temperature and current density. As SEI formation is exothermic with increased entropy, elevated temperatures promote greater entropy acquisition, inducing instability. Simultane-

ously, temperature enhances Li-ion diffusion assisted by stress, making particles more prone to cracking and leading to battery failure after prolonged cycling. High C-rates contribute to increased entropy and stress, indicating that as SEI entropy approaches its maximum, stress peaks. Maintaining moderate SEI entropy is crucial, as excessive initial entropy causes substantial stress, while too small an initial entropy prolongs reaching the maximum, leading to excessive Li-ion consumption.

All the influence of temperature and current density on SEI formation underscores the need for a tailored approach in LIB manufacturing. Engineers and researchers must carefully select and optimize these parameters to meet the requirements of different applications, whether they prioritize rapid charging, long-term cycling stability, or other performance metrics. The choice between higher temperatures and current densities for faster formation or lower temperatures for improved stability should align with the specific needs of the battery system under consideration. Striking a balance between SEI characteristics, including stability, conductivity, and resistance, is essential. This balance depends on the specific goals of the battery application, and trade-offs may be necessary.

In addition to temperature and current density, the formation of the SEI in LIBs is influenced by a multitude of other factors.[73] These factors encompass specific surface area (SSA), particle size, surface chemical groups, choice of solvents, ion types, and more. However, it is important to note that these factors often exhibit interconnected relationships with the thermodynamics of SEI formation. For instance, the SSA of an electrode is intimately linked with its surface energy and formation enthalpy.[74] This relationship impacts the surface thermodynamics of the electrode during SEI formation. Additionally, as per Eq.(2) and Eq.(4), a low interface resistance resulting from a large SSA can reduce irreversible heat generation.[17] Consequently, electrodes with higher SSA may exhibit superior performance at elevated current densities.[75] However, a high SSA can also increase the likelihood of surface reactivity,[76] which can lead to capacity loss,[77] particularly in the initial cycle.[78] Therefore, selecting the appropriate SSA for a given electrode cannot rely solely on one or two factors but should be carefully considered in the context of the overall battery requirements. Particle size is another parameter closely related to SSA, and it significantly influences battery performance.[79] Furthermore, factors such as surface chemical groups, choice of solvents, and ion types play crucial roles in SEI formation. These factors have been extensively studied, and there is a wealth of literature discussing their effects. However, summarizing their precise impact is a complex challenge due to the multitude of conditions and complexities that influence their decision-making processes. Furthermore, our analysis, perspectives, and thermodynamic model can be applied to investigate SEI in next-generation batteries, such as Li metal batteries. While the reactions on graphite and Li metal anodes differ, the transport of Li-ions through the SEI shares similar characteristics. Common SEI species contribute to these similarities. However, it is crucial to note that Li metal deposition/stripping induces volume changes at the interface,

creating numerous defects between SEI and the Li metal anode. These voids may produce more complicated energy and entropy gradients in SEI on the Li metal anode from a materials science standpoint.

Conflict of Interests

The authors declare no conflict of interest.

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