Interfacing Si-Based Electrodes: Impact of Liquid Electrolyte and Its Components

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As the demand for mobile energy storage devices has steadily increased during the past decades due to the rising popularity of portable electronics as well as the continued implementation of electromobility, energy density has become a crucial metric in the development of modern batteries. It was realized early on that the successful utilization of silicon as negative electrode material in lithium-ion batteries would be a quantum leap in improving achievable energy densities due to the roughly ten-fold increase in specific capacity compared to the state-of-the-art graphite material. However, being an alloying type material rather than an intercalation/insertion type, silicon poses numerous obstacles that need to be overcome for its successful implementation as a negative electrode material with the most prominent one being its extreme volume changes on (de-)lithiation. While, as of today, a plethora of different types of Si-based electrodes have been reported, a universally common feature is the interface between Si-based electrode and electrolyte. This review focuses on the knowledge gained thus far on the impact of different liquid electrolyte components/formulations on the interfaces and interphases encountered at Si-based electrodes.

1. Introduction

Lithium-ion batteries (LIBs) are considered one of the best candidates to continuously satisfy the growing demand for future energy storage. To revolutionize emerging applications such as electromobility, next-generation LIBs need to provide higher energy densities, fast-charging possibilities, and longer lifetimes than state-of-the-art (SOTA) analogues (e. g., layered oxidel[graphite batteries). The negative electrode, as one of the main components of LIBs, contributes significantly to the output power and energy density of the battery. The success story of graphite as negative electrode material in the SOTA LIBs is due to its abundance (i. e., low cost), low discharge potential, long cycle life, and significantly improved safety over bare lithium metal. However, to obtain a desirable improvement in energy density for future energy demands, a shift in the electrode active materials beyond conventional LIBs is inevitable (Figure 1).

One of the most promising alternative negative electrode material to realize higher energy density LIBs is the utilization of metallic materials that form intermetallic phases with Li with defined stoichiometry and structure, so called “alloying” electrode materials, such as silicon or Sn. In analogy to hydrogen storage materials in nickel-metal hydride batteries, these materials can be called Li storage materials. In particular Si-based electrodes have attracted significant attention among academics and industries in the last decade due to their beneficial properties, such as high theoretical specific gravimetric capacity of 4200 mAh·g⁻¹ (at 450 °C for the Li₁₄Si phase) and 3590 mAh·g⁻¹ (at room temperature for the Li₁₄.₅Si phase), which is more than 10-times higher than that of graphite,[8-11] still attractive operating potential (~0.2–0.5 V vs Li/Li⁺), high natural abundance and thus low cost accompanied by negligible toxicity.[12] However, despite all these resilient features, intrinsic challenges such as extreme volume changes upon (de-)lithiation (200–400%), low diffusivity (δ~ and D_li), a dynamic solid-electrolyte interphase (SEI), and low initial Coulombic efficiency (ICE) and related Li and thus capacity losses[14] make application of Si (as well as of other Li-alloying metals) as negative electrode material extremely difficult (Figure 2).
The large volume variation causes fractures in the active material as well as the SEI, leading to mechanical deformation of the electrode. Furthermore, the fractures re-expose active material to the electrolyte during cycling, resulting in additional formation of solid electrolyte interphase (SEI) and thus in continuous active lithium consumption,\textsuperscript{[18]} which in turn results in low Coulombic efficiency (CE) and severe capacity fading (Figure 3) which can be seen very clearly in full cell operation.

Figure 1. Capacity and voltage ranges of selected negative electrode and positive electrode materials currently considered for lithium-based batteries.

Figure 2. Anode/electrolyte interface considerations: SEI stability and flexibility during cycling with graphite, lithium storage metals (such as silicon or tin) and metallic lithium. Reproduced with permission.\textsuperscript{[17]} Copyright 2015, IOP Publishing Ltd.
configuration.[19] Recent studies revealed that on prolonged cycling, SEI grows into the silicon bulk, generating a porous Si structure which in turn leads to additional SEI formation. This contributes to electrode swelling and results in an additional fading mechanism for Si-based electrode materials.[20,21]

As Si electrodes will be inevitably subject to SEI formation (which depends on the type of Si surface[22,23]) and dynamic interface/interphase evolution (somehow a bit similar to Li metal[16]), measures to overcome or at least diminish the large and continuous volume and surface/interface changes are required.

To overcome the challenges of Si-based electrodes, several different strategies have been developed—among them, the modification of the active material structure. It has for example been shown that nanoscale Si,[25] as like other Li storage metal[26] particles are less susceptible to mechanical stress during cycling. Another strategy to further improve the performance of Si-based active materials is combining Si with other materials like graphite. For instance, blending Si and graphite can provide the benefits of both components while avoiding their inherent drawbacks. However, it should be kept in mind that this strategy always comes with compromises in practical terms and does not mitigate the fundamental challenges of Si.[27] The mechanical challenges imposed by alloying type active materials have led to a reconsideration of the role of the binder in electrodes.[28] Another important strategy is tailoring the electrolyte composition to the specific requirements imposed by Si-based active materials.[29,30] In principle, the same considerations regarding the role of the electrolyte with respect to ion transport and interphase formation apply, regardless of the specific negative electrode materials employed. Therefore, rather than recapping these considerations, we would like to point the reader to previously published extensive and excellent reviews regarding the role of the electrolyte in LIBs.[31–34] However, with Si-based electrodes, the mechanical stability of the formed SEI becomes a much more critical property.

This review aims to provide a comprehensive overview of the interfacial reactivity of liquid electrolytes at the vicinity of the polarized Si-based electrodes. The utilized compounds will be grouped into i) solvents/cosolvents, ii) conducting salts, and iii) functional additives, and, when possible, their individual impact on the SEI layer will be summarized. Due to their intrinsic difference in physical, chemical, and electrochemical properties compared to “conventional” liquid organic solvent based electrolytes, ionic liquids and solid electrolytes as well as their hybrids will however not be included in this contribution. Among the numerous studies covered here, several research contributions stand out by utilizing exotic or highly sophisticated analysis techniques in order to gain a deep level of understanding of the interphasial processes taking place at the silicon surface during battery operation. These studies and the employed techniques will be highlighted in a separate section.

2. Electrolyte Interfacing Si-Based Electrode

The utilization of Si as a negative electrode does not change any of the fundamental working principles of a LIB other than the way the lithium-ion is incorporated into the active material. Therefore, it was only logical to utilize electrolytes that were already well-studied and understood in graphite based systems, as re-invention of the wheel is rarely feasible.[35–38] Organic carbonate-based solutions containing LiPF6 with fluoroethylene carbonate (FEC) as an additive or cosolvent are current SOTA electrolytes for LIBs that utilize Si-based electrodes. However, as Si poses numerous challenges when used as a negative electrode, a large effort is put into developing novel electrolyte
formulations that are able to tackle these challenges more effectively than the SOTA electrolytes.[28,35]

The following sections will summarize literature reports that use electrolytes which differ from SOTA formulations, i.e., solutions of LiPF₆ in mixtures of ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC). There is no clearly defined threshold above which an additive is considered a cosolvent. However, as most of the reviewed literature treats added substances in an amount of up to 10% as additives, this threshold will be adopted here as well. Higher amounts will be considered as cosolvents. If possible, the impact of individual components on the interphasial chemistry will be highlighted.

2.1. Impact of Solvents/Cosolvents

The primary role of electrolyte solvents is to facilitate complete salt dissociation and fast ion transport. Since single compounds usually only allow one of the two requirements, often a compromise in the form of mixed solvents has to be used. For SOTA electrolytes, EC, endowed with high a dielectric constant but also high viscosity, together with one more linear carbonates (e. g., DMC, DEC, and EMC) with low dielectric constant but low viscosity, are usually employed.[31] Moreover, electrolyte solvents facilitate the formation of effective interphases (SEI and CEI) on the electrode active materials, and thus enable continued operation of the LIB.[32,33] This implies that the nature and composition of electrolyte formulations have dramatic effects on the interphase chemistry. This section will highlight studies where electrolyte solvents other than the SOTA components were used (Figures 4–8).

