

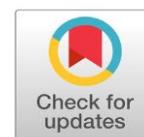


Review Article

A review on advanced functional electrolyte additives for silicon-based lithium-ion batteries

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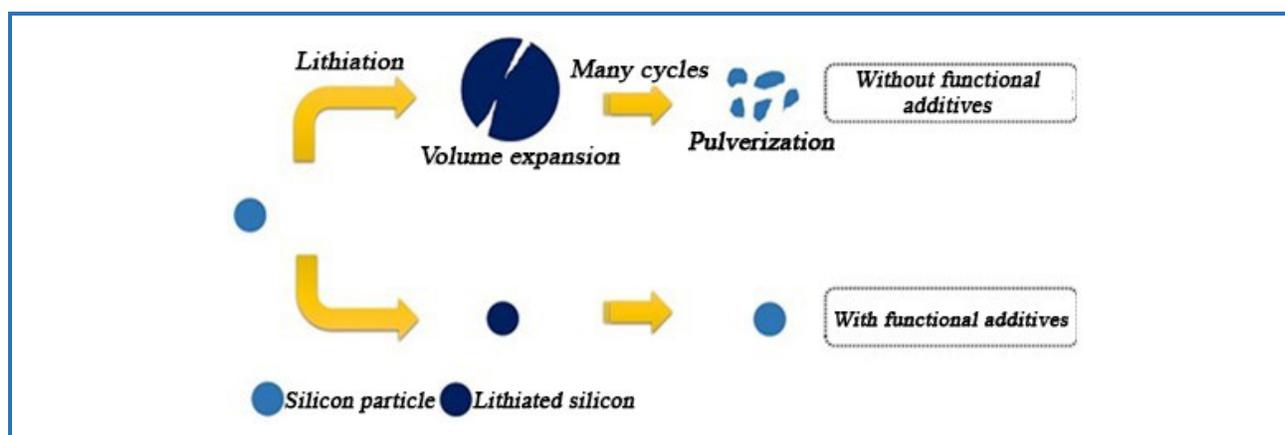
Lithium-ion battery
 Electrolyte additive
 Silicon anode
 Solid electrolyte interface

ABSTRACT

In last decades, many efforts have been made to commercialize the silicon (Si) as anode material with a capacity of ten times higher than that of conventional graphite anode to enhance the energy and power density of the state of the art lithium-ion batteries (LIBs). However, the Si anodes suffer from large volume expansion during the charge/discharge process and continuous formation breaking reformation process of solid electrolyte interface (SEI) layer that may cause poor cycle life, hindering the commercialization of the Si anode. Various strategies have been used to overcome the above-mentioned problems, and one of those strategies is the use of the functional electrolyte additives. Among these additives, fluoroethylene carbonate (FEC) has been known as the most effective additive for the Si-based LIBs. This was found to be attributed to the ability of this compound to form a robust and stable SEI layer on the Si surface. This review comprehensively studies the diverse additives used in Si-based LIBs in last years.

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Graphical Abstract



Biographies



Behrooz Mosallanejad received his BSc degree from Malayer University in Applied Chemistry. After that, he got his MSc degree at Amirkabir University of Technology (Tehran Polytechnic) in Analytical Chemistry. His studies are mainly focused on electrolyte of lithium-ion battery.

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Introduction

In recent years, the concerns on climate, environment, and human health problems due to the consumption of non-renewable fossil fuel have increased the number of research conducted on developing the sustainable and clean energies including solar and wind powers [1, 2]. One of the strategies to reduce the dependence on petroleum is the electrification of vehicles. The utilization of renewable energies meets the demand for conversion and storage devices [2]. Lithium-ion batteries (LIBs) are one of the most promising candidates for the storage device of electrical energy due to

