

Review

Development, retainment, and assessment of the graphite-electrolyte interphase in Li-ion batteries regarding the functionality of SEI-forming additives

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SUMMARY

Formation of a decent solid-electrolyte interphase (SEI) is recognized as an approach to improve the performance of lithium-ion batteries. SEI is a passivation layer generated on the anode during the initial cycles. Characteristics of the graphite SEI depend on the operational parameters, state of the anode, and the content of the electrolyte. Introducing reduction-type additives to the carbonate electrolytes has been one of the most practiced methods to generate an effective SEI on carbonous anodes. To track the role of additives in SEI evolution, first, we have presented a general review on what is currently understood about the SEI formation processes and the impacting parameters. In the second step, the most reported methods to study and analyze the functionality of the SEI-forming additives are classified. As the third part, different reduction-type additives are categorized, and their performances are comparatively reviewed.

INTRODUCTION

We live in the era of electrification in which lithium-ion batteries (LIB) have globally become a mainstream in electrical energy storage. A glance at the constantly growing market of electric vehicles would bring the potentials of LIB technology into the picture. It is predicted that the current dominance of the combustion engine vehicles will decrease from 99% in 2015 to 68% in 2030 showing the immense potential for the market of electric vehicles to grow by a factor of 52 (Berckmans et al., 2017). The contemporary transition happening in the transportation industry demands better batteries every passing day to provide satisfactory features in terms of safety, capacity, cyclability, shelf life, and energy density. The fact that many of these determinative parameters are correlated with the characteristics of the solid-electrolyte interphase (SEI) (Funabiki et al., 1999; Peled et al., 1995, 1997) signifies the importance of the SEI layer in lithium-ion batteries. As a general description, the SEI could be figured as a thin film covering the electrode particles due to the decomposition reactions of the electrolyte which can preserve the active material from latter degradative mechanisms. However, the intercalation of lithium ions inside the carbonous structure is the main reaction happening while the graphite anode is getting charged, there will be a competition among many electrolyte components to reduce at the surface of the electrode due to the suitability of their reduction potential (Peled and Menkin, 2017; Verma et al., 2010). The SEI will be formed during the initial cycles of the cell (Formation Cycles) as a complex product of the anodic electrolyte reduction reactions (Peled, 1979; Xu, 2004; Xu et al., 2009). In addition to the *in situ* formation, an *ex situ* approach (Artificial SEI in some literature) has been practiced to coat the SEI layer on the anode before the cell is fabricated (Joshi et al., 2018; Wu et al., 2015; Xu, 2014) but its long process and higher preparation costs are not in favor of the battery value chain. However, the *in situ* SEI is commercially established, the *ex situ* approach is still in the R&D stage (Nair et al., 2019). *In situ* formation of the SEI layer has been studied and reported in different anode chemistries (Nie et al., 2013a; Shu, 2008), but considering graphite as the most common anodic material used in standard LIBs, this work is devoted to studying the graphite anode.

Progress of the SEI formation irreversibly consumes the solvated lithium ions and the solvent molecules causing into decrement of the initial capacity. Regarding this inevitable and irreversible capacity loss, an appropriate SEI must be mechanically stable and it should have good adhesion to the anodic particles

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(Peled and Menkin, 2017) as otherwise would be detached from the electrode surface leading to the continuation of electrolyte degradation mechanisms and consequently more capacity loss. To suppress further reduction reactions and retain the capacity of the cell, a good SEI must be electrolyte insoluble and also should be able to tolerate volumetric changes of the anode particles during the cycle-life of the battery (expansions and contractions during Li-ion intercalation and deintercalation) (Heiskanen et al., 2019). Stability within a wide temperature range and consistency in the operating potential window of the cell is considered as another essential feature of a proper SEI (Peled and Menkin, 2017). Because the development of a thick SEI film could result in higher resistance against Li-ion transportation, a favorable thickness for the SEI is reported from few Angstroms and would not exceed a few nanometers (Edström et al., 2006; Yoshida et al., 2006). Such a perfect SEI, however, should not be expected in practice as it has been found that although the main part of the SEI layer forms during the first cycles, it continues to grow over repeated charge/discharge cycles (An et al., 2016; Horstmann et al., 2019). However, the SEI film is intended to prevent electrolyte degradative reactions, it should not become a barrier for lithium intercalation/deintercalation as the main electrochemical charge transfer process. Therefore, high Li-ion permeability is an essential feature of the solid-electrolyte interphase as otherwise would sabotage the capacity and power output of the cell. On the other hand, transfer of electrons should be hampered from the electrode to the electrolyte as it causes self-discharge of the active materials and disrates the performance of the battery; hence, the SEI is needed to be an electron insulator (Heiskanen et al., 2019; Peled and Menkin, 2017).

To generate the SEI layer inside the cell while it cycles, electrolyte additives have been applied. The basic LIB electrolytes are composed of the lithium salt and solvent(s) as the Li-ion source and the ion carrier, respectively. Studies have shown that carbonate solvents like ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) which are used as common solvents in LIBs (Xu, 2014), are not thermodynamically stable in a LIB cell (Gauthier et al., 2015), and could result in an unstable SEI. The addition of a reduction-type additive as the SEI-forming agent to the electrolyte which reacts prior to the other components has been followed as an efficient method to form an interphase with deliberate features on the anode. In this review paper, we have tried to depict a clear picture from the graphite SEI based on the reported formation/evolution mechanisms in literature. We have then categorized the affecting parameters on the SEI composition. As the next step, we have figured the most common techniques which were applied to study and assess the efficiency and features of the graphite-electrolyte interface and considering the utilization of carbonates as the standard electrolyte in LIB (Heiskanen et al., 2019), we have been focused on the performance of this type of electrolyte on the SEI formation process. Sensing the necessity of a fundamental essay in literature to illustrate the role of the reduction-type additives, we have reviewed the efficiency of the reduction-type SEI-forming compounds in carbonate electrolytes where we have tried to elucidate and compare the effects of their molecular structure on SEI generation considering the most recent advancements. Given the fact that the SEI features affect the battery performance from different aspects including cell capacity, power output, cycle life, and even safety, this review has also targeted to assess and compare the impact of SEI forming agents on cell performance, so further than a classified probing of the subject for those who are particularly focused on the SEI layer, researchers working on the other scopes of LIB technology can realize the contribution of the SEI-improving additives in the big picture.

STRUCTURE AND COMPOSITION

Added to protecting the electrolyte from sustained reduction, the SEI is supposed to prohibit solvent co-intercalation into the graphite and protect the carbonous anode from disintegration where the structure and composition of the SEI is a cornerstone to determine these features (Xu, 2014). Owing to the recent understandings, it is collectively concluded that generation of the graphite SEI by reduction of the carbonate electrolytes within the formation cycles will be followed by further evolutionary phenomena resulting in the development of a multisectional complex as the interfacial layer. The development process of the graphite SEI could be described in two phases: Firstly, Formation as the stage which composes the initial structure of the SEI and secondly, Evolution as a combination of several happenings leading to gradual structural changes in the SEI composition.

Formation

The initial solid-electrolyte interphase gets formed during the charging step of the early cycles through various mechanisms. Figure 1 depicts an outline of the SEI formation versus lithium intercalation as the main anodic processes. As the preliminary SEI forms, it hinders transportation of solvent molecules and

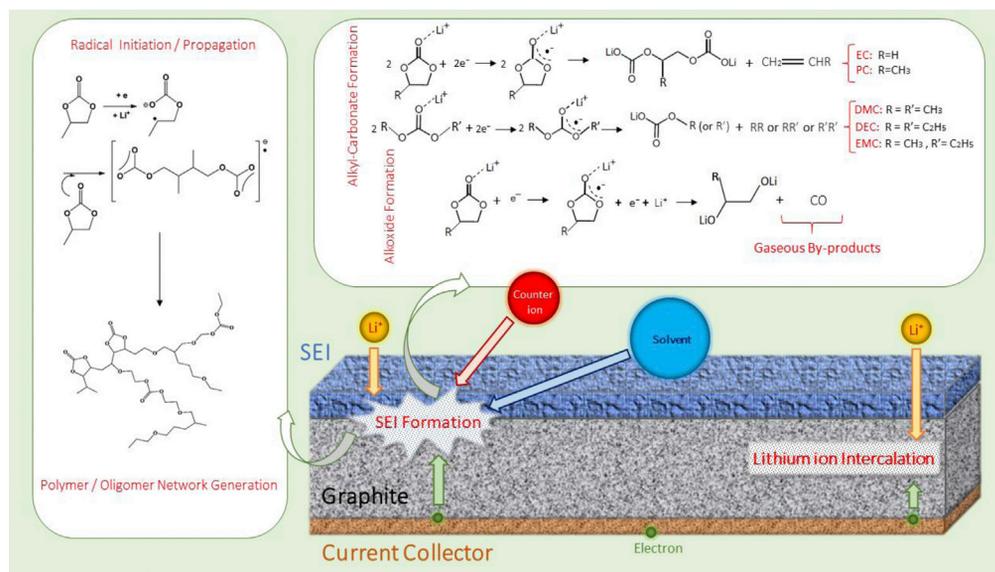


Figure 1. SEI formation process at the graphite anode in carbonate electrolyte vs lithium intercalation

lithium salt counter ions, and therefore after the formation of early SEI, the continuation of its growth is expected to occur at the interface between the SEI and the electrolyte.