2.1.1. Organic Carbonate-Based Solvents

**Fluoroethylene Carbonate (FEC):** Jin et al. studied Si nanowire electrodes by means of solid state NMR using LiPF₆ in FEC as electrolyte formulation. The achieved cycling performance was superior to all other considered electrolytes, including electrolytes employing FEC as additive in the first 50 charge/discharge cycles. Unfortunately, no long-term cycling data was disclosed. The authors reported that the SEI in the pure solvents is rich in branched or cross-linked poly(ethylene oxide) (PEO), similarly to the SEI found in FEC additive containing electrolyte, but different from the mostly linear PEO found in FEC additive-free electrolyte.[36] Kong et al. used FEC as a cosolvent together with DMC, sulfolane and a fluorinated ether and successfully increased the cycling performance of NMC811||SiOₓ-Gr batteries under high voltage conditions (up to 4.5 V). However, due to the presence of several solvents it is difficult to pinpoint the influence of FEC in the formulation.[37]

When FEC is not used as an additive, it is commonly employed to replace EC, leading to an improved cycling performance for a variety of Si-based electrodes compared to conventional organic carbonate-based electrolytes.[38–41] Several groups have performed detailed analyses of the SEIs formed in electrolytes consisting of significant portions of FEC with different techniques. The results typically suggest the formation of thin SEIs that are rich in lithium fluoride (LiF) and different organic polymers.[42–46]

**Propylene Carbonate (PC):** Dalavi et al. studied the effect of different functional additives on the cycling performance of Si thin film electrodes. In one of the studied electrolytes, they replaced EC by propylene carbonate (PC). Interestingly, PC-based electrolyte was found to perform significantly worse than the EC-based counterpart, leading to a steady decrease in CE. The authors detected only a thin, fluorine rich SEI and concluded that the SEI formed in presence of PC-based electrolyte may be soluble in the electrolyte and therefore fails to sufficiently passivate the Si electrode.[47] Ulldemolins et al. used an electrolyte containing PC as a cosolvent with Si thin film electrodes but focused on the effect of VC additive. However, from the presented galvanostatic cycling data, it is evident that the capacity fading they observed was much less severe than in the work of Dalavi et al. which may in part be attributed to the much thicker Si electrodes used.[48] Later, Domi et al. used...
a solution of LiTFSI in PC as an electrolyte with Si thick film electrodes and observed a similarly severe capacity fading as Dalavi et al. Also here the cycling performance could be dramatically improved by adding VC or FEC as additives, which further supports the conclusion that PC alone is not able to form an effective SEI, independent of the used conducting salt.[49]

Vinylene Carbonate (VC): In order to understand the effects of the most popular electrolyte additives, FEC and VC, Jin et al. studied Si nanowire electrodes by means of solid state NMR. One of the electrolytes studied was a solution of LiPF₆ in pure VC. Surprisingly, the achieved cycling performance was on par with cells that used an organic carbonate-based electrolyte with FEC additive or pure FEC and thus superior to the benchmark electrolyte in the first 50 charge/discharge cycles. Unfortunately, no long-term cycling data was reported. They found the SEI formed in the pure solvents to be rich in branched or cross-linked poly(ethylene oxide) (PEO), similarly to the SEI found in FEC additive containing electrolyte, but different from the mostly linear PEO found in additive-free electrolyte.[36]

2.1.3. Ether-Based Solvents

1,1,2,2-Tetrafluoroethyl-2,2,3,3-tetrafluoropropyl Ether (TTE): In order to understand the effects of the most popular electrolyte additives, FEC and VC, Jin et al. studied Si nanowire electrodes by means of solid state NMR. One of the electrolytes studied was a solution of LiPF₆ in pure VC. Surprisingly, the achieved cycling performance was on par with cells that used an organic carbonate-based electrolyte with FEC additive or pure FEC and thus superior to the benchmark electrolyte in the first 50 charge/discharge cycles. Unfortunately, no long-term cycling data was reported. They found the SEI formed in the pure solvents to be rich in branched or cross-linked poly(ethylene oxide) (PEO), similarly to the SEI found in FEC additive containing electrolyte, but different from the mostly linear PEO found in additive-free electrolyte.[36]

2.1.2. 2,2,2-Trifluoroethyl Methyl Carbonate (FEMC)

Yang et al. used FEMC as a cosolvent in a non-flammable LiFSI-based electrolyte for SiO electrodes and demonstrated significantly improved galvanostatic cycling performance compared to additive-free organic carbonate-based electrolyte. Compared to the classical electrolyte, they found a thin SEI that is both rich in organic and inorganic compounds. They attributed the increased cycling performance to the formation of elastic polyphosphoesters, stemming from the cosolvent TFEP, as major SEI constituents.[50]

2.1.3. Ether-Based Solvents

1,1,2,2-Tetrafluoroethyl-2,2,3,3-tetrafluoropropyl Ether (TTE): Haruta et al. used TTE as solvent for a LiTFSI tetraglyme complex with silicon flake powder electrodes. The cycling performance was found to be similar to conventional LiPF₆/organic carbonate-based electrolyte. Addition of FEC to the electrolyte system led to increased performance, a comparison with conventional organic carbonate-based electrolyte with FEC additive was however not given.[51] In several other studies, TTE was employed as a cosolvent in the context of sulfonamide salts together with other unusual solvents.[52] Where the TTE containing electrolytes were compared to the TTE free variants, a significant improvement in cycling performance was observed. Yang et al. found smaller interface resistance and significantly lower SEI fracture in glyme-based electrolytes with higher TTE contents.[53] In their phosphate-based electrolyte, Yang et al. attributed the improved cycling performance to a stronger participation of LiFSI in the SEI formation induced by TTE through alteration of Li⁺ coordination in the bulk electrolyte.[90] Kong et al. used TTE together with DMC, sulfolane and FEC in a LiPF₆-based electrolyte. However, as no comparison with different compositions is reported, the specific impact of TTE on the interphasial chemistry remains unknown in this case.[77]

Bis(2,2,2-trifluoroethyl) Ether (BTFE): BTFE was used by Jia et al. as a cosolvent in a LiFSI-based non-flammable electrolyte that showed increased cycling performance with Si/Gr composite electrodes. However, the impact of BTFE on the SEI composition is hard to judge as several non-standard components were used in this electrolyte.[34] In a follow-up study, Jia et al. utilized BTFE as a diluent in LiFSI/organic carbonate-based electrolytes. However, no analysis of the formed interphases was reported.[55]

Dimethoxymethylene (DME): Recently, Yang et al. reported a LiFSI-based electrolyte using dimethoxymethylene (DME) and TTE as solvents, outperforming the SOTA organic carbonate-based analogue on Si thin film electrodes. The authors found the SEI to have a layered structure with an inner layer rich in LiF, silicates and sulfites while the outer layer was rich in polyethers. They attributed the increased galvanostatic cycling performance to the special SEI structure allowing for structural changes while maintaining the elastic polyether SEI-building layer.[58] Jaumann et al. used DME as a cosolvent together with 1,3-dioxolane (DOL) for LiTFSI-based electrolytes with Si nanocomposite electrodes. However, the focus was set on the impact of LiNO₃ additive on the SEI rather than that of DME.[56]

Tetrahydrofuran (THF) and 1-Methyltetrahydrofuran (MTHF): Chen et al. demonstrated the application of a solvent blend of THF and MTHF with high concentrations of LiPF₆ for silicon microparticle and other alloying type electrodes, achieved a remarkable cycling performance in half cells with very little capacity fading and demonstrated feasibility of the electrolyte in full cells with LiFePO₄ positive electrodes. They found the formed thin SEI to possess a bilayer structure that is rich in LiF close to the Si|SEI interface and rich in organics at the SEI|electrolyte interface with an additional Li₂SiO₃ layer under the LiF. The increased cycling stability was attributed to an unusual stability of the SEI resulting from the described layer structure.[57]

1,3-Dioxolane (DOL): Etacheri et al. used DOL as a solvent for LiTFSI-based for Si nanowire electrodes and found a remarkable cycling performance compared to conventional organic carbonate-based electrolytes at a high current rate of 6C at 60 °C by identifying poly(DOL) as well as fluorocarbon species formed on the electrode surface. LiNO₃ additive can significantly improve the cycling performance and dramatically reduces the amount of decomposition products of LiTFSI in the SEI, underlining the critical role of DOL decomposition for the SEI.[58] Later Jaumann et al. introduced DME as a cosolvent with DOL and studied the influence of LiNO₃ on the SEI formation on Si nanocomposite electrodes. Authors confirmed the ability of LiNO₃ to limit LiTFSI decomposition and thus to increase the cycling performance.[56]
2.1.4. Ester-Based Solvents

**Trifluoroethyl Butyrate (TFEB):** Smart et al. used TFEB as a substitute for EMC in one of FEC-based electrolytes and found a significant drop in achievable capacity with Si-C composite electrodes. However, it has to be noted that the LiPF₆ concentration was halved at the same time, making a solid conclusion of TFEB’s effect on the SEI impossible.[50]