their high voltage, high energy density, and cycleability [3, 4]. The state of the art LIBs consist of a graphite anode and a transition metal oxide cathode such as LiCoO_2 , LiMnO_2 , and LiFePO_4 which are soaked in a Li-ion rich electrolyte and disconnected by a separator [5, 6]. In addition to the electric vehicles (EVs), LIBs are vastly utilized in portable electronic devices including, laptop computers, cell phones, and digital cameras [3–5]. Low power density and energy density of conventional electrodes used in LIBs (the theoretical capacities of graphite anode and well-known cathodes are 372 mAh/g^{-1} and less than 200 mAh/g^{-1} respectively) have restricted some applications of the LIBs such as in EVs [1, 7]. To tackle with the aforementioned problems, tremendous efforts have been made. For instance, alloy-type anode materials have been explored due to their high theoretical capacity [8, 9]. Among the alloy-type anode materials, silicon (Si) has achieved incredible attention as anode material in recent years due to the following reasons: (I) Si possesses a capacity of 4200 mAh/g^{-1} upon full lithiation to $\text{Li}_{22}\text{Si}_5$ which is 10 times higher than that of the graphite electrode, (II) Si shows a relatively low discharge potential at about 0.4 V versus Li^+/Li which can be paired with a high voltage cathode to form a full LIB with high working voltage, and (III) Si is copious in earth's crust and other merits of Si are environment friendly, cheapness, and non-toxic [10–12]. There are some bottlenecks that may put off the use of Si as anode material in LIBs. During complete lithiation of Si, a dramatic volume expansion (more than 300%) may occur which causes pulverization of Si morphology. Successive volume changes and pulverizations led to loss of the electrical path between the active material and current collector and also the continuous formation breaking reformation process of the solid electrolyte interface (SEI) layer (Figure 1). All these issues hasten electrode collapse and capacity fading [11, 12]. Tremendous efforts have been made to tackle these issues. Using Si particles in nano-scale, compositing of Si with stress-relief buffer matrix, and also designing of new binders can diminish the effects of the problems in Si [12].

Apart from these strategies, engagement of the functional electrolyte additives or SEI additives can improve the performance of Si electrode [13, 14]. The SEI additives have a higher reduction potentials than those of carbonate solvents, so they can form a robust and stable passivation layer on the surface of Si [6, 15, 16]. In recent years, a great deal of attention has been given to electrolyte additives as one of the avenues to resolve the problems of Si anode. Figure 2 depicts the number of publications from 2006 to 2019 on the use of electrolyte additives in Si-based LIBs, showing rapid growth in the research activity of electrolyte additives for Si anode.

SEI additives have been playing a vital and important role in graphite-based LIBs [17–19]. Therefore, they have been widely used for improving the performance of Si-based LIBs. Although part of some review papers investigated the functional additives for Si anodes [11, 20], in this review, we intend to present a comprehensive studying on the functional additives used in Si-based LIBs. A

variety of SEI additives have been examined in recent years. The fluoroethylene carbonate (FEC) [21], vinylene carbonate (VC) [22], succinic anhydride (SA) [23], and lithium bis(oxalato)borate (LiBOB) [24] are the most well-known additives which can promote the performance of Si through the formation of a passivation layer (Figure 3).

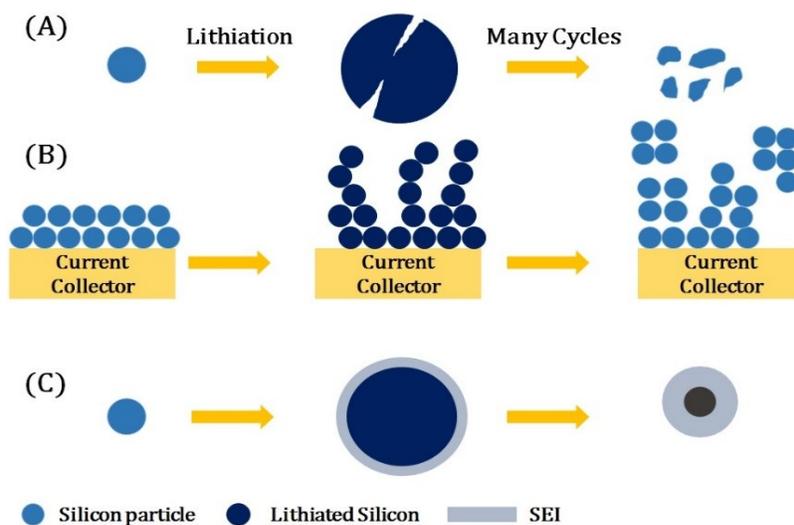


Figure 1. The different failure mechanisms of Si anode: A) electrode pulverization, B) collapse of the entire electrode, and C) the continuous formation-breaking-reformation process of the SEI layer