The well-known single-electron reduction of carbonates which proceeds through the nucleophilic interactions between generated radical anions formed by electron addition to the carbonate molecules assisted by the vicinity of lithium ions to their carbonyl group would generate lithium salts of semi-carbonates or alkyl carbonates. Ethylene and propylene are reported as the gaseous side-produced alkenes in the reduction of cyclic carbonates attributed to the decomposition of EC and PC, respectively. Alkanes on the other hand will be the reduction side-products of linear carbonates through the same mechanism (Dedryvère et al., 2005, 2006; Marom et al., 2010; Nie et al., 2013b; Tsubouchi et al., 2012; Xu et al., 2006a; Zhuang et al., 2006). Added to the well-accepted single-electron reduction of carbonates, a two-electron pathway is suggested which explains the process considering the carbonate molecule going through two consecutive one-electron electronation steps with a radical intermediate. The products of this mechanism are also reported as alkyl carbonates and gaseous by-products (Collins et al., 2015).

Reduction products of salt anions are typically inorganic species like LiF, LiCl, and Li₂O which precipitate on the electrode surface (Peled and Menkin, 2017). Alongside the lithium semi-carbonates, LiF is repeatedly reported as an SEI component in electrolytes containing LiPF₆ as the lithium salt. Investigating the SEI formation in a simple two-component electrolyte of LiP₆/EC, lithium ethylene dicarbonate (LEDC), LiF, and ethylene are reported as the main components of the initial SEI layer. The dominance of EC reduction products has been reported repeatedly in graphite SEI showing the priority of EC to take part in SEI formation mechanisms among different carbonates (Nie et al., 2013b; Xu et al., 2007; Zhuang et al., 2005a). Comparing the SEI formation mechanisms in an electrolyte containing linear alkyl carbonates, it was concluded that the initial SEI in an EC-containing electrolyte will remain majorly consisted of LEDC and LiF as the contribution of the linear alkyl carbonates are lower than the EC (Liu et al., 2019; Nie et al., 2013b; Strehle et al., 2017; Zhuang et al., 2005a). Detecting the dominance of ring-opening reactions and the absence of cyclic radicals, some studies have reported the formation of carbonate radical anion as a determinant step within the SEI formation mechanisms (Shkrob et al., 2013) which is in agreement with the gaseous side-products explained by the single electron reduction mechanism of the carbonate molecules. To simplify the system and understand the SEI formation process in a clearer way, researchers have synthesized lithium naphthalene as a representative material for lithiated graphite which reacts with the electrolyte components within a single electron process. Having imitated the SEI formation reactions with different molecules, they finally concluded that, however, various products could be observed by reaction of different electrolyte components, the main SEI constructors will remain as LiF and LEDC (Nie et al., 2013b; Parimalam and Lucht, 2018).

In addition to the lithium alkyl carbonates, oxalates and succinates are reported as SEI species in EC/PC and EC/DMC electrolytes where the appearance of these carboxylates has been attributed to different reduction pathways due to the necessity of a radical recombination process following the generation of acyl radicals in the formation of new carbon-carbon bonds (Augustsson et al., 2004; Zhao et al., 2006; Zhuang et al., 2006). Also, tracking the SEI content by ^{13}C NMR has revealed that, however, the carbonyl group of the solvent molecules is expected to stay intact during the SEI formation, following some transformative mechanisms could lead to saturation into ether bonds causing the appearance of new SEI components such as acetals and ortho-esters (Leifer et al., 2011).

However, generation of CO_2 has been detected during the SEI formation with a low abundance (Mantia and Nova, 2008), some research groups have reported CO instead of CO_2 as a gaseous by-product (Kong et al., 2005; Mogi et al., 2003; Onuki et al., 2008; Xiao et al., 2009) where the low amount of CO_2 is interpreted as it probably appears in form of an intermediate. Lithium carbonate (Li_2CO_3) is also reported as an SEI component. Considering the semi-carbonates as the main product of electrolyte reduction, generation of Li_2CO_3 within the formation phase has been attributed to inefficient moisture elimination during cell fabrication explained through the reaction of Li_2O with CO_2 (Bryngelsson et al., 2007; Edström et al., 2006; Harilal et al., 2009).

In addition to the organic and inorganic salts, polymeric and oligomeric side-products are reported in SEI composition (Ota et al., 2004; Shu, 2008; Tsubouchi et al., 2012; Xiao et al., 2009). Long-chain structures with mass to charge ratios of 1500–3000 are reported from EC/DMC and PC electrolytes, respectively (Tavassol et al., 2012, 2013). It is suggested by some literature that in comparison with the short-chained semi-carbonates the polymeric species bring a better protecting function to the SEI and also, it is the presence of densely branched polymers containing carbonate/ethylene oxide units that give an electrolyte nature to the interface assisting the lithium ions to pass through the layer (Shkrob et al., 2013). In terms of stability though, it has been argued that polymeric components and semi-carbonates are partially soluble in an electrolyte where the inorganic species show more stability versus dissolution (Peled and Menkin, 2017).

Evolution

The initial SEI evolves and changes gradually as the cell cycles especially under accelerated aging conditions (Herstedt et al., 2004; Vetter et al., 2005). This evolution originates from the instability of the initially formed interphase leading to phenomena like SEI dissolution or mechanical breakdown, and consequently, the local formation of new decomposition products or structural changes occurred by the progress of further electrochemical mechanisms. Figure 2 simplifies the gradual changes which occur to the SEI layer as the graphite anode cycles.

Studies on SEI evolution have suggested changes within the interphase in long-term cycling, toward a more inorganic content (Louli et al., 2019; Nanda et al., 2019). Some proposed models explain the SEI evolution proceeding with the formation of interphase which consists of multiple layers, with a mostly inorganic section containing lithium salts such as Li_2O , LiF, and Li_2CO_3 close to the electrode and a more organic part composed from semi-carbonates and polymeric structures close to the electrolyte (Edström et al., 2006; Lu et al., 2014; Takenaka et al., 2014; Verma et al., 2010). Comparing the features of these two fractions, studies have shown that the organic outer layer is less conductive than the inorganic inner section (Lu et al., 2014). During the SEI evolution process, the less stable organic part would gradually transform into a more stable inorganic content. To understand the content of these two fractions, the reaction mechanisms of the lithium alkyl carbonates as an organic unit and Li_2CO_3 as an inorganic unit are investigated in presence of moisture, LiPF_6 , and at elevated temperature. It has been observed that the decomposition reactions of lithium alkyl carbonates would form Li_2CO_3 or LiF and decomposition of Li_2CO_3 would lead to the formation of LiF. This confirms the possibility of the gradual transformation of the organic content of the SEI into the inorganic units. Raising the ratio of the electrolyte to the electrode material increases the effective concentration of impurities causing a more rapid decomposition of the initial SEI (Heiskanen et al., 2019).

Some of the radicals produced in the initial stages of SEI formation can get adsorbed on the anode surface and some might remain in the liquid phase, and once some of the SEI blocks begin to nucleate on the anode, these reactive radicals can transfer charge to their surrounding components. Radical propagation

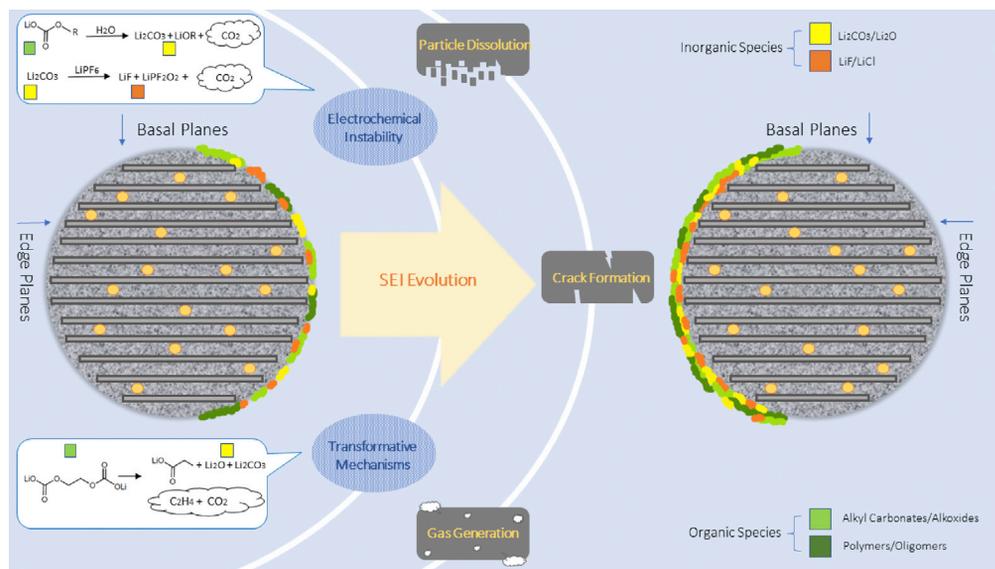


Figure 2. Evolution of the SEI layer and the affecting phenomena

The SEI structure experiences gradual changes as the cell cycles. The evolution of the interphase is influenced by the electrochemical instability of the SEI components and the consequent proceeding of transformative mechanisms. These conversions assisted by physical defects of the electrode particles, namely particle dissolution, crack formation, and gas generation lead to transformation within the SEI composition. Further progress of this process elevates the inorganic content of the interphase and eventually results in a two-sectional SEI with a mostly inorganic part close to the anode and a mostly organic part close to the electrolyte. Given the higher activity of the graphite edge planes, such conversions are more probable at these sections compared to the basal planes.

would proceed especially through the organic layers, and once the radical reaches a molecule and reacts with it, new radicals will be generated and this circle can continue (Peled and Menkin, 2017).