**Dimethyl 2,2,3,4,4-hexafluoropentanedioato (DMHFDP):** Piwko et al. studied dilute solutions of LiTFSI in DMHFDP with Si thin film electrodes. The DMHFDP-based electrolyte led to lower capacity fading than organic carbonate-based electrolytes at current rates lower than C/5. However, galvanostatic cycling at C/2 dropped the reversible capacity to less than 10% of the initial value within the first 15 charge/discharge cycles. By means of XPS, the authors found perfluorocarboxylates being initially formed in the SEI that are completely defluorinated upon further lithiation of the negative electrode. Re-appearance of the C-F peaks upon de-lithiation was interpreted as the partial reversibility of the defluorination reaction rather than a continuous SEI growth.[59]

2.1.5. Phosphate-Based Organic Solvents

**Triethyl Phosphate (TEP):** Matsumoto et al. applied TEP together with FEC as electrolyte solvents with LiPF₆ as conducting salt for carbon coated SiO electrodes. With this non-flammable electrolyte, they achieved the same capacity retention as a conventional, albeit FEC free electrolyte over 250 charge/discharge cycles. TEP as standalone solvent failed to enable any practical cyclability. However, no studies of the interstitial composition were performed.[60] Jia et al. used TEP as a cosolvent in their non-flammable TFSI-based electrolyte formulation and reported LiF rich SEI, but did not discuss the impact of TEP in detail.[54]

2-(2,2,2-Trifluoroethoxy)-1,3,2-dioxaphospholane-2-oxide (TFEP): Yang et al. utilized TFEP as a cosolvent in a LiFSI-based non-flammable electrolyte with SiO electrodes. A significantly better cycle performance than with FEC free organic carbonate-based electrolyte was demonstrated. The authors found a thin SEI rich in inorganic compounds as well as polyphosphoesters resulting from TFEP decomposition. They attributed the high performance to an increased elasticity of the SEI due to the presence of the polyphosphoesters.[50]

2.1.6. Sulfur-Based Organic Solvent

**Sulfolane:** Piwko et al. used sulfolane as a cosolvent together with the fluorinated ether TTE for LiTFSI-based electrolyte and were able to demonstrate increased galvanostatic cycling performance compared to FEC containing conventional electrolyte in NCA[Si]Si cells when additional amount of FEC was introduced. Even without FEC, the electrolyte led to significantly reduced SEI fracture.[52] Li et al. replaced EC by sulfolane in LNMO[SiOC] cells and demonstrated improved cycling performance with drastically reduced gas evolution compared to the conventional organic carbonate-based electrolyte. This indicates the formation of an SEI that can more effectively prevent continuous electrolyte decomposition. However, no insights into the interphasical chemistry were reported.[61] Kong et al. used sulfolane together with DMC, TTE and FEC in a LiPF₆-based electrolyte. However, no comparison with different compositions is reported, and thus the specific impact of sulfolane on the interphasical chemistry remains unknown in this case.[37]

**Dimethyl Sulfite (DMS) and Diethyl Sulfite (DES):** Liu et al. used DMS and DES as solvents together with EC and FEC as an additive in LiTFSI-based electrolytes. Significant improvement in galvanostatic cycling performance of Si/graphite compositive electrodes cycled at -20 °C was demonstrated. DES was found to be a crucial component in allowing long-term cycling stability and forming uniform and dense SEIs. XPS analysis revealed SEIs rich in LiF and sulfonates. A comparison to conventional electrolytes was however not reported.[62]

2.2. Impact of Conducting Salts

Any given electrolyte salt for rechargeable LIBs has to meet the following minimal requirements: (1) It should be able to completely dissociate in the solvent. (2) The anion should be stable against electrochemical decomposition at the electrodes. (3) The anion should enable the long-term stability of other cell components, either by inertness or by formation of a protective film, e.g. for aluminum current collector protection.[63] In addition to that, it should result in a high ionic conductivity when dissolved, have a high thermal and chemical stability, low toxicity and low cost while not disturbing the formation of effective interphasess on the used electrodes. Despite tremendous efforts, a single compound that meets all mentioned criteria is yet to be found. LiPF₆ has been the SOTA electrolyte salt in LIBs for several decades now as it usually offers the best compromise between all the above-mentioned requirements.[31,32,64,65] However, its proneness to hydrolysis, low thermal stability and the formation of highly toxic compounds, such as HF, POF₃ and various organofluorophosphates[66] on decomposition drive significant research effort towards partly substituting LiPF₆ or its complete replacement.

This section focuses on publications where a lithium salt other than LiPF₆ is the main electrolyte salt (Figure 9). Additions of smaller amounts of other salts to electrolytes are considered additives and will be covered in the appropriate section.

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**Figure 9.** Chemical structures of selected lithium salts.
2.2.1. Sulfonimide-Based Salts

Lithium Bis(trifluoromethylsulfonyl)imide (LiTFSI): LiTFSI is well known from the domain of polymer electrolytes, but suffers from its pronounced Al dissolution issues.[32] While it has been used with Si-based electrodes, many of the studies also utilize non-carbonate solvents, making conclusions on the specific effect of LiTFSI as compared to LiPF₆ challenging. While studying the use of fluorinated esters with Si thin film electrodes, Fears et al. found that LiTFSI significantly reduces the capacity fading in EC/DMC solvent as compared to LiPF₆. XPS results showed that LiTFSI is readily decomposed and is an important contributor to the SEI.[39] Haruta et al. used LiTFSI to substitute LiPF₆ in an EC/DEC solvent mixture in order to protect the utilized in situ AFM setup from HF. They found non-uniform SEI formation on Si thin film electrodes, to which they attributed the poor cycling performance, but did not compare it directly to the LiPF₆-based electrolyte.[67] Etacheri et al. used 1,3-dioxolane (DOL) as solvent for TFSI and were able to demonstrate a remarkable capacity retention of crystalline Si nanowire electrodes cycled at a rate of 6C at 60 °C whereas the conventional LiPF₆/organic carbonate electrolyte led to very rapid capacity fading. Addition of LiNO₃ to the electrolyte increased the capacity retention even further. XPS analysis revealed a large fraction of LiTFSI decomposition products in the SEI.[88] However, as such dramatic improvements are not observed in organic carbonate-based electrolytes, the main contributor is likely to be the DOL. Later Jaumann et al. studied the positive effect of LiNO₃ on the LiTFSI/DOL system and demonstrated by detailed XPS analysis that LiTFSI degradation was significantly reduced upon the addition of LiNO₃ to LiTFSI/DOL system. Furthermore, further improvement of the capacity retention of nanostructured Si/C composite electrodes was achieved by using dimethoxyethane (DME) as a cosolvent.[56] Piwoń et al. developed an electrolyte for lithium silicide|carbon/sulfur batteries consisting of LiTFSI in sulfolane and TTE. Interestingly, this electrolyte formulation led only to minor Al dissolution up to 4.5 V.[32] Liu et al. used LiTFSI in sulfite-based electrolytes for Si/graphite composite electrodes at low temperature (~20 °C). However, as LiTFSI is not the only sulfur source and no comparison to LiPF₆-based electrolyte was reported, the particular influence of LiTFSI cannot be deducted.[62]

Lithium Bis(oxalato)borate (LiBOB): Choi et al. compared the performance of Si thin-film electrodes in organic carbonate-based electrolytes using LiPF₆ and LiBOB as conducting salts. In case of the LiBOB-based electrolyte, the formed SEI was much denser than in the LiPF₆-based one, reaching to a conclusion that the SEI formed in the LiBOB-based electrolyte limits the formation of electrochemically inactive Si phases and thus leads to an increase in galvanostatic cycling performance.[70] Li et al. investigated the influence of mixed electrolytes containing LiBOB and LiPF₆ in organic carbonate solvents on the cycling performance of Si/graphite composite electrodes. The blended salt electrolyte with LiBOB as the major components showed a more stable long-term cycling stability than either of the single salt-based electrolytes. In the case of single salt-based electrolytes, cells with the LiBOB electrolyte yield lower discharge capacities but less capacity fading in the first 60 charge/discharge cycles than the LiPF₆ electrolyte. Unfortunately, no long-term cycling data was presented for these electrolytes.[71,72] In an attempt to develop environmentally more friendly electrolytes, Hernández et al. studied the effect of fluorine free electrolytes on silicon-graphite composite electrodes in full cell configuration. Using LiBOB as the electrolyte salt, an oxygen-containing compounds rich SEI was found to be formed as opposed to the LiF rich SEI in the case of LiPF₆. While the fluorine free electrolyte failed to outperform the LiPF₆-based electrolyte under typical cycling conditions, it showed better performance at lower currents and higher temperatures.[59]

Lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide (LiTDI): A unique feature of LiTDI is that the desired delocalization of the negative charge is achieved with an aromatic core. In an initial in-depth study of the first cycle, compatibility of an electrolyte comprising the salt and organic carbonate in cycling performance between the LiPF₆-based and the LiFSI-based electrolytes. Thus, authors concluded that the conducting salt plays a minor role for the cycling performance compared to the solvents. However, the SEI chemistry responsible for aforementioned findings was not studied.[69] Jia et al. utilized previously reported non-flammable electrolytes based on LiFSI, BTFE and TEP with silicon-graphite composite electrodes and demonstrated significantly improved cycling performance in full cells at elevated temperatures (45 °C) compared to a LiPF₆-based organic carbonate electrolyte containing FEC as an additive. This improvement was attributed to a LiF rich SEI, formed from the electrochemical decomposition of LiFSI.[54] In a follow-up study, Jia et al. developed highly concentrated LiFSI-based electrolytes that utilize BTFE and organic carbonates as cosolvents. The study demonstrated that considered electrolytes show significant improvement in the cycling stability of full cells utilizing silicon-graphite composite electrodes as compared to the LiPF₆ baseline even at an upper cutoff voltage of 4.5 V.[55] Recently other groups also successfully developed LiFSI-based electrolytes for SiO and Si electrodes, but also utilize different electrolyte solvents, which makes it hard to reach conclusive remarks on the influence of LiFSI salt anion on the formed interphases.[50,51]
solvents with a Si composite electrode was established by Lindgren et al. Only a small portion of the salt was found to decompose and no unwanted side reactions with the Si active material occur, however the formed SEI thickness was higher than with similar LiPF₆-based electrolytes. In a follow-up study, it became clear that the formed SEI is ineffective on prolonged cycling and thus leads to poor cycling performance. This can be counteracted by using VC and FEC additives and results in good cycling performance. The electrolyte formulation was then further optimized by Niedzicki et al. to achieve an overall better performance than with commercial LiPF₆-based electrolytes.

Lithium Tris(pentafluoroethyl)trifluorophosphate (LiFAP): The rather exotic LiFAP was used by Farmakis et al. as a conducting salt in EC/DMC together with Si film electrodes but fails to achieve the same improvement as on graphite electrodes. In fact, on the utilized Si electrodes it performs poorer than LiPF₆ analogue.

2.2.3. Inorganic Salts

Lithium Perchlorate (LiClO₄) and Lithium Tetrafluoroborate (LiBF₄): Han et al. used an organic carbonate-based electrolyte with LiClO₄ as conducting salt for Si thin film electrodes. Most notably the use of LiClO₄ leads to poor CE around 96% and a pronounced impedance growth of the Si electrodes as well as electrode pulverization on prolonged cycling. These effects could however be alleviated with the use of different additives.

Li et al. considered a number of lithium salts in organic carbonate solvents with Si/graphite/carbon composite electrodes. In the case of single salt-based electrolytes, LiClO₄ showed more pronounced capacity fading than the LiPF₆ benchmark while the use of LiBF₄ led to rapid fading of the reversible capacity. They furthermore studied blends of LiBOB with LiPF₆ and LiClO₄ and demonstrated that an increasing amount of LiClO₄ deteriorated cycling performance, which could be correlated with a significant increase in electrode impedance.

2.3. Impact of Functional Additives

Among the different approaches in adjusting certain characteristics of LIBs, such as cycling performance, shelf life or flammability, the methodically simplest, economically viable and scalable approach by far is the introduction of small amounts (e.g., ≤ 10% by weight, volume or moles) of compounds, called electrolyte additives. The goal is usually to enhance a specific property of the battery chemistry in question without negatively impacting other desired properties like the bulk properties such as viscosity, ionic conductivity etc. of the electrolyte.

A plethora of compounds has been studied and reported in graphite-based battery chemistries, many of which have been (more or less successfully) transferred to silicon-based battery chemistries. Compared to solvents and conducting salts, the required properties of functional additives may be severely relaxed as for example many additives are specifically added to the electrolyte to be decomposed on the electrodes. Therefore, for additives, the required properties strongly depend on their intended function within the battery. This section will highlight the application of different types of functional additives in batteries that utilize Si-based negative electrodes (Figures 10, 12–17).

2.3.1. Organic Carbonate-Based Additives

Fluoroethylene Carbonate (FEC) and Vinylene Carbonate (VC): FEC is by far the most popular electrolyte additive for Si-based electrodes, closely followed by VC. Therefore, instead of summarizing the main findings of all the individual reports, we will focus on the in-depth studies of the decomposition mechanisms of these additives on Si electrodes.

Due to its outstanding positive effect on the cycling performance of Si-based electrodes, FEC quickly became the SOTA electrolyte additive for systems utilizing silicon. Naturally, several groups have suggested different mechanisms to explain the effect of FEC based on their findings, making use of experimental and computational studies. However, no consensus was reached. To settle the debate as to what really happens at the Si interface when FEC is present, Shkrob et al. utilized low-temperature radiolysis and photolysis, pulse radiolysis-transient absorption spectroscopy and matrix isolation continuous wave electron paramagnetic resonance (EPR) spectroscopy to study the oxidation and especially reduction chemistry of FEC in great detail. An evidence for a two-electron reduction close to the surface was found, which leads to complete mineralization of FEC in the inner SEI layer. In the outer SEI layer, FEC is only incompletely reduced by a one-electron reduction process and results in a cross-linked polymeric outer SEI. The difference to non-fluorinated organic carbonates is that in the case of FEC, one-electron reduction leads to the liberation of LiF and CO₂, leaving behind a vinoxyl radical while the non-fluorinated carbonates undergo ring opening. The vinoxyl radical then serves as an initiator for the formation of a poly(VC) like polymer. Overall, the author's
findings strongly support the conclusions from the computational studies of Leung et al. [87]

Further reduction of the polymer can generate radical moieties in the polymer backbone that can move via 1,2-shift and recombine to form cross-links between different polymer chains (Scheme 2). The authors attribute the outstanding positive effect of FEC as electrolyte additive to this intrinsic ability to form cross-linked polymer networks.

Later, in a similarly elaborate study, Jin et al. used a combination of liquid and solid state nuclear magnetic resonance (NMR) spectroscopy with 13C-labelled FEC to gain additional insights into the mechanism of FEC reduction by studying the formed SEI and the electrolyte after different stages of cycling. [91] Authors were able to directly observe soluble vinoxyl species and cross-linking groups in oligomeric and polymeric species, thus supporting the previously discussed formation of vinoxyl radicals and the suggested cross-linking mechanism (Scheme 3). None of these were detected in the absence of FEC. Notably, the experiments furthermore proved that FEC can indeed be converted to VC in a battery under operating conditions. In case of the FEC free electrolyte, soluble species like lithium ethylenedicarbonate (LEDLC), lithium formate (from CO₂ reduction) and ethylene oxide-based oligomers are formed. The insoluble part of the SEI mainly consists of ethylene oxide and carbonate species. The experiments indicated an increase in concentration of the soluble species upon cycling, which is in line with the inability of the SEI to suppress electrolyte decomposition.

In a follow-up study, Jin et al. further consolidated these findings and especially the nature of the cross-linking units by 13C-13C correlation experiments. [36] But most notably, the authors have extended the methodology to 29Si NMR and studied the evolution of the Si surface with cycling. Organosiloxane species that contain Si-C bonds were identified, thus indicating that the organic SEI layer is at least partially covalently bonded to the Si surface (Figure 11). However, the authors point out that the presence of Si-C bonds does not necessarily correlate with an increased cycling performance. In this study, pure VC was used as a solvent, however not too many details on the findings were provided as the formed polymeric SEI species are practically the same as with FEC.

To the best of our knowledge, with the exception of the work of Jin et al., [36] no similarly in-depth study on the impact of VC on Si-based electrodes has been performed. This is likely the case why VC is not as popular as FEC for Si-based electrodes and early computational work already suggested the mechanisms for VC and FEC to be closely connected, which was later confirmed by the experimental studies discussed above.

For the sake of completeness, reports where FEC is utilized as an electrolyte additive can be found in references [45–47, 51–55, 60–62, 67, 69, 73, 75–77, 92–125] and reports utilizing VC as electrolyte additive can be found in references [40, 45, 47–49, 69, 71, 73, 75–77, 98, 99, 102–104, 106, 113, 115, 119, 122, 123, 126–132].