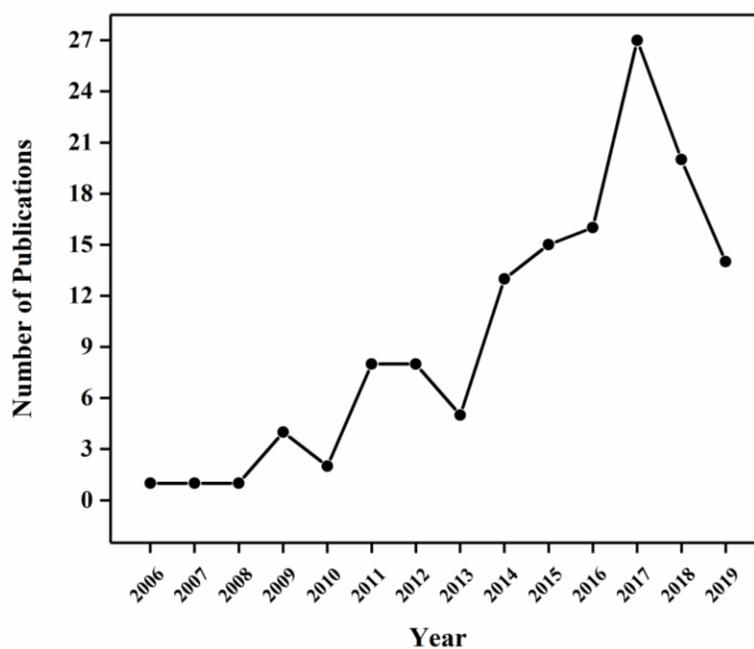
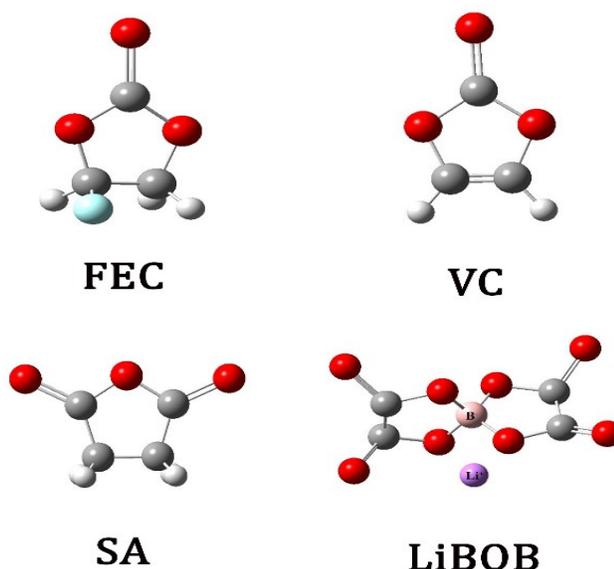


Figure 2. Evolution of publications on the using of electrolyte additives in Si-based LIBs. The keywords used in this evolution were: lithium-ion battery and silicon anode and electrolyte additive (last Scopus data updated on 29/06/2019)

Figure 3. Chemical structures of the most well-known electrolyte additives for Si anode



Nitrogen-containing additives

Pentafluorophenyl isocyanate (PFPS) is a nitrogen-containing additive used to improve the performance of Si anode [25, 26]. Many reports revealed that additives containing isocyanate group can undergo reductive polymerization reaction, forming a passivation layer on the graphite anode which prevents further reduction of electrolyte [27, 28]. *Nolle et al.* [25] found that addition of 2 wt% PFPS to ethylene carbonate (EC): diethyl carbonate (DEC) (3:7, weight ratio) containing 1 M lithium hexafluorophosphate (LiPF_6) as baseline electrolyte significantly improves capacity retention and coulombic efficiency (CE) of Si/NMC111 full cell after 103 cycles. It was believed that PFPS could compete with FEC and VC highly used additives. The ability of this additive to improve the performance of the Si electrode was evaluated by XPS. The existence of isocyanate group enables additive to undergo an electron-induced reductive polymerization and form a passivation layer on the Si surface, which may prevent further reduction of the electrolyte [25]. Addition of 2.5 wt% dimethylacrylamide (DMAA) to 1 M LiPF_6 EC:DEC:FEC:dimethyl carbonate (DMC) (3:3:1:3, weight ratio) electrolyte can form a low-impedance and compact SEI layer on the Si electrode, which improves the performance of battery after 500 cycles [26].