Generation of gaseous by-products is detected as a source of capacity fade during the evolution processes (Ma et al., 2018). Because a part of the decomposition products is gasses and soluble species, the number of insoluble SEI products can decrease gradually under aging conditions (Campion et al., 2005; Kim et al., 2017; Sloop et al., 2003; R. Wang et al., 2017). Added to the anodic side, crossover reactions happening on the cathodic side can generate some products like CO₂ which can diffuse inside the anode layers that on one hand may destabilize the SEI and on the other hand could get reduced into Li₂CO₃ at the anode resulting in interphase which contains more lithium carbonate as the SEI evolves (D. J. Xiong et al., 2016). Studies have shown that the aging of the graphite anode would facilitate the formation of Li₂CO₃ (Zhao et al., 2006).

The mechanical breakdown can be the result of the local dissolution of the soluble products or could happen by stresses in the SEI due to uneven recess of the carbonous structure. In the case of fast-forming cracks, the electrolyte flows into the crack and the fresh anode surface exposed to the electrolyte, immediately reacts with it to form a new thin protective film that slows further local reactions. In the case of slow-forming cracks though, the SEI becomes thinner and electrons pass through the thin region and reduce the electrolyte further (Peled and Menkin, 2017). To compare the stability of SEI-composing lithium salts in the electrolyte, it has been reported that salts with a larger size are more soluble in carbonate solvents in comparison with smaller ones (Tasaki and Harris, 2010).

The initial SEI mainly contains LEDC and LiF but the instability of LEDC can cause further decomposition and changes in the SEI content some of which are soluble in the electrolyte or gasses. The remaining insoluble SEI close to the electrode side which majorly contains inorganic species like LiF, Li₂CO₃, and Li₂O gradually becomes less dense and more porous. If the more porous layer passes the electrolyte to the surface of the graphite, it would result in the progress of further reduction mechanisms and the generation of additional LEDC and LiF. The new electrolyte decomposition processes result in the formation of the second, more organic section of the SEI. Repetition of these stages thickens the SEI with an overall increase in the content of insoluble inorganic components (Heiskanen et al., 2019).

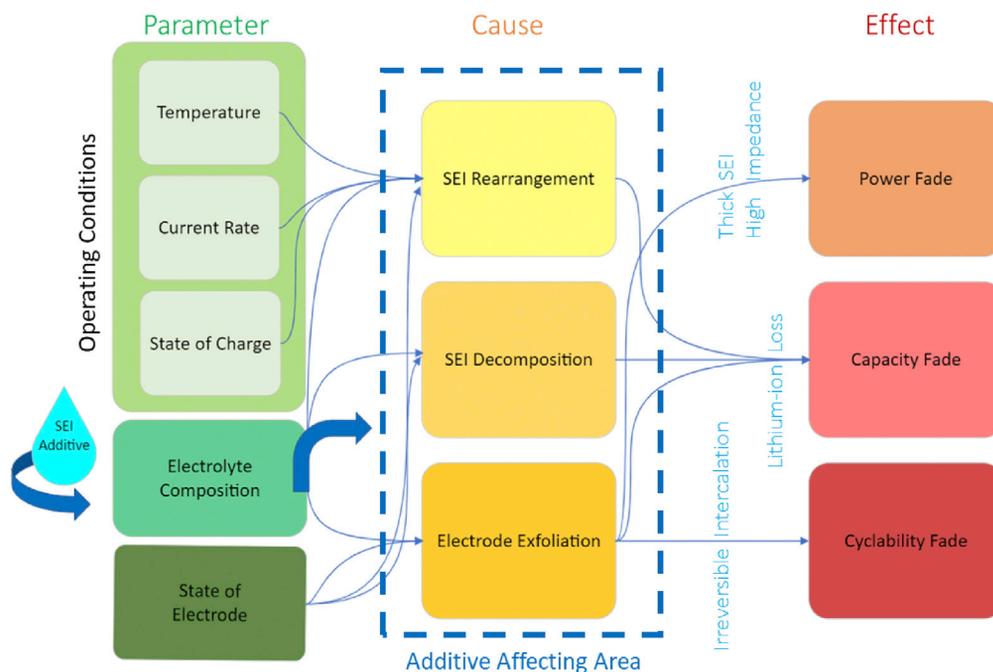


Figure 3. The SEI-affecting parameters and their consequences on battery performance
Introducing the SEI-improving additives could suppress the causes of battery performance fade.

Affecting parameters

In addition to the priority of electrochemical pathways and stability of reduction products, the SEI formation/evolution process on graphite anodes could be affected by several other factors such as operating conditions, state of the electrode, and composition of the electrolyte. Figure 3 briefly categorizes the SEI-affecting parameters and classifies the consequently affected properties in the LIB cell.

Operating condition

Major operational parameters affecting SEI properties could be counted as the applied current rate, the current density at the electrode, SOC (state of charge), and operating temperature (Verma et al., 2010; Vetter et al., 2005; Xiong et al., 2020). Cycling the cell with high current rates would accelerate SEI growth and cause significant capacity loss (Ning et al., 2003). Therefore, low current rates are applied for the initial formation cycles during the preparation step of LIBs. Increasing the electrode current density can lower the irreversible capacity loss during SEI formation (Peled and Menkin, 2017). Cycling the cell at high temperature causes a severe increase in the thickness of the SEI (Waldmann et al., 2014), and also it can lead to the dissolution of thermally unstable SEI components (Peled and Menkin, 2017) which reduces the battery power and capacity. High SOC values and overcharging the cell will also cause structural changes in the SEI layer resulting in power and capacity fade (Vetter et al., 2005).

State of the electrode

Characteristics of the graphite electrode are an important factor to determine SEI properties. Both the natural and the highly oriented pyrolytic (HOP) graphite are structured from two characteristic surfaces referred to as basal planes (parallel to the graphene layers) and cross-sectional edge planes (intersecting the graphene layers). The presence of oxygen-containing groups on graphite surfaces increases the reduction potential and can assist SEI formation before lithium intercalation (An et al., 2016; Peled and Menkin, 2017; Verma et al., 2010). Lack of these SEI nucleation sites would hinder electrolyte decomposition during interphase formation and may lead to electrode exfoliation (Yan et al., 2008). From one side, the abundance of these groups is more on edge sites and from the other side, lithium intercalation into the graphene layers mainly proceeds through edge planes. Therefore, the ratio of the edge planes to the basal planes determines the electrochemical performance of graphite in SEI formation. Because this ratio differs in different forms of graphite, the formation process, chemical composition, and physical properties of the SEI layer

will be different (An et al., 2016; Peled and Menkin, 2017; Verma et al., 2010). It is reported that the SEI on the cross section of the graphite contains more inorganic components like LiF whereas the SEI on the basal planes mostly consists of organic compounds (Gauthier et al., 2015; Verma et al., 2010). Added to the ratio of the edge-to-basal plane, particle size, pore size, degree of crystallinity, and surface chemical composition are key factors in SEI formation (Joho et al., 2001; Winter et al., 1998; Zheng et al., 1999). Smaller particles provide more edge sites, as well as a more active surface for SEI formation. Thus, decreasing the surface area and increasing the particle size would raise the chance of exfoliating in graphite layers. According to the higher rate of reduction at the edge planes, SEI thickness was found to be greater in cross-sectional planes than that of the basal planes (An et al., 2016). The surface chemical composition of the carbonous anode affects the chemical adhesion of graphite to the SEI after decomposition as well as its interactions with the electrolyte before decomposition (Naoui et al., 2005; Peled et al., 1996).

Electrolyte composition

Being involved in both formation and evolution processes, the solvent is an affecting element to determine SEI features. Application of solvents with a lower lithium-binding energy or in other words weakening the interactions between the solvent molecules and Li^+ ion could prevent graphite exfoliation as the cell gets charged. As a comparison, EC which has been an essential (co)solvent in almost any LIB electrolyte, has a lower interaction with lithium ions and therefore instead of severe co-intercalating into the graphite it can participate in SEI formation at the interface. PC on the other hand tends to sustain the co-intercalation process into graphite layers and gradually exfoliates the anode without further lithium intercalation (Peled and Menkin, 2017; Xu, 2014). Studies have shown that increasing the ratio of DMC in a PC/DMC electrolyte would suppress electrode fracture by modifying the solvation number of PC molecules per Li^+ ions (Yamada et al., 2009). The type of solvent can affect the SEI content as well. Li_2CO_3 is reported as the main interfacial species in PC-based electrolytes, while a mixture of the previously mentioned organic and inorganic reduction products including semi-carbonates, oxalates, and oligoethers was observed in the case of EC-based electrolytes (Zhuang et al., 2005b). From another aspect, solvent properties could impact the stability of SEI components. Higher solubility of SEI-composing lithium salts in EC in comparison with DMC is an example of this complication which originates from differences in polarity, size, and shape of the solvent molecules (Tasaki and Harris, 2010).

As the other electrolyte component, different types of lithium salt can bring different features to the SEI composition. For instance, Li_2CO_3 was detected as the main SEI component in LiTFSI-based electrolytes, while a mixture of Li_2CO_3 and semi-carbonates was reported with LiBETI as the lithium salt (Dedryvère et al., 2006). As another example, it is reported that semi-carbonates as SEI components are more sensitive in presence of acidic by-products of LiPF_6 salt which could result in further decomposition mechanisms and change the composition of the interphase layer (Marom et al., 2010). Given the anions' structural differences among lithium salts, these compositional variations could be attributed to the decomposition chemistry of counter ions (Wu et al., 2021a, 2021b). For example, added to Li_2O , Li_2CO_3 , and LiF which is a common reduction product of the fluorine-containing salts, LiPF_6 (lithium hexafluorophosphate) leads to the formation of Li_xPF_y and $\text{Li}_x\text{PF}_y\text{O}_z$ compounds whereas LiBF_4 (lithium tetrafluoroborate) generates Li_xBF_y species, LiDFOB (lithium difluoro(oxalato)borate) forms lithium oxalates, and LiFSI (lithium bis(fluorosulfonyl) imide) causes the appearance of $\text{Li}_3\text{N}(\text{SO}_2)_2$ in the SEI. Shifting to LiTFSI as another fluorine-containing salt (lithium bis(trifluoromethane) sulfonimide), a wider range of decomposition products will appear along with LiF, Li_2O , and Li_2CO_3 including Li_2S , Li_3N , $\text{Li}_2\text{NSO}_2\text{CF}_3$, and LiSO_2CF_3 as well as the Li_xCF_y and Li_xSO_y compounds (Eshetu et al., 2016; Parimalam and Lucht, 2018). Comparing particularly TFSI⁻ with FSI⁻ where the two fluorine atoms are replaced with $-\text{CF}_3$ groups, it is evident how the anion's structure could influence the SEI content.