**Methylene Ethylene Carbonate (MEC):** Nguyen and Lucht studied MEC as electrolyte additive in different Si-based systems. When used in an amount of 10% in conventional electrolyte for Si/C composite electrodes, MEC was able to improve the cycling performance by a very similar extent as FEC. The authors found the formation of poly(MEC) on the negative
electrode surface while the additive did not significantly change the positive electrode.\cite{105} On Si nanoparticle-based electrodes, addition of 10% MEC to the conventional electrolyte also led to a very similar improvement as the addition of FEC. The authors were able to reduce, however not completely prevent electrode cracking and found the formed SEI to be rich in poly(MEC), Li$_2$CO$_3$ and lithium carboxylates.\cite{121}

5-Methyl-4-((trifluoromethoxy)methyl)-1,3-dioxol-2-one (DMVC-OCF$_3$) and 5-Methyl-4-((trimethylsilyloxy)methyl)-1,3-dioxol-2-one (DMVC-OTMS): Park et al. designed and synthesized the two VC-derived additives DMVC-OCF$_3$ and DMVC-OTMS and used them in a small amount of 0.5 wt% each together with VC in conventional electrolyte for NMC811|Si/C cells. Additives were found to alter the VC-based SEI in a way that significantly increases its flexibility and thus prevents particle fracture. Increased amounts of LiF and less signs of LiPF$_6$ decomposition were observed as well. Furthermore, the trimethylsilyl group of DMVC-OTMS was found to act as an HF scavenger, which effectively reduces transition metal dissolution and is thus beneficial for the cycling performance.\cite{106}

Trifluoropropylene Carbonate (TFPC): Hu et al. used TFPC as an additive in conventional electrolyte with Si nanowire electrodes and demonstrated that an addition of 10% of TFPC leads to a superior performance than an addition of 10% FEC. An effective SEI was formed that resisted fracture and thus more effectively protected the electrode. The authors attributed the improved performance to a favorable ratio of polyolefins to LiF, resulting in a mechanically stable SEI that effectively hinders salt and solvent decomposition.\cite{133}

Vinyl Ethylene Carbonate (VEC): Kennedy et al. studied VEC as an additive in conventional electrolyte for Si nanowire electrodes. While an addition of 3 wt% if VEC did lead to an improved cycling performance, the performance was highly

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**Scheme 3.** Possible reaction schemes based on the experimentally observed chemical motifs in electrolyte and SEI after cycling with Si-based electrode. Reproduced with permission.\cite{91} Copyright 2017, American Chemical Society.

**Figure 11.** Possible Si surface structures and their corresponding chemical shifts; R denotes an alkyl group. $^{29}$Si shifts of SiO$_x$ and Si species are summarized: crystalline silicon (c-Si) ~82 ppm; amorphous silicon (a-Si) ~40 to ~70 ppm. Reproduced with permission.\cite{36} Copyright 2018, American Chemical Society.
unstable with large fluctuations in capacity during prolonged cycling. Analysis of the SEI composition that VEC does not form poly(VC) on the electrode and therefore does not effectively protect the active material from irreversible consumption, which is evident by the increased amount of $\text{Li}_x\text{SiO}_y$ species found on electrodes cycled in the VEC containing electrolyte.\cite{115}

1,2,3-Trifluoroethyl Methyl Carbonate (FEMC) and Di(2,2,2-trifluoroethyl) Carbonate (DFDEC): Nguyen et al. studied FEC-based electrolytes for NMC532||Si/C cells under high voltage conditions and found an addition of 5% of FEMC to significantly improve the cycling performance due to an increase in CE. XPS analysis suggests that FEMC effectively reduces the transition metal dissolution from the positive electrode.\cite{45}

Jo et al. used 10% each of FEMC and DFDEC in conventional electrolyte with Si/C composite electrodes. They found DFDEC to result in a very similar performance increase compared to FEC while the cells with FEMC containing electrolyte performed slightly worse. They could however achieve a significant improvement over just FEC when an additional 1 wt% of DFDEC was added. The authors found an SEI rich in LiF and (organofluorophosphates, which they attributed to the presence of DFDEC.\cite{114}

1,2-Difluoroethylene Carbonate (DFEC): Shen et al. reported the use of 2% of DFEC in conventional electrolyte for NCA||SiO_x/C cells. Interestingly, they found a significantly improved cycling performance when 2% of DFEC were used and a drastic reduction in cycling performance when 3% were used. XPS results indicate that DFEC is strongly participating in SEI formation resulting in an increased amount of C-F species and $\text{Li}_2\text{CO}_3$ on the negative electrode surface. From reduced Si-O and SiO_x signals, the authors conclude that DFEC effectively stabilizes the silicon particles and prevents their degradation. Unfortunately, no comparison to the structurally very similar FEC is presented.\cite{135}

Lactic Acid O-Carboxyanhydride (lacOCA) and Diethyl Dicarbonate (DEDC): In a comparative additive study Nölle et al. designed an additive to combine beneficial effects of two additives, one of which was DEDC (see LAC for the other additive). When added in 2 wt% to a conventional electrolyte, it was demonstrated to significantly improve the cycling performance of NMC111||Si thin film cells. Giving slightly better results than the also studied LAC. Similar to LAC, addition of DEDC to the baseline electrolyte led to an increased ratio of lithium fluorophosphates to LiF as well as an increased amount of $\text{Li}_2\text{CO}_3$ in

Figure 12. Chemical structures of selected carbonyl-based electrolyte additives.

Figure 13. Chemical structures of selected salt-based electrolyte additives.

Figure 14. Chemical structures of selected phosphorus-based electrolyte additives.

Figure 15. Chemical structures of selected boron-based electrolyte additives.
the SEI. In order to combine the characteristics of both DEDC and LAC, the authors synthesized lacOCA and found that by using 2 wt% of lacOCA the cycling performance could be significantly increased as compared to the single additives DEDC and LAC, but also compared to a simple blend of both additives. XPS analysis revealed that the amount of lithium fluorophosphate species in the SEI was significantly reduced and evidence of simultaneous formation of poly(lactic acid) (PLA) and Li$_2$CO$_3$ as the main SEI components was found.\[136\]

2.3.2. Carbonyl-Based Additives

**Succinic Anhydride (SA):** Han et al. used 3 wt% of SA in a conventional electrolyte for Si thin film electrodes. They found a significant increase in the cycling performance and found an SEI that is rich in hydrocarbons and Li$_2$CO$_3$ and did not change significantly over prolonged 100 charge/discharge cycles. From low LiF content, the authors concluded that the formed SEI effectively hinders LiPF$_6$ decomposition.\[137\] Li et al. later applied a similar electrolyte to improve the cycling performance of Si/C nanofiber electrodes by increasing CE by 2% upon addition of SA.\[138\] Farmakis et al. used SA in conventional electrolyte as well as electrolyte based on the LiFAP salt anion with Si film electrodes. Contrary to other reports, they observed a significant decline in cycling performance as compared to the additive-free electrolyte, but do not elaborate why this might be the case.\[77\] Rezqita et al. used 5 wt% of SA in conventional electrolyte with Si/C composite electrodes. In their study, they observed a slightly better cycling performance of the SA containing electrolyte compared to the baseline electrolyte. The authors found increased amounts of lithium carbonate, ROCO$_2$Li, as well as LiF in the overall SEI composition. The increased amount of SA as compared to the other studies might be a reason for the different effect.\[139\]

**Carbon Dioxide (CO$_2$):** Krause et al. reported the use of CO$_2$ in conventional electrolytes with LCO|Si/C machine wound pouch cells. While highly impractical, because of excessive bloating of the pouch cells, the authors demonstrated an impressive improvement in cycling performance when CO$_2$ was used. They demonstrated a synergistic effect when additional FEC was added and that FEC could effectively slow down the gradual consumption of CO$_2$ during prolonged cycling. The authors attributed the beneficial effects of CO$_2$ to the formation of a thinner SEI and improved CE.\[139\] Later Hopkins et al. used a special pouch cell setup to add exactly 2.00 mL of CO$_2$ gas to the cells using conventional electrolyte and Si thin film electrodes with Li counter electrodes. They demonstrated that the presence of CO$_2$ leads to formation of more PEO-like species that are only loosely bound to the surface and washed away when the electrodes are rinsed. For the insoluble part of the SEI, the authors could show that CO$_2$ containing electrolyte forms a thinner, highly LiF rich SEI as compared to the CO$_2$-free electrolyte. Overall the SEI formed in CO$_2$ containing electrolyte is thinner and electronically insulating, resulting in an improved CE.\[139\]