Succinic anhydride

SA is one of the most well-known additives for graphite-based LIBs [29, 30]. *Han et al.* [23] introduced a thin-film Si electrode in 1 M LiPF_6 EC:DEC (1:1, volume ratio) with 3 wt% SA. The half-

cells without and with SA respectively showed 40% and 80% discharge capacity retentions after 100 cycles compared to their initial discharge capacities. The good performance of the electrode with SA was arisen from a smooth SEI layer formed by this additive. In contrast, due to the pulverization and consecutive SEI formation-deformation process, the SEI layer originated from electrolyte without additive had a porous morphology, causing the poor performance of the thin-film Si electrode [23]. The effect of SA on the performance of Si/C composite nanofiber was investigated [31]. The composite electrode containing 3 wt% SA in 1 M LiPF₆ EC:DMC:DEC (1:1:1, volume ratio) electrolyte achieved an 802 mAh/g⁻¹ discharge capacity and 82.8% discharge capacity retention compared to its initial capacity after 50 cycles which were higher than that of electrolyte without additive with 598 mAh/g⁻¹ discharge capacity and 63% discharge capacity retention [31].

Silane-based additives

Silane-based additives are the other family of SEI additives used to modify the surface of the Si electrode through the formation of a passivation layer [32–34]. One of the reasons for the irreversible capacity loss in Si electrode is that the surface of Si consists of silicon oxide (-Si-O-Si-) and silanol (-Si-OH) which can reductively react with lithium ions and cause irreversible capacity loss. Therefore, silane-based additives can form a siloxane network on the Si electrode, suppressing the reaction between Si and electrolyte and subsequently reducing the capacity loss [34]. Song et al. [33] evaluated the effect of trimethoxy methyl silane (TMMS) as an electrolyte additive on the performance of Si thin-film on the stainless steel (Si/SS) substrate. They found that, addition of 5 wt% TMMS to the 1 M LiPF₆ EC:DEC (1:1, volume ratio) can increase the capacity retention of the electrode from 17% in electrolyte without additive to the 84% in the electrolyte with additive [33]. Recently, vinyl tris(2-methoxyethoxy) silane (VTMS) was utilized in 1 M LiPF₆ EC:EMC (3:7, weight ratio) baseline electrolyte [32]. It is reported that addition of 5 wt% VTMS to the baseline electrolyte can significantly promote the charge capacity of Si/C composite electrode from 503.3 mAh/g⁻¹ in the baseline electrolyte to 584.6 mAh/g⁻¹ after 50 cycles. The improvement of charge capacity was attributed to the ability of VTMS to form SEI layer on the surface of the composite. The XPS of the Si 2p spectrum of the fresh electrode (electrode before cycling) showed three peaks in 104, 103.2, and 99.6 eV which were attributed to the SiO₂, SiO_x-Si, and Si-Si bondings respectively. These three peaks were not found in the spectrum of electrode cycled in the baseline electrolyte. In contrast, the cycled electrode in the 5 wt% VTMS electrolyte showed two new peaks in 102.5 and 101.5 eV, which were ascribed to the C-Si-O and Si-O-Si bondings [32].

Vinylene carbonate

Vinylene carbonate is widely used in graphite-based LIBs as a commercial functional electrolyte additive [35]. However, there are only handful articles, which reported the effect of this additive on the Si-based LIBs. *Chen et al.* [36] added 1 wt% VC to the 1 M LiPF₆ EC:DMC (1:1, volume ratio) electrolyte to promote the performance of Si film anode. The reversible capacity of Si electrode in VC-containing electrolyte kept over 50% of the first charge capacity even up to 500 cycles, but, in VC-free electrolyte, the electrode can not cycle at all after 200 cycles. Except in the initial three cycles, the CEs of the cell with VC in other cycles were about 100%. The semiquantitative analysis of the XPS spectra