As another finding, it is reported that increasing the lithium salt concentration in the electrolyte could lead to a weaker Li^+ ion solvation sheath and consequently protect graphite against exfoliation and facilitate lithium intercalation (Jeong et al., 2008). Type of the lithium salt can affect the conductivity of SEI as well. As a comparison, LiClO_4 is reported to form less resistive interphase layers than LiPF_6 or LiBF_4 due to no LiF decomposition (An et al., 2016).

The exploitation of SEI formation additives inside the electrolyte is another factor that can affect the interphase composition. The effectiveness of these species is reviewed in the last section.

PROTECTION AND RETAINMENT

As mentioned before, several phenomena could destabilize the formed SEI. To address some of these processes and prevent them from happening, a number of approaches have been introduced to retain the functionality of the interphase and protect it in long-term cycling. These techniques are based on electrode surface modification, application of self-healable material, and electrolyte engineering to compensate for the gradual deterioration and sustain the cell performance. Crack formation and weak adhesion in electrode particles are understood as interphase-destabilizing phenomena that interfere in the SEI development process and lead to changes in its characteristics and structure. Introduction of self-healing binders to the electrode composition has been attempted to diminish this problem (Gendensuren and Oh, 2018). Considering the severe cracking issues in silicon-containing anodes, the application of this method could significantly improve the electrode stability in that chemistry (Chen et al., 2021; Rajeev et al., 2021; Wang et al., 2021). Despite its benefit, however, the requirement of high binder content and consequently low loading of active material has limited the practicality of this technique especially in commercial cells (Narayan et al., 2021).

Lithium dendrite growth is another issue threatening the performance and safety of LIBs. Considering the correlation between lithium plating and the intercalation process, the formation of inefficient SEI assists the lithium deposition reaction (Beheshti et al., 2021). Surface coating and application of artificial SEI are followed as an approach to inhibit lithium plating. For instance, it is shown that coating of high-polarity β -phase polyvinylidene difluoride (PVDF) on graphite particles would decrease lithium dendrite formation at the anode and significantly improve its cyclability (Luo et al., 2018). Because lithium metal is a promising anode for the next-generation high-energy-density batteries, SEI film coating has been a point of interest in this chemistry as well to achieve a non-dendrite anode and reduce the dead lithium (Wang et al., 2020a). Besides the positive achievements of the surface modification techniques, it should be mentioned that rare reports have tested the protective strategies to the level of practical standards, and sustainability of protective coatings are not always verified under high current or high-capacity conditions (Narayan et al., 2021) and therefore the method requires further improvements.

Electrolyte degradation is a parameter that could affect the SEI features. As mentioned before, introducing SEI-forming agents has been followed as a feasible and practical approach to develop efficient interphase and protect the electrolyte components from continuous decomposition. Given the liquid nature of the common LIB electrolytes, it is difficult to address their issues via other self-healing approaches because these mechanisms are mostly developed for solid materials, and at present, no significant studies have been reported in the literature in the liquid phase (Mezzomo et al., 2020). However, given the new emerging types of electrolytes like solid polymer systems, self-healing approaches are applied to prevent electrolyte disintegration in such cells (Jo et al., 2020; Whiteley et al., 2015). Nevertheless, there are many challenges to overcome for globalizing these new electrolytes and that could be the reason why the LIB market currently relies on conventional solvent-containing LIBs. Achieving desirable room temperature ionic conductivity values ($>10^{-3} \text{ S cm}^{-1}$), proper interfacial contact with low resistance, high Li-ion transference number, and more feasible yet less complex preparation methods could be counted as the main difficulties to develop this new class of electrolytes (Narayan et al., 2021).

ASSESSMENT AND ANALYSIS

To monitor SEI evolution and investigate the functionality of an additive in the development process of the interfacial layer and also to evaluate the performance and characteristics of the generated SEI, a various number of techniques have been applied during the past five decades. Hence, development of these methods had become an undetachable chapter of the SEI studies.

Primary understandings about the anode-electrolyte interphase were achieved by performing microscopic observations on the surface of the lithium electrode (Dey, 1977) which eventually led to introducing the concept of SEI by the late 70s (Peled, 1979). Coupling the initial comprehensions with the obtained results from the electrochemical analysis, especially impedance spectroscopy, the interphase was described as a multilayer structure with thin compact interphase close to the lithium electrode and a thicker porous layer near the electrolyte (Peled, 1983). Implementation of characterization techniques including IR, XPS, and XRD by the middle 80s shaped the early pictures from the SEI composition by reporting lithium carbonate, lithium alkyl carbonates, and polymeric compounds among the decomposition products (Aurbach et al., 1987; Nazri and Muller, 1985). These new grasps from one side and the introduction of the intercalation

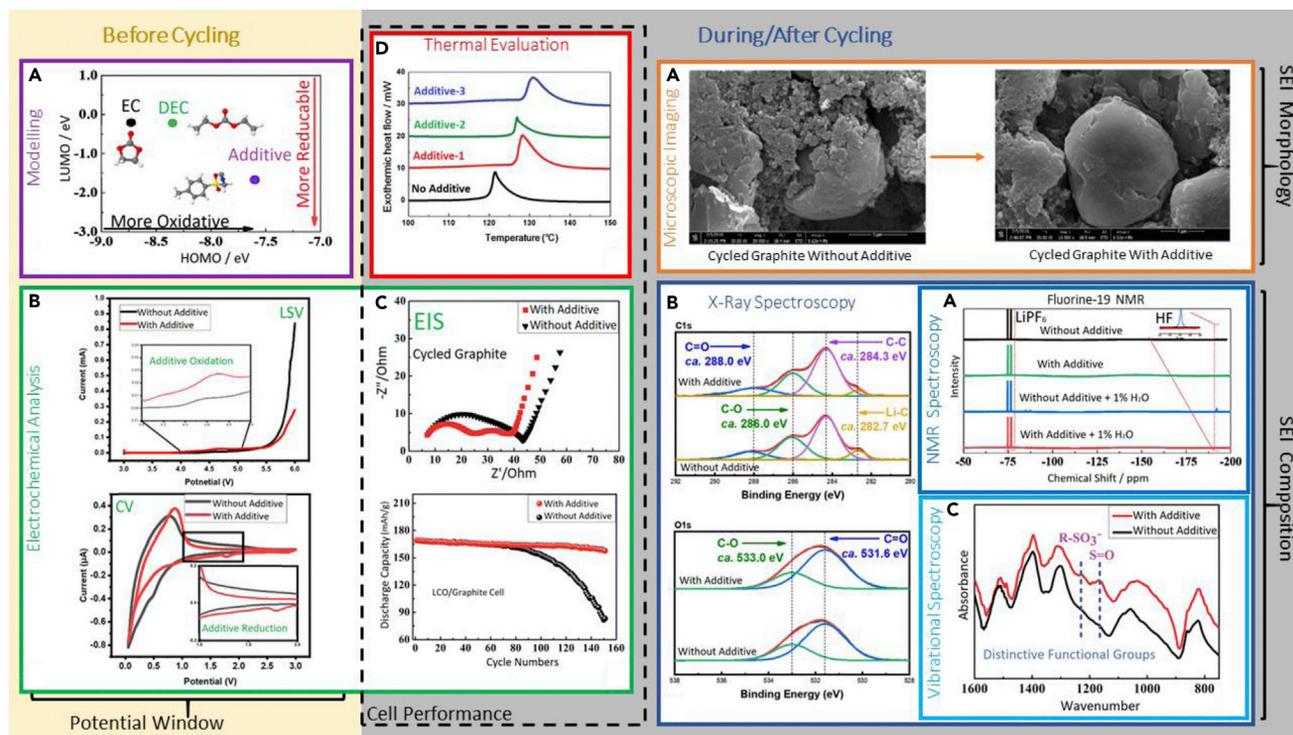


Figure 4. Application of different analytical techniques to evaluate the generated SEI on the graphite anode

The shown data are borrowed from A (Li et al., 2020), B (Park et al., 2020), C (Zuo et al., 2018), and D (Jung et al., 2013) where the studies have investigated the functionality of SEI-improving additives to ameliorate the performance of carbonate electrolyte in SEI formation.

chemistry from the other side led to suggesting a three-dimensional formation model for the SEI, based on co-intercalation/decomposition of the solvent molecules inside the graphite electrode (Besenhard et al., 1995). Later advancements in characterization techniques detected other remarkable species such as lithium fluoride inside the interphase and refined the SEI's portrait further (Kanamura et al., 1995). Accordingly, the presence of different organic and inorganic compounds within the SEI structure was analogized to a mosaic array proposing a new concept by the late 90s (Peled et al., 1997). Application of the *in situ/operando* methods has been the next step to authenticate the adopted interphase model resulting in our current idea from the SEI structure (Gauthier et al., 2015; Wu et al., 2021b). In parallel with various types of experimental assessment, development of computational techniques has featured an important contribution on understanding the SEI generation process.