**Sarc-N-CA, Ala-N-CA, and PhGly-N-CA:** Schmiegel et al. investigated three amino acid derived compounds 3-methyl-oxazolidine-2,5-dione (Sarc-N-CA), 3,4-dimethyloxazolidin-2,5-dione (Ala-N-CA), and 3-methyl-4-phenyloxazolidin-2,5-dione (PhGly-N-CA) that all share the same oxazolidine core structure with different substituents on the alkyl carbon. They were used as functional additives in conventional electrolytes and compared to 2 wt% FEC in machine wound NMC532|SiO$_2$/C pouch cells. It is worth pointing out that the authors adjusted the additive amounts to account for the differences in molar mass so that all electrolytes contained the same molar amount of additive rather than using the same weight fraction for all additives. Even though the difference in molar mass can lead to tremendous differences in additive concentration when different molecules are compared, it is usually ignored in additive studies. Sarc-N-CA showed very similar cycling performance to the FEC containing electrolyte with a rollover failure\[141\] setting in after approximately 200 charge/discharge cycles. Interestingly, for the other two additives (i. e. the ones bearing a substituent on the alkyl carbon atom), the rollover failure is delayed by 100 charge/discharge cycles. From a series of different analysis techniques, the authors conclude that the additives work by ring-opening polymerization with decarboxylation and thus generate effective SEI layers.\[96\]

**Lactide (LAC):** Nölle et al. designed an additive to combine the beneficial effects of two other additives, one of which was LAC (see lacOCA and DEDC). LAC is able to form effective layers by forming poly(lactic acid) (PLA). When added in 2 wt% to a conventional electrolyte, it was demonstrated to significantly improve the cycling performance of NMC111|Si thin film cells.
Studies of the formed SEI however, indicated that LAC is not able to completely prevent the decomposition of EC on the Si negative electrode. Furthermore, addition of LAC leads to an increased ratio of lithium fluorophosphates to LiF in the SEI.\textsuperscript{[116]}

**Pentafluorophenyl Isocyanate (PFPI):** Nölle et al. studied PFPI as an additive to conventional electrolytes for Si thin film electrodes in NMC111|Si cell configuration. The study demonstrated that addition of 2 wt% to the baseline electrolyte has a similarly beneficial effect as the addition of 2 wt% of VC or FEC. XPS analysis revealed PFPI to be a main part of the formed, presumably more flexible SEI. The authors propose a reductive polymerization reaction of the isocyanate functional group to be responsible. Interestingly, addition of PFPI lowers the CE of the cells by approximately 1% compared to the other additives without any significant negative effect on the discharge capacities. This effect was traced back to oxidative parasitic reactions on the positive electrode.\textsuperscript{[99]}

**Dimethylacrylamide (DMAA):** Zhu et al. found that the addition of 2.5 wt% of DMAA to a conventional, FEC containing electrolyte can significantly enhance the cycling performance of Si nanoparticle electrodes. DMAA decomposes at higher potentials than the other electrolyte components and thus effectively reduces their decomposition. The formed SEI has lower Li\(_2\)CO\(_3\) and higher ROCO\(_2\)Li contents.\textsuperscript{[101]}

**N,N-Dimethyl trifluoroacetamide (DMTFA):** Xu et al. studied conventional electrolytes with 2% of DMTFA as well as 1% of LiPF\(_2\)O\(_2\) in Si|SiS cells in comparison to a baseline electrolyte containing FEC. The authors found that unlike the baseline electrolyte, the additive containing electrolyte did not show any significant changes (neither optically, nor in NMR spectra) after storage at 60 °C for a week. Similarly, the authors were able to demonstrate a remarkable cycling performance of the full cells at 60 °C with no significant capacity loss within 2000 charge/discharge cycles and a remarkable rate capability. They found reduction of DMTFA additive to dominate the SEI chemistry, resulting in a uniform, N rich layer.\textsuperscript{[111]}

### 2.3.3. Li Salts as Functional Additives

**Lithium Bis(oxalato)borate (LiBOB):** Dalavi et al. used 5% of LiBOB in conventional electrolyte with Si thin film electrodes. The findings were mostly the same as with LiDFOB as an additive (see LiDFOB).\textsuperscript{[47]} Smart et al. used LiBOB as an additive in several electrolytes with Si/C electrodes. However, the variation of several components at the same time makes it difficult to conclude the specific effect of LiBOB.\textsuperscript{[40]} By adding 5% of LiBOB to different electrolytes with Si thin film electrodes, Dunn et al. were able to completely mitigate the drastic capacity fading they observed with their TPP and DMMP containing electrolytes. XPS measurement detected high amounts of oxalates and low amounts of LiF and borates in the SEI, which remains mostly unchanged upon prolonged cycling, indicating an effective SEI.\textsuperscript{[142]} Interestingly, when Rezqita et al. used 5% LiBOB to a conventional electrolyte for Si/C electrodes, initially the achievable capacity was the lowest of the considered electrolytes but increased upon continuous cycling and became the second highest after 100 charge/discharge cycles. The XPS analysis is found to be in agreement with previously reported findings.\textsuperscript{[129]}

In the work of Kennedy et al. where they used different additives in conventional electrolyte with Si nanowire electrodes, LiBOB showed a similarly strange fluctuating behavior in the cycling that they observed for VEC. Notably, in their XPS analysis, the authors found a small fraction of poly(VC) in the SEI despite the absence of any compounds that are known to form poly(VC). The other reported species in the SEI are in line with previous reports.\textsuperscript{[135]}

**Lithium Difluoro(oxalato)borate (LiDFOB):** Dalavi et al. used 1% of LiDFOB in conventional electrolyte with Si thin film electrodes. They found the addition of LiDFOB to improve the cycling performance and detected increased amounts of oxalates and lithium fluorophosphates as well as a reduced amount of LiF in the SEI.\textsuperscript{[47]} Lee et al. used 1 wt% LiDFOB as an additive for conventional electrolytes with Si/C composite electrodes and demonstrated an increased cycling performance at 45 °C in full cells. In their system, however, they detected a decreased amount of lithium fluorophosphates, indicating that LiDFOB mitigates decomposition of LiPF\(_6\).\textsuperscript{[143]} An et al. studied a number of different additives in high capacity NMC811|SiO\(_2\) cells. The baseline electrolyte used was a conventional LiPF\(_6\)/organic carbonate-based electrolyte that already contained several additives, one of which was LiDFOB. However, as boron-species were not analyzed, the specific impact of LiDFOB cannot be deduced due to the presence of numerous other additives.\textsuperscript{[100]}

**Lithium Nitrate (LiNO\(_3\)):** Etacheri et al. used LiNO\(_3\) as an additive in DOL-based electrolyte with Si nanowire electrodes. The addition of LiNO\(_3\) significantly increased the cycling performance, which could be correlated to a distinctively different SEI composition. In the case of LiNO\(_3\) containing electrolyte, the authors found organic fluorides to be the dominant fluorinated species with only 30% LiF content as opposed to 60% LiF content in the nitrate free electrolyte. The authors suggest that early reduction of LiNO\(_3\) to LiO and Li\(_2\)NO\(_3\) quickly passivates the electrode surface and LiNO\(_3\) promotes surface polymerization of DOL.\textsuperscript{[58]} Nguyen and Lucht used LiNO\(_3\) together with MEC and could thereby further improve the cycling performance of Si/C composite electrodes. The authors detected nitrate species as well as amine/ammonium species in the SEI of electrodes cycled in the presence of LiNO\(_3\). Furthermore, they found increased amounts of Li\(_2\)CO\(_3\) and a reduced amount of lithium alkyl carbonates in the SEI.\textsuperscript{[105]}

**Lithium Difluorophosphate (LiPF\(_2\)O\(_2\)):** Li et al. used LiPF\(_2\)O\(_2\) as an additive for conventional electrolyte with Si nanoparticle electrodes. They found the addition of 2% LiPF\(_2\)O\(_2\) dramatically increases the long-term cycling performance as compared to the LiPF\(_2\)O\(_2\) free baseline electrolyte. XPS analysis depicted an increase in the ratio of LiF to C-O, O-C = O and CO\(_3\) species with the electrolyte containing LiPF\(_2\)O\(_2\) additive, which results in a more stable SEI.\textsuperscript{[144]} Earlier, Xu et al. used LiPF\(_2\)O\(_2\) together with DMTFA and demonstrated a remarkable temperature tolerance of the resulting electrolyte and cells cycled with it. However, as a second additive was always present, the exact impact of LiPF\(_2\)O\(_2\) is difficult to judge in this case.\textsuperscript{[111]}

**Lithium Bis(fluorosulfone)imide (LiFSI):** An et al. studied a number of different additives in high capacity NMC811|SiO\(_2\) cells. The baseline electrolyte used was a conventional LiPF\(_6\)/organic carbonate-based electrolyte that already contained several additives, one of which was LiFSI. However, as another
sulfur containing additive was present in the baseline electrolyte, the specific impact of LiFSI cannot be deducted.[100]