Given the evident footprints of these evaluation methods in SEI history, in this section, the most common approaches to assess the interphase layer are categorized into the modeling and the experimental aspects. Some of these studies could be performed before cycling the electrolyte whereas the others should be followed in a lithium-ion cell configuration. The overall classification of these methods is demonstrated by Figure 4 where the examples of different approaches are brought together in one frame. As is categorized by the figure, some studies could be performed to assess the potential window of the electrolyte, some others analyze the SEI composition/morphology, and some techniques are implemented to evaluate the cell performance after the SEI is formed. Therefore, to clarify the features of the SEI or functionality of the correlating additive, a combination of these analytical approaches is required.

Computational modeling

The computational simulation could be performed as an early-stage study to investigate the formation process of the SEI layer. From one side, this method has been used to predict the most probable formation mechanisms aiming to clarify the composition of the SEI (Vollmer et al., 2004), and from the other side, it has been used as a determinative sieve to assess the applicability of additives prior to the experimental studies. Density-functional theory (DFT) (Li et al., 2020) and molecular dynamics (MD) (Wang et al., 2020b) are common computer simulation

methods for this purpose (Wang et al., 2018a). However, the exact electrochemical behavior of an additive might vary from what was calculated by means of simulation; modeling can help to scratch out the molecules with characteristics far away from requirements and thus can save time and expenses. Determinant features of a reduction-type additive to be studied by simulation techniques could be counted as the reduction/oxidation potential acquirable by the energy level of the lowest unoccupied and highest occupied molecular orbital (LUMO and HOMO, respectively), the lithium-ion binding energy, and the polarity of the molecule. The energy difference between the Fermi level of the electrode and the LUMO/HOMO energy levels of the electrolyte determines the thermodynamic stability of the electrolyte components (Goodenough and Kim, 2010). Additives with a LUMO energy level lower than the solvent tend to obtain electrons prior to the solvent and reduce before the solvent molecules are decomposed. The lower energy level of HOMO, on the other hand, shows a lower tendency in electron donation meaning more stability against oxidation at the cathodic side (Yoon et al., 2013; Zhang et al., 2013). The value of Li^+ ion binding energy elucidates the stability of the solvation sheath where lower values mean easier Li^+ ion de-solvation (Park et al., 2011; Wang et al., 2018a). As explained previously, the strength of the solvation sheath could lead to co-intercalation of the molecule, severe decomposition, and excessive gas generation causing SEI instability (Xu, 2014). Large values of dipole moment showing higher polarity could cause stronger non-bonded interactions with Li^+ ion resulting in more lithium salts in SEI composition (Halls and Tasaki, 2010) and therefore modeling has been implemented to obtain this parameter for SEI-forming additives (Park et al., 2011).

Electrochemical analysis

The actual efficiency of an electrolyte additive in an LIB cell requires to be validated by experiment through electrochemical evaluation techniques. Interpretation of responses collected from the electrochemical system through different modes of scanning portraits the SEI development process and could be used as a comparative tool to evaluate the efficiency of the applied additives.

Galvanostatic charge-discharge of the cell, based on measuring the potential in a cell polarized with a constant current, reveals the irreversible capacity loss during SEI formation and illustrates the stability of the evolved interphase by tracking the capacity retention as the cell cycles. The initial SEI formation occurring through the first intercalation process could be recognized with the appearance of a voltage plateau during the first charge step in full-cell measurements but proceeds in the first discharge step in the case of half-cell studies. The detectable difference in capacity compared to the deintercalation step displays the charge which was consumed in SEI formation.

Voltammetric techniques provide essential information about the decomposition potential of the electrolyte. Performing the cyclic voltammetry (CV), the potential in which the solvent/additive reduces to the decomposition products will be obtained versus Li/Li^+ reference. Reversibility of the Li^+ ion intercalation is another matter which could be verified with a reversible CV. Linear sweep voltammetry (LSV), on the other side, could be used to assess the stability of the solvent/additive in oxidation mechanisms which might proceed at the cathodic side (Beheshti et al., 2021).

The acquired data from the electrochemical impedance spectroscopy (EIS) would draw an equivalent circuit for the cell in which the resistive/capacitive behavior of the SEI element could be interpreted to the characteristics of the formed interphase such as resistance, thickness, and morphology of the layer. The evolution mechanism of the SEI layer could also be studied by comparing the EIS results at different potential/cycles (Habte and Jiang, 2018; Lu et al., 2014). Temperature-dependant characteristics of the interphase could be monitored via EIS analysis as well by measuring the impedance at different temperatures (Huang et al., 2018; Steinhauer et al., 2017).

Structural characterization

Application of different characterization methods has been followed as an approach to obtain reliable information about the complex content of the SEI layer. Synthesis of pure carbonate reduction products pursued by characterization (Dedryvère et al., 2005; Xu et al., 2006a) has provided researchers a valuable database to recognize the composing units of the interphase.

Spectroscopic analysis

Given the various measuring possibilities in different ranges of frequency, the structure and composition of SEI have been studied by radiofrequency spectroscopy, IR spectroscopy, and X-ray spectroscopic

methods. Nuclear magnetic resonance (NMR) spectroscopy could be used to obtain bulk information about the SEI composition. Distinctive signatures, such as chemical shift differences between the dilute and the concentrated stages of graphite lithiation in ^7Li NMR spectra, detect phase changes used for a detailed study of the lithiation process during SEI formation (Krachkovskiy et al., 2018; Lorie Lopez et al., 2017). Targeting particular elements, NMR spectroscopy could be implemented to characterize the formed SEI on graphite anode; however, a low signal-to-noise ratio of measurement may cause some limitations (Hall et al., 2017; Wang et al., 2019). Vibrating spectroscopy including Fourier transform infrared spectroscopy (FT-IR) and Raman analysis could provide valuable surface information in order to investigate SEI composition (Li et al., 2021; Nanda et al., 2019) but several shortcomings such as weak vibration signals in thin films, hard peak detection due to the inhomogeneous nature of the SEI, and appearance of similar functional groups from different components may limit the precision of measurement (Verma et al., 2010). Tracking changes among absorption bands in different operating conditions such as temperature (Saqib et al., 2018) and voltage (Rikka et al., 2018) is an approach to study affecting parameters on SEI composition. The structural changes of the electrode could be followed with another approach by interpretation of the appeared shifts in the wavelength during the Raman measurement.

X-ray photoelectron spectroscopy (XPS) as a non-destructive and surface-sensitive method of analysis has been used to investigate SEI composition and its contribution to Li^+ ion intercalation (Nakatani et al., 2018). XPS could detect which elements are present on the surface and reveal the nature of chemical bonds between them; thus, it has been widely used to diagnose the decomposition products of the carbonate electrolytes, especially with differentiating C-C, C-O, and C=O bonds by C 1s/O 1s spectra (Malmgren et al., 2013; Zhao et al., 2020a). Depending on the constructing atoms present in the structure of the additive/salt, XPS analysis of F 1s, B 1s, P 2p, S 2p, and N 1s could become a tool to clarify the SEI content (Andersson et al., 2003; Cao et al., 2013; Chalasani et al., 2012; Li et al., 2013a; Wang et al., 2009; Xu et al., 2010; Zhang et al., 2015; Zhao et al., 2020a). Considering the information it provides about the content of the interfacial layer, XPS spectroscopy enables researchers to analyze the structure of the generated SEI after additive reduction by attributing the tracked elements and bonds to the decomposition products of the applied additive. The size of chemical shifts that occurred within the measurement depends on the conductivity and the microstructure of the component, and therefore in the inhomogeneous and complex SEI, rectifying the results will be difficult. From the other side, investigating such an inhomogeneous film, the etching rate during a destructive depth analysis requires to be different for hard/inorganic particles and soft/organic ones because the hard species need longer sputtering time to etch a particular depth as compared to the soft material (Verma et al., 2010).

X-ray diffraction technique (XRD) has been the other X-ray analysis applied to study the structure of the SEI layer and track the effect of the electrolyte additives in the formation process (Lee et al., 2004; Li et al., 2013c; Nakatani et al., 2018). Given the fact that electrolyte additives would react at the cathodic side as well, XRD has been exploited to monitor the structural changes of the cathode as an effect of additive application (Li et al., 2013a). Also, the effect of temperature on the structure of the formed SEI could be followed by applying the XRD method (Cho et al., 2010).

Mass spectrometry (MS) has been another characterization tool implemented to study the SEI layer. Following a transition phase that generates ionic particles, quantitative information about the chemical identity of a system could be acquired by tracking the intensity of mass signals versus the mass-to-charge ratio of the separated corresponding ions in the mass spectrum. Considering the mode of analysis, different methods of mass spectrometry, namely thermal gravimetry MS (TGMS) and secondary ion MS (SIMS) have been applied to investigate the SEI chemistry. Because the interphase development proceeds with gas-generating reactions, TGMS has been used to detect the evolved gasses during the SEI formation/decomposition process in order to determine the probable pathways. Implementation of this technique with diversifying the affecting parameters such as temperature, current density, and voltage could reveal their role on SEI decomposition (Watanabe and Yamaki, 2006; Zhao et al., 2006). Such approaches could be used also for mechanistic studies. For instance, online electrochemical assessment along with mass spectrometry has been applied to monitor the initiation stage of the interphase formation process (Mozhukhina et al., 2020). SIMS technique is capable to provide in-depth information about the content of solid surfaces and thin films. Therefore, this type of spectrometry can be employed to analyze the SEI composition and the surface structure growth (Wu et al., 2021b). Application of SIMS has also provided distinctive information about the SEI formation mechanism, supporting its two-sectional structure (Zhou et al., 2020).

Considering representation of organic and inorganic compounds with CH_3^+ and Li_2O^+ ions, respectively, SIMS studies had investigated the two sectional structure and shown that polymeric species are mainly generated at higher voltages whereas the inorganic components appear as the voltage decreases, partially through conversion of the organic content (Lu et al., 2014).

Microscopic imaging

Imaging the electrode surface in order to investigate the SEI structure at the particle level and detecting the effect of electrolyte additives has been followed using different techniques such as scanning electron microscopy (SEM) (Bian et al., 2018; Chalasani et al., 2012; Hamidah et al., 2019; H. Park et al., 2020), transmission electron microscopy (TEM) (Li et al., 2020; Mai et al., 2014; Nie et al., 2013b), scanning tunneling microscopy (STM) (Seidl, 2015; Wang et al., 2012), and atomic force microscopy (AFM) (Huang et al., 2018; Luchkin et al., 2020). Changes that occurred to the morphology, particle size, and arrangement of the SEI layer including electrode volume expansion/shrinkage, crack formation, and delamination during battery operation could be tracked by imaging techniques (Harks et al., 2015). Morphological evolution through different voltage steps (Deng et al., 2014; Luchkin et al., 2020) or at different temperatures (Huang et al., 2018) could be detected as well by comparative microscopic imaging investigations.

Thermal evaluation

Differential scanning calorimetry (DSC) has been implemented to evaluate the thermal stability of the SEI layer where the appearance of exothermic peaks at elevated temperatures would show the degradation of the formed interphase and reveal its thermal stability (Forestier et al., 2016; Jung et al., 2013). This method could be executed to assess the efficiency of an electrolyte additive to improve the thermal stability in the resulted SEI (Cao et al., 2013). Thermal gravimetry followed by gas chromatography/mass spectroscopy is reported as an approach to analyze the electrolyte decomposition products and study SEI composition (Zhao, 2005). Temperature programmed desorption coupled with mass spectroscopy has been another reported thermal analysis conducted to study the surface chemistry of the electrode in order to study the SEI layer (Ng et al., 2009).

Sampling and handling

To study the SEI characteristics with the aforementioned methods, the cycled electrode could be either collected with a postmortem treatment and get analyzed by an *ex situ* approach or it could be investigated through an *in situ* procedure where it is kept in its original position inside the cell. In an *ex situ* procedure, first, the cycled electrode will be collected from the disassembled cell inside a glove box filled with an inert gas. As the next step, the sample will be washed with dimethyl carbonate (DMC) and as (vacuum) dried, it will be transferred for characterization in an air-sealed vessel to avoid exposure to the atmosphere (Chalasani et al., 2012; Kubota et al., 2012; Xu et al., 2013). However, *ex situ* measurements are exploited for SEI analysis given the risk of contamination during sample preparation and vulnerability of reduction products against air and moisture, implementation of the analytical techniques with an *in-situ* approach would draw a more reliable picture from the interphase composition. Despite all the advantages, demanding specific cell designs in order to conduct the experiments has hindered the extensive application of *in situ* techniques (Harks et al., 2015). Operando analysis as an advanced *in situ* method has been developed to elucidate the less understood aspects of the SEI formation/evolution process. Monitoring the phenomena as the cell cycles, the operando approach provides a live demonstration from the composition/decomposition process of the SEI under operation where it could be used to determine the SEI composition and the absolute charge consumption during the formation and Li^+ intercalation (Kawaura et al., 2016). Operando analysis could unravel the complex dynamics of Li^+ ion solvation/coordination and electrolyte/impurities side-reactions to show the material origin and even the formation potential of SEI components (Mozhzhukhina et al., 2020).

ADDITIVE FUNCTIONALITY

The addition of SEI forming additives to the electrolyte is an approach to ameliorate the interfacial layer, decrease gas generation, and lower the irreversible capacity loss. In the case of EC-based electrolytes, given their suitable Li^+ -binding energy and its capability to form SEI, the additives are applied as an interphase-improving agent. In PC-based electrolytes though, using additives is necessary as otherwise, co-intercalation of solvent followed by reduction would lead to a crucial graphite exfoliation. SEI forming additives could be divided into different types based on how they contribute to the formation process;

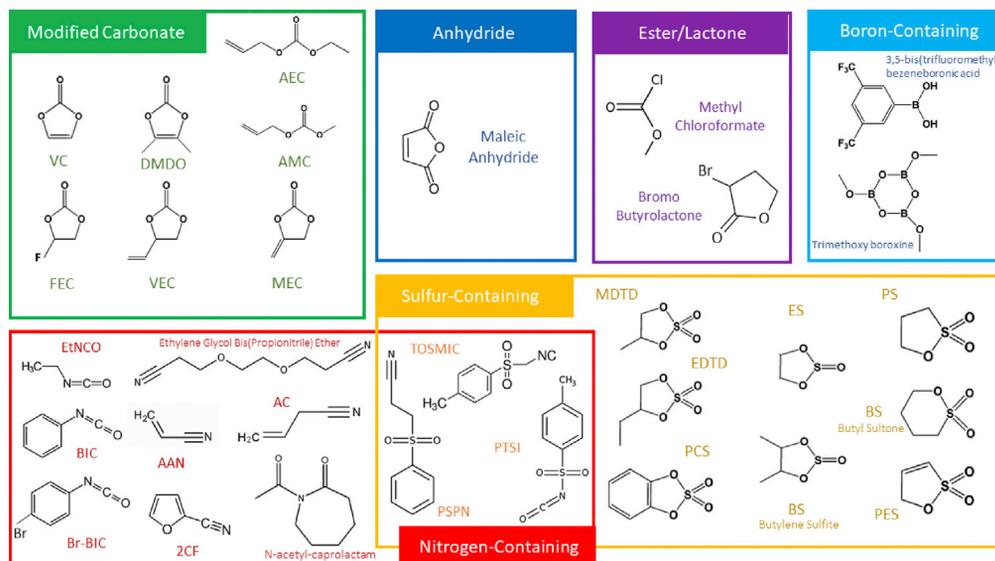


Figure 5. Categorization of the reduction-type additives considering their molecular structure

The first group referred to as reduction-type additives, intervene in the SEI formation process by getting reduced prior to the solvent molecules as they present a higher reduction potential than the other electrolyte components. The early reduction of the additive before lithium intercalation could be observed by the emerging signals in the initial cycles of CV measurement (Figure 4). The reaction-type additives, on the other hand, do not contribute directly to the reduction process within the potential range of Li^+ ion intercalation and their role is either scavenging the radical anions (generated as the intermediates in solvent reduction pathway) or combining with the decomposition products to form a more stable SEI (Zhang, 2006).

The reduction-type additives can affect the SEI formation process through different mechanisms. A group of this type is polymerizable compounds in which presence of unsaturated bonds in their structure can particularly facilitate the polymerization reaction via a nucleophilic addition. Because the polymerization process could progress via both reductive and oxidative pathways, the concentration of such additives should be optimized in order to prevent the irreversibility of the cathode. The performance of these additives will be determined by the characteristics of the formed SEI where a good adhesion to the graphite, insolubility of the structure in the electrolyte, and resistance against further decomposition are required. Reduction-type additives can also contribute to SEI improvement by affecting the activity of the reducible oxygen-containing sites present on the cross section of graphite planes. Sulfur-containing additives are reported as an example of such compounds. A diverse range of the SEI-improving agents is introduced in literature including derivatives of carbonates, anhydrides, esters, and many other organic compounds containing a distinctive functional group based on sulfur, nitrogen, and boron. With a patent landscape on liquid electrolytes of LIBs, carbonate derivatives and sulfur-containing additives could be accounted as common SEI-improving additives (Ershadi et al., 2018). Also, considerable research is reported on additives based on organic derivatives of isocyanates and cyanides. In order to understand the functionality of these compounds, modified carbonates, sulfur-containing, and nitrogen-containing additives are reviewed and compared based on their molecular structure and their performance in the SEI evolution process. Figure 5 provides a brief overview of the molecular structure of these compounds where several examples of each group are presented. Also, considering their reported advantages and drawbacks, Figure 6 provides an overall comparison between the additives given the affecting level which they have on carbonate electrolytes.

VC, FEC, and other modified carbonates

Structural modification of cyclic carbonates has been followed as an approach to introduce SEI-improving additives. Vinylene carbonate (VC) and fluoroethylene carbonate (FEC) which are arguably the most prevalent SEI additives have been developed by pursuing this strategy. Comparing the molecular structure of these two additives with EC could clarify the big impact of the small differences. In the case of VC, the

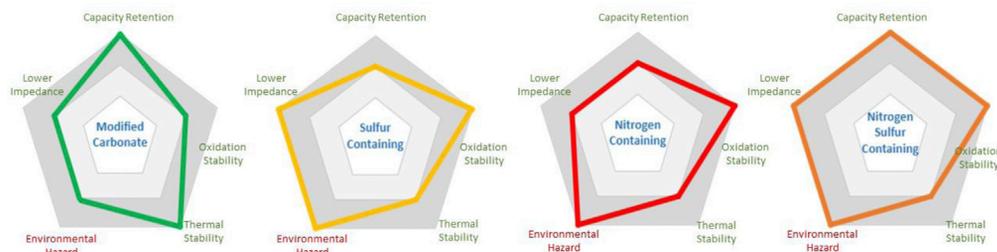


Figure 6. Overall qualitative comparison of the affecting level of different SEI improving additives on LIB characteristics

Considering the irreversible Li-ion intercalation in PC-based electrolytes, the radar charts are comparing the reported performance of additives in EC-based electrolytes

existence of the unsaturated C=C bond turns the molecule into a polymerizable compound during the SEI formation process. The lower level of LUMO which is a desirable factor for a reduction-type additive is also the result of this slight structural change as it helps the molecule to delocalize the excessive charge leading to a more stable radical anion and consequently, an easier reduction pathway. In the case of FEC, the presence of fluorine as an electron-withdrawing group reduces the LUMO energy and facilitates the reduction process at the carbonate ring. It is understood that reduction of FEC proceeds through the formation of VC and HF as intermediates, where VC will get polymerized to form a stable SEI and HF, would lead to the formation of LiF as an inorganic SEI particle (Zhang, 2006).