$M(TFSI)_x$: Han et al. studied doping of Si electrodes by introduction of other metals by using TFSI salts as electrolyte additives in conventional electrolyte. The salts considered were $M(TFSI)_x$ with $M = \text{Li, Mg, Zn, Al, Ca}$. However, as this approach is more of an in situ modification of the active material rather than the SEI, the reader is referred directly to the publication.[92]

2.3.4. Phosphorus-Based Additives

Triphenyl Phosphate (TPP) and Dimethyl Methyl Phosphonate (DMMP): TPP was used by Smart et al. as a flame retardant additive in a variety of solvents with LiPF$_6$ and Si/C composite electrodes. The focus however was set on finding a suitable solvent composition to enable long-term cycling of Si/C electrodes and thus the particular effect of TPP was not investigated. Results regarding the flammability of the solvents were not reported either.[48] In two related studies, Dunn et al. investigated TPP and dimethyl phosphonate (DMMP) as flame retardant additives in conventional organic carbonate-based electrolyte in contents of 10%. They demonstrated that addition of LiBOB or FEC as coadditives enable reasonable cycling performance of Si thin-film and Si nanoparticle electrodes for the first 50 charge/discharge cycles and showed that TPP and DMMP do not significantly alter the SEI composition. However, a reduced flammability of the electrolytes was not demonstrated.[142,145]

Tris(trimethylsilyl) Phosphate (TTSP): An et al. studied a number of different additives in high capacity NMC811[$\text{SiO_x}$ cells. The baseline electrolyte used was a conventional LiPF$_6$/organic carbonate-based electrolyte that already contained several additives (see the sections on boron- and sulfur-based additives). Among the tested additives, addition of 0.5% of TTSP led to the best cycling performance of all tested additives with a retention of 84% of the initial capacity after 560 cycles as compared to 77% for the baseline electrolyte. However, as with the boron-based analogue TMSB, the authors attribute the improved performance primarily to effects of the silicon containing additives on the CEI rather than the SEI.[100]

Tris(trimethylsilyl) Phosphite (TMSPi): In an in-depth study, Liu et al. analyzed the effects of TMSPi on NMC811[$\text{Si/C}$ cells. Addition of 2 wt% TMSPi to a conventional, but FEC free electrolyte could significantly enhance the cycling performance. Detailed XPS analysis revealed that TMSPi participated in SEI formation, leading to the presence P-O-Si-based compounds, which the authors concluded to be stabilizing the SEI. Furthermore, they found evidence that in addition to contributing to the SEI layer, TMSPi acts as an HF scavenger and effectively reduces electrode cross-talk by suppressing PvdF degradation on the positive electrode.[146] Deng et al. combined TMSPi with FEC in a conventional electrolyte for NMC622[$\text{SiO_x/C}$ cells and demonstrated that a combination of 3% TMSPi with 5% of FEC resulted in the best cycling performance, which was significantly better than that of the baseline electrolyte as well as commercial electrolytes. TMSPi was found to actively participate in formation of both SEI and CEI.[97] Later, Haridas et al. studied similar electrolyte systems with NMC532[$\text{Si/PAN}$ cells, drawing similar conclusions. The authors reported TMSPi to reduce HF mediated transition metal loss and slow the rise in cell resistance on prolonged cycling while FEC helps in the formation of a uniform SEI.[100] The limited lifetime of TMSPi in LIB cells has been reported in.[547]

2.3.5. Boron-Based Additives

Tris(trimethylsilyl) Borate (TMSB): An et al. investigated different additives in high capacity NMC811[$\text{SiO_x}$ cells. The baseline used was conventional LiPF$_6$/organic carbonate-based electrolyte that already contained several additives. The cells containing 0.5 wt.% of TMSB showed a significant improvement in cycle performance compared to the baseline electrolyte, retaining 83% of the initial capacity after 560 charge/discharge cycles as compared to 77% for the baseline electrolyte. However, the authors attribute the improvement to a stabilization of the positive electrode and thus the cathode electrolyte interface (CEI) rather than the SEI.[100]

Tris(pentafluorophenyl)borane (TPFPB): TPFPB was used by Han et al. in up to 5% among other additives to improve the cycling performance of Si thin-film electrodes in LiClO$_4$/organic carbonate-based electrolyte. While the additive did not significantly influence the salt decomposition, it was able to significantly improve the cycling performance by reducing surface pulverization of the electrode. XPS results indicated that electrolyte decomposition, including additive, continues on prolonged cycling.[78]

2.3.6. Sulfur-Based Additives

1,3,2-Dioxathiolane-2,2-dioxide (DTD): Zhang et al. used different amounts of DTD in conventional FEC containing electrolyte with Si/C composite electrodes. 3 wt% was found to be the optimum amount which increased the cycling performance by mitigating electrode fracture and pulverization. XPS analysis suggested the formation of a thinner SEI containing sulfate and sulfonate species.[93] An et al. studied a number of different additives in high capacity NMC811[$\text{SiO_x}$ cells. The baseline electrolyte used was a conventional LiPF$_6$/organic carbonate-based electrolyte that already contained several additives. While an amount of 1.5 wt% DTD was able to increase long term cycling performance, the improvements of other Si-based additives were significantly better.[100]

Prop-1-ene-1,3-sultone (PES), Propylene Sulfite (PS), and Methylene Methanedisulfonate (MMDS): PS was one of the additives in the baseline electrolyte used by An et al. (see DTD). However, as the baseline electrolyte was not studied in detail, the specific impact of PS remains unclear. 0.5 wt% of PES was used as a coaditive together with 1 wt% of DTD. The addition of PES led to a slight decrease in cycling performance compared to DTD alone, which can be attributed to an altered SEI composition as revealed by XPS analysis. Addition of 0.5 wt% methylene methanedisulfonate (MMDS) initially leads to a slightly better cycling performance than the other sulfur-based additives.

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However, after 300 cycles, a much more severe capacity fading is seen, negating the initially better performance. Interestingly, MMDS leads to the lowest impedance of half cells compared to other sulfur containing additives and the best storage performance overall (i.e., least capacity loss of fully charged cells stored at 55 °C for 7 days). The authors attribute this to a decrease of parasitic reactions at the positive electrode, which could also be related to the change in capacity fading behavior of MMDS containing electrolyte.

1.3.2-Dioxathiane 2,2-dioxide (PCS): Xu et al. used 1% of PCS together with 1% of FEC in a conventional electrolyte with SiO/C|LNMO cells and could significantly improve the cycling performance. However, the improvement in SiO/C|Li cells was only minor, indicating that the effect mainly stems from the positive electrode. Nevertheless, the authors demonstrated that the electrolyte containing PCS effectively suppresses carbonate decomposition and thus gas generation on the negative electrode. XPS analysis revealed that the SEI contains sulfate and sulfonate species.

2.3.7. Silicon-Based Additives

Alkoxy Silanes: Ryu et al. used 5 wt% of methoxy methyl silanes with different numbers of methoxy groups in LiPF6/organic carbonate-based electrolyte to study the interfacial reactions on Si thin film electrodes. They found that the alkoxy silanes effectively suppressed electrolyte reduction and thus improved cycling performance, but only studied the initial 10 charge/discharge cycles.

Triethoxy Silane (TEOS): Aupperle et al. used TEOS as an additive in 5 wt% in conventional LiPF6/organic carbonate-based electrolyte. However, the study focuses strongly on the nitrile derivative TEOSCN and not much detail is given on the effects of TEOS.

(2-Cyanoethyl)tripethoxy Silane (TEOSCN): 5 wt% of TEOSCN in conventional electrolyte was utilized by Aupperle et al. to increase the cycling performance of Si-Alloy|NMC622 cells. They found that the formed SEI is rich in inorganic species, leading to the hypothesis that the formation of a polymeric network is potentially the cause of the increase in performance. The same authors demonstrated that addition of 1 wt% of TEOSCN to a conventional FEC and VC additives containing electrolyte increased the cycling performance of NMC622|Si-Gr cells dramatically at 45 °C. They found that TEOSCN effectively prevents transition metal dissolution on the positive electrode which otherwise leads to formation of MFx species on the negative electrode.

Vinyl Tris(2-methoxyethoxy) Silane (VTMS): VTMS was used as an additive in conventional organic carbonate-based electrolyte with Si/C composite electrodes by Wang et al. They found the optimum amount to be 5 wt% and demonstrated that the formed SEI is much thinner than in the baseline electrolyte, interfacial resistance significantly reduced and achievable reversible capacity overall higher, although the rate of capacity fading does not seem to be influenced by the presence of VTMS. XPS analysis of the electrodes after cycling revealed the presence of siloxane and oxysilane species in the SEI that were not detected in the baseline electrolyte.