It is well accepted that using VC and FEC ameliorates the cyclability and capacity retention of a LIB cell through forming a more stable SEI. The composition of the SEI has been studied as a function of VC and FEC additives using a set of coupled analytical techniques including XPS, IR, TEM, and NMR concluding that the addition of these two agents to the electrolyte (LiPF₆ in EC/EMC) would generate a thinner layer containing polymeric decomposition products (referred to as poly(VC) and poly(FEC), respectively) with less amount of unstable alkyl carbonates (Nie et al., 2015). The functionality of VC and FEC could be explained through inhibition of reductive reactions correlated with the carbonate solvent which consequently reduces the number of alkyl carbonates and gaseous by-products during the SEI formation process. It is investigated that reduction of VC would form CO₂ added to the polymeric structures where in the next step CO₂ would be reduced to generate Li₂CO₃ and LiHCO₂ leading to strengthened interphase resulting in a better cyclic performance (Michan et al., 2016; Schwenke et al., 2019). Comparing the SEI formed by the two additives, the concentration of the crosslinked polymeric compounds is reported to be relatively higher in the case of VC (Nie et al., 2015). Also, owing to the differences in reduction mechanisms, the concentration of lithium carbonate is higher in the interphase correlated with VC whereas the inorganic section of the SEI formed by FEC is richer of lithium fluoride (Michan et al., 2016). Over than the better coulombic efficiency (Winkler et al., 2017), optimized addition of VC and FEC reduces the impedance values (Chang et al., 2011; Zhao et al., 2015) which is in agreement with the formation of a thinner SEI layer. Looking at the two additives from another aspect, however, some studies have reported less oxidation stability by introducing VC to the base electrolyte (LiPF₆ in EC/EMC) (Jung et al., 2013); other investigations have shown improved potential stability in an FEC-containing electrolyte (Wang et al., 2018b). Considering the reinforced SEI generated by FEC, it is also reported that application of fluoroethylene carbonate would significantly improve the capacity retention and decreases the impedance value at elevated temperatures (Shin et al., 2015).

Added to VC and FEC, structures such as vinyl ethylene carbonate (VEC) (Xu et al., 2013), Methylene Ethylene Carbonate (MEC) (Chalasanani et al., 2012), Allyl Ethyl Carbonate (AEC) (Lee et al., 2004), Allyl Methyl Carbonate (AMC) (Abe et al., 2004), dimethyl 2-oxo-1,3-dioxolane-4,5-dicarboxylate (ODC) (Khasanov et al., 2015), and 4,5-dimethyl-[1,3]dioxol-2-one (DMDO) (Xu et al., 2010) are examples of modified carbonates reported as SEI-improving additives. In general, having a higher reduction potential than the solvent molecules and a polymerizable C=C bond in the structure enables unsaturated carbonates to reduce prior to the solvent and form a more stable SEI leading to diminution of capacity loss.

Sulfur-containing additives

Considering the molecular structure, the reported sulfur-containing additives could be generally sorted into organic sulfites, sulfates, and sulfonates (Sultones). Reduction of these molecules prior to the solvent through cleavage of the S-O bond at reductive potentials explains their functionality during the SEI

formation process. Added to the saturated sulfur-based additives, polymerizable structures with unsaturated bonds have been the other reported SEI-improving agents. The formation of lithium sulfite (Li_2SO_3) and lithium alkyl sulfonates (ROSO_2Li) has been detected as the emerging SEI components produced by sulfur-containing additives resulting in a compact and stable interphase that resists further decomposition and capacity loss.

Butylene sulfite (BS) (Chen et al., 2007) and ethylene sulfite (ES) (Xing et al., 2011) have been studied as sulfites that can suppress extensive decomposition of solvent in PC-based electrolytes where Li_2SO_3 and ROSO_2Li are reported to be present in SEI composition. Trimethylene sulfite (TMS) has been recently used as an SEI improver in EC-based electrolyte (LiPF_6 in EC/EMC) where it has formed a smooth, uniform, thin SEI film on the surface of the graphite electrode, which enhanced the electrochemical performance of the electrode in terms of impedance, reversible capacity, and cycle stability (Zhao et al., 2020b).

Sulfates have been investigated as the other type of sulfur-containing additives which can form a stable SEI in PC-based electrolytes. Application of 4-methyl-1,3,2-dioxathiolane-2,2-dioxide (MDTD), 4-ethyl-1,3,2-dioxathiolane-2,2-dioxide (EDTD), and phenyl cyclic sulfate (PCS) has prevented PC decomposition and semi-carbonates were replaced with sulfate reduction products in the SEI (Sano and Maruyama, 2009).

Sulfonates have been the other group of sulfur-containing additives reported as SEI improvers where 1,3-propane sultone (PS) (Lee et al., 2007), butyl sultone (BS) (Xu et al., 2006b), methylene methanedisulfonate (MMDS) (Mai et al., 2014), and propargyl methanesulfonate (PMS) (Ciosek Högström et al., 2014) could be counted as some examples. Composition study of the interphase has revealed that the addition of sultones can thicken the protective layer during the initial cycles with a gradual raise of lithium content and formation of a compact SEI in long-term cycling, whereas the layer formed without it is thinner in the early stage but thickens significantly with an excessive raise of lithium content as is cycled further resulting in a less stable interphase (Ciosek Högström et al., 2014). In general, sulfonates have been observed as a group of SEI improvers which ameliorates thermal and oxidation stability of the electrolyte and results in a more stable and less resistive interphase. Modification of the cyclic sulfonates has been studied as an approach to assess the effect of functionalization or structural change on additive performance. Prop-1-ene-1,3-sultone which contains an unsaturated bond different from PS, has resulted in an increased cyclic stability in comparison with PS in PC-based electrolytes (Li et al., 2013b). 2, 3-Epoxypropyl methanesulfonate (OMS) is another sulfonate that has been used recently in EC-based electrolyte (LiPF_6 in EC/EMC) which has developed an SEI layer containing lithium alkyl sulfonates. Upon cycling at elevated temperature, less lithium alkyl-carbonate decomposition has been observed, suggesting that the SEI composition was more stable in presence of OMS (Zhang et al., 2018). Performance of PES has been compared with VC in an EC-based electrolyte where the modified sulfonate has shown better capacity retention in LMO/graphite system especially at high temperature (60 °C) (Li et al., 2013a). Fluoro propane sultone (FPS) is another example that contains fluorine bonded to the PS ring. Studies have shown that in comparison with PS and VC, the addition of FPS has increased thermal and oxidation stability of the electrolyte (LiPF_6 in EC/EMC) and improved the capacity retention of the LCO/graphite cells at both room temperature and elevated temperatures (Jung et al., 2013). In another research, simultaneous addition of PS and VC to the electrolyte is studied where anodes cycled with both VC and PS were found to contain lithium alkyl sulfonate and poly (VC), leading to a layer with improved conductivity and thermal stability. Diminution of gas generation during cycling via reducing the evolution of ethylene has been the other conclusion of using the two additives in a same time (Zhang et al., 2015).

To understand the impact of the sulfur-containing functional groups, interesting research has evaluated the performance of the three groups of sulfites, sulfates, and sulfonates as SEI formation additives. Comparing the functionality of ethylene sulfate, 1,3-propane sultone, and ethylene sulfite have revealed the better performance of ethylene sulfate and 1,3-propane sultone in terms of cell impedance and capacity retention with superiority of the sulfate compound (Wu et al., 2018). The observed variations in the performance of the different SEI layers could be attributed to the results obtained from XPS analysis where a higher ratio of organic to inorganic sulfide species has resulted in a better performing and more stable interphase.

Nitrogen-containing additives

Isocyanates are a group of Nitrogen-containing additives used to protect the electrolyte from extensive decomposition. The presence of two unsaturated bonds in the structure of the isocyanate group facilitates

its reduction process through the formation of a stable radical anion resulting in a molecule that reduces in higher potentials than the carbonate solvent. The generated radical anion could attack another isocyanate where repetition of the mechanism leads to the formation of a polymeric product through nucleophilic addition. The stability of the formed SEI by isocyanates is attributed to the formation of the polymeric structure with similarities to polyimides (Korepp et al., 2007a). Ethyl isocyanate (EtNCO) is reported as an additive that lowers solvent decomposition in PC-based electrolytes and protects graphite anode against exfoliation (Korepp et al., 2007b). The application of EtNCO has been studied in EC-based electrolytes as well where it has improved capacity retention of LCO/graphite cells. In the same work, the application of aromatic isocyanates has been evaluated as well, and however changing the additive to benzyl isocyanate (BIC) has slightly improved the cyclic stability of the base electrolyte, it has not ameliorated the performance of EtNCO. The addition of a bromine atom to the para-position, however, has turned 4-bromobenzyl isocyanate (Br-BIC) into a better-performing additive (Korepp et al., 2007a).

Organic cyanides have been another group of nitrogen-containing additives investigated for SEI improvement in which existence of a triple $C\equiv N$ bond in their structure assists the reduction process of the molecule. Acrylic acid nitrile (AAN) (Santner et al., 2003), 2-cyanofuran (2CF) (Korepp et al., 2006), and allyl cyanide (AC) (Yong et al., 2013) are reported as SEI-improving agents which protect the solvent in a PC-based electrolyte and make lithium intercalation a reversible process at the graphite anode. Dicyanoketene alkylene acetals (DCK) (Forestier et al., 2016) are a more recent example of organic cyanides which have been used as reduction-type additives in EC-based electrolytes ($LiPF_6$ in EC/DMC). Lithium carbonate-like $Li_2CO_2C(CN)_2$ and $RCHCH_2(CO_2C(CN)_2Li)_2$ are reported as the decomposition products of dicyanoketene ethylene (or propylene) acetal along with ethylene or propylene as gaseous by-products. By forming a more stable SEI layer, dicyanoketene alkylene acetals have improved the capacity retention of the NMC/graphite cells both at room temperature and high temperature (45°C). Ethylene glycol bis(propionitrile) ether has been recently applied as an additive containing two cyanide groups in the EC-based electrolyte ($LiPF_6$ in EC/DMC) where it has facilitated the formation of a thin and uniform SEI with a lower impedance and improved its stability on the graphite electrode (Liu et al., 2020).

Imides can be mentioned as the other group of nitrogen-containing additives used to form a better SEI layer where a nitrogen atom is connected to two acyl groups. The addition of aromatic maleimide compounds to the electrolyte containing PC and EC has resulted in a thinner yet more stable SEI which increases cell cyclability at different capacity rates (Wang et al., 2009). As another example, N-acetyl-caprolactam is reported as an additive that has maintained the room temperature capacity of LCO/graphite cells more efficient than VC and performed better stability against oxidation in comparison to vinylene carbonate in an EC-based electrolyte. However, the thermal stability of the SEI has been also improved by introducing N-acetyl-caprolactam to the base electrolyte; performance of VC has been reported slightly better at high temperatures (60°C) (Yoon et al., 2013).

Sulfur- and nitrogen-containing additives

Considering the observed advantages of nitrogen-containing and sulfur-containing additives, a new type of SEI-improving additives is developed with emplacement of both nitrogen- and sulfur-based groups in molecular structure. In general, the application of such additives in EC-based electrolytes has turned the composition of the SEI to possess sulfur-based reduction products like Li_2S , Li_2SO_3 , and $ROSO_2Li$ and polymeric structures containing amides or nitriles instead of unstable components. This modified SEI is expected to be stable against HF leading to less LiF content.

p-Toluenesulfonyl isocyanate (PTSI) is reported as an electrolyte ($LiPF_6$ in EC/EMC/DEC) additive which has reduced the impedance and enhanced the cycling capacity of Li/graphite cell especially at high current densities attributed to the formation of a stable SEI film inhibiting extended reductive decomposition processes upon cycling. Composition analysis of the SEI has detected Li_2S , Li_2SO_3 , and $ROSO_2Li$ as the sulfur-based decomposition products and a polyamide-like structure as a nitrogen-based species in the interphase revealing the contribution of both nitrogen- and sulfur-containing groups of the molecule in the formation process. Replacement of lithium carbonate and lithium alkyl carbonates with this composition has been reported as the reason for SEI improvement (Wang et al., 2017). 3-(phenylsulfonyl) propionitrile (PSPN) has been investigated as another example where the XPS analysis has confirmed the presence of Li_2S , Li_2SO_3 , and $ROSO_2Li$ in the SEI composition resulting in a more stable interphase against a prolonged decomposition. In terms of performance, the SEI formed by PSPN has presented a lower impedance than

the base electrolyte (LiPF_6 in EC/EMC) and the cyclic stability of the electrode was improved (Zuo et al., 2018). A similar combination of sulfur-based decomposition products has been reported by introducing fluorosulfonyl isocyanate (FI) to the EC-based electrolyte (LiPF_6 in EC/DMC) and the improved performance of the SEI has been correlated with this modified composition (Shi et al., 2019). In another work, effects of adding *p*-toluenesulfonylmethyl isocyanide (TOSMIC) to the electrolyte (LiPF_6 in EC/DEC) have been evaluated and added to Li_2SO_3 and ROSO_2Li ; XPS analysis has revealed the presence of nitrile compounds in the ameliorated SEI showing the contribution of both the nitrogen- and sulfur-containing parts of the additive in the formation process (Li et al., 2020).

Added to EC-based electrolytes, this type of additive has been used in PC-based electrolytes to protect the graphite against exfoliation and give reversibility to the lithium intercalation process. Introducing ethyl isothiocyanate (EITC) to a PC-based electrolyte has led to the formation of a polymeric structure containing $\text{N}=\text{C}-\text{S}$ units which have improved the cyclability of the electrode by protecting the electrolyte from an extended co-intercalation/decomposition process (Li et al., 2021).

Despite many positive features of sulfonates and isocyanates, the toxicity of compounds that contain such functional groups is an important drawback to be considered, particularly in the large-scale application of these additives.

CONCLUSION AND PERSPECTIVES

- Despite the new approaches followed to introduce more efficient battery chemistries namely all-solid-state lithium batteries, lithium-ion batteries composed from carbonous anodes and based on liquid electrolytes are still an interesting system due to their well-developed chemistry and well-adapted industry. Further globalization of the LIB-dependant markets, particularly the EV sector, from one side requires performance advancements in cell capacity, power density, and safety, where from the other side demands diminution of the environmental impacts caused by toxicity of the material. Solid-electrolyte interphase (SEI) formed on the anode by decomposition of the electrolyte components during the initial charging steps affects the performance of LIBs from different aspects.
- The generation of a stable SEI inhibits a continuous electrolyte decomposition process and consequently diminishes the extended Li^+ ion dissipation leading to better capacity retention especially under severe aging factors like elevated temperature and high current rate. Considering its interfacial quiddity, the formation of a thin SEI layer featuring good Li^+ ion conduction leads to impedance diminution and improves the power output of the cell. From another perspective, a decent SEI could detract detrimental side-reactions such as extensive gas generation and gradual lithium plating caused by long-term degradation of the anode and therefore could reduce the relevant safety concerns. Introducing SEI-improving additives to the electrolyte has been followed as a cost-effective approach to ameliorate SEI features.
- The efficiency of the formed SEI layer depends on its composition and morphology. The graphite SEI formed in carbonate electrolytes is reported to be composed partially of inorganic species such as lithium carbonate, lithium oxide, and lithium fluoride and partially from organic species mainly including lithium alkyl carbonates and lithium alkoxides. The SEI formed during the initial intercalation processes gradually evolves as the cell cycles leading to a two-sectional configuration with an organic part close to the electrolyte and an inorganic section adjacent to the electrode. Electrochemical instability of the SEI components followed by a continuation of transformative mechanisms leads to further electrolyte decomposition which reduces lithium inventory. Therefore, the generation of stable components within the SEI structure is the target of interface modification.
- Decomposition of the reduction-type additives which reduce prior to the other electrolyte components brings a new composition to the SEI layer causing improvements in cell performance. VC and FEC as modified carbonates, stabilize the interphase by transforming the unstable species into the more stable inorganic lithium salts and forming a polymeric structure as the organic section. Sulfur-containing additives, mainly organic sulfates, and sulfonates generate sulfur-based decomposition products in the SEI with high electrochemical stability and improved Li^+ ion conductivity. Nitrogen-containing additives such as organic cyanides, isocyanates, and imides can also stabilize the interphase against a prolonged decomposition process by forming a polymeric network and turning the degradable components into more stable nitrogen-based compounds. Also, a new type of

electrolyte additives, containing both the nitrogen-based and sulfur-based functional groups, are introduced which form a stable SEI with a combination of sulfur-based lithium salts and nitrogen-based polymeric species.

- Although the performance of the SEI layer is significantly ameliorated via electrolyte engineering, there are further modifications required due to the stability concerns under prolonged cycles, extended storage, high current rates, and elevated temperatures. Given the flexible structure of organic compounds in molecular design, progress could be made by the development of additives benefiting from various capabilities of different functional groups in their structure.
- Further optimization of the interphase and the additives relies on a profound understanding of the SEI-affecting parameters. Development of non-invasive analytical techniques with *in situ/operando* approaches to observe the actual SEI as the battery cycles will provide essential details on its affecting factors. Picturing the SEI as a mosaic-like structure, such studies could also help researchers to obtain a better idea about the grain boundaries of its nanosized components and how it impacts the Li⁺ ion transportation within the interphase. Combination of such analytical methods with advanced computational studies would help researchers to compare the expected decomposition products with the factual components hence predicting the most probable formation/evolution mechanisms which lead us to improved battery materials.
- Despite all the achieved advancements in SEI-improving additives, if we look from the environmental aspect most of these compounds, especially sulfonates, cyanides, and isocyanates are toxic materials. An electric world is appearing to become inevitable meaning an exponential growth in LIB production. However, the amount of SEI additives in the electrolyte is relatively low; multiplying that small amount into the enormous yet growing number of produced cells would bring the negative environmental influence on the picture. Therefore, performing further research and development studies in the field of SEI improvement appears to be essential in order to decrease the environmental footprints while the LIB industry goes forward.

LIMITATIONS OF THE STUDY

This review has mainly studied the SEI layer formed on the carbonous anodes and the applied additives in carbonate-based electrolytes as the common system in LIB cells and therefore the other anode chemistries were not included in the performance analysis. The qualitative comparison between different additives is achieved by an aggregative approach and hence represents the overall features of the reviewed compounds in each category.

AUTHOR CONTRIBUTIONS

The study was performed by S.H.B.; The paper was written by S.H.B.; The paper was reviewed and edited by M.B., J.V.M., A.H., M.S.H., H.O., and M.J.; Supervision by M.B., J.V.M., A.H., H.O., and M.J.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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