3. Characterization Methods

In order to gain insight into the various processes and working mechanisms at the interface between Si-based electrodes and liquid electrolytes, a variety of complementary analytical techniques is necessary. Over the decades of research on LIBs, a set of techniques has become standard tools even though some of them are quite sophisticated in terms of equipment and analysis. Besides the obvious electrochemical techniques like galvanostatic cycling, electrochemical impedance spectroscopy (EIS), cyclic- and linear sweep voltammetry (CV and LSV), different electron microscopy techniques, energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) have become standard techniques due to the invaluable information they can provide on interfacial properties. However, the individual facets of the standard techniques in their different implementations are beyond the scope of this review. Readers are encouraged to read references for more details.

This section aims at highlighting selected non-standard analytical techniques and unusual implementations of standard techniques that have been employed in the study of interfaces and interphases on Si-based electrodes for LIBs.

3.1. IR/Raman Spectroscopy

A great advantage of IR-based techniques is their intrinsic non-destructiveness and the possibility to be employed in situ. Several groups have utilized attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to study the interfacial composition of Si-based electrodes under different conditions. Sum frequency generation vibrational spectroscopy (SFGVS) is an unusual technique where infrared and visible light are combined to gain information about the chemical composition of an interface as well as the orientation of molecules located at this interface. In a number of studies, Horowitz et al. used this technique under in operando conditions to study the chemical transformations taking place at the Si|electrolyte interface at different potentials as well as the influence of FEC on EC-based electrolytes and the adsorption behavior of the electrolyte constituents.

3.2. Atomic Force Microscopy (AFM)

Martin et al. used AFM to study the morphology of Si thin film electrodes after cycling in standard electrolytes with and without VC additive. They were able to show that the mean surface roughness increases on prolonged cycling due to crack formation. However, the increase in surface roughness was much less severe when VC was present in the electrolyte, indicating the formation of an effective SEI layer. Later, other groups used in situ AFM for in-depth studies of the SEI formation in the first cycle and demonstrated that the SEI formation is strongly impacted by the current rate of the first cycle and the most significant changes occur between 0.6 and 0.2 V versus Li/Li+ i.e., before Li is inserted into
the bulk Si material. In a unique benchmarking study, Han et al. used AFM-based techniques to study the physical, electrochemical, and mechanical properties of thin films of numerous inorganic compounds frequently encountered in the SEI on Si-based electrodes. Stetson et al. reported the use of AFM in contact mode to generate nm resolution 3D-resistivity maps of the SEIs formed on silicon wafers. They found that the resistivity to be relatively uniform in the lateral direction, but shows a steep decrease in the vertical direction towards the SEI/Si interface. Among several tested electrolytes, the FEC containing one resulted in the largest increase in SEI resistivity.

### 3.3. X-Ray Spectroscopy

Through the unique utilization of a combination of soft and hard X-rays generated from two synchrotron facilities, Philippe et al. were able to perform non-destructive depth-profiling by means of XPS and thereby monitoring the transformations on the silicon electrode surface as a function of the electrode potential. In a follow-up study, the authors demonstrated that the beneficial effect of LiFSI compared to LiPF 6 is a result of its lower sensitivity to hydrolysis. Because of that less HF is generated in case of LiFSI and lithium silicate as well as lithium oxide species on the surface are preserved, which in turn helps retaining the beneficial interactions of binder and active material. Young et al. later used hard X-ray photoelectron spectroscopy to compare the effects of FEC containing electrolytes on the SEI compared to standard electrolytes. They found that the SEI formed in the FEC-free electrolyte experienced the most pronounced changes in composition during prolonged cycling and concluded this to be the reason for the comparatively poor cycling performance.

Horowitz et al. used X-ray reflectivity together with sum frequency generation (SFG) and found that the orientation of solvent molecules, specifically of EC, in the first surface layer becomes more perpendicular to the surface with increasing FEC content of the electrolyte while the outer layers are unaffected and retain a parallel orientation.

### 3.4. Neutron Reflectivity

Jerliu et al. constructed a three-electrode cell for in operando neutron reflectivity (NR) experiments to study the lithiation of amorphous silicon electrodes and noticed the appearance of a several nanometer thin, lithium-rich layer upon de-lithiation. Later Veith et al. used a similar technique, but focused on the SEI rather than the bulk electrode. They were able to determine the SEI thickness as a function of lithiation degree and found it to be thinning upon lithiation and thickening upon de-lithiation. Previously, Veith et al. demonstrated that silicon reacts with a standard LiPF 6-based electrolyte without electrochemical influence and observed the formation of a 35 Å layer on the electrode. They pointed out that depending on the surface area of the silicon, this process could consume a significant portion of the electrode active material and thus lead to an irreversible capacity loss.

### 3.5. NMR Spectroscopy

Solid state nuclear magnetic resonance (ssNMR) spectroscopy has been employed to identify the chemical species formed on the surfaces of Si-based electrodes under different conditions. Delpuech et al. used a quantification technique for ssNMR spectra and found that the lithium salt degrades only in the first cycles and thus only accounts for a negligible part of the irreversible capacity loss. Furthermore, authors found that the amount of lithiated surface species grows upon continued cycling and concluded from 13C NMR spectra that more than two-thirds of the electrode’s mass gain stems from non-lithiated oligomers and polymers formed from the degradation of the organic carbonate solvents. In a quite elaborate study, Michan et al. used isotope labelled electrolyte components to identify distinct chemical species formed on the electrode surface depending on the applied voltage. Interestingly, they did not detect any fluorinated species except LiPF 6 and LiF even though other species are frequently reported in XPS studies. EC decomposition products were identified as main contributors to the SEI. In follow-up studies, Jin et al. studied the SEIs formed in pure FEC and VC electrolytes in comparison to standard electrolytes with and without 10% FEC as an additive. Large amounts of branched or cross-linked PEO in the case of FEC and VC electrolytes were identified, similar to the ones found in the additive containing standard electrolyte, but different from the species found in case of the standard electrolyte without additive. Furthermore, they did not detect fluorinated polymer species, which supports computational results suggesting FEC de-fluorination takes place prior to polymerization.

### 3.6. EPR Spectroscopy

By combining room temperature pulse radiolysis and matrix isolation continuous wave electron paramagnetic resonance (cwEPR) spectroscopy Shkrob et al. studied the FEC reduction mechanism in great detail. They were able to experimentally confirm the mechanistic difference in the one-electron reduction of non-fluorinated cyclic carbonates, which undergo a ring-opening, and the one-electron reduction of FEC, which undergoes de-fluorination and liberation of CO 2 while forming a vinylxyl radical. This in turn results in a higher degree of cross-linking in FEC derived polymers as compared to EC derived ones.

### 3.7. Microscopy

By applying a combination of cryogenic (scanning) transmission electron microscopy (cryo-(S)TEM) and electron energy loss spectroscopy (EELS) Huang et al. confirmed that the SEI on silicon undergoes dimensional changes on (de-)lithiation as was previously demonstrated by NR. They furthermore showed that in addition to the dimensional changes, the SEI undergoes chemical changes as well and confirmed the formation of poly(VC) as part of the SEI in the presence of FEC.
4. Concluding Remarks and Perspective

Compared to the well-established graphite-based negative electrode materials, that were subject to several decades of research and development, silicon-based negative electrode materials are still emerging technologies. The tremendous knowledge base gained from graphite-based and Sn-based electrode systems undoubtedly helped Si-based electrodes along significantly in the early stages of development, especially in the case of composite materials. However, due to its fundamentally different working mechanism, silicon still poses numerous significant challenges to be overcome. Tailoring the employed electrolyte to the unique requirements of silicon-based materials is only one of several directions being taken in order to overcome the numerous hurdles imposed by silicon. The main culprit of poor electrochemical performance, the dramatic volume change on (de-)lithiation coming with a highly dynamic interface against the electrolyte, is at the same time a large incentive to explore the potential of micro- and nanostructured materials and thus, a large fraction of the conducted research is dedicated to the silicon-based active materials themselves. Furthermore, it was realized that the electrode binders in silicon-based materials require tailoring in their own right.

In the end, the long sought-after breakthrough in the application of silicon-based materials as negative electrodes in LIBs will most likely not come from a singular of these directions, but rather from a synergistic combination of insights from all different paths of research.

Acknowledgements

This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No. 875548.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrolytes, functional additives, lithium salt, lithium-ion batteries, silicon electrode

Received: October 1, 2021
Revised: November 18, 2021
Published online: January 6, 2022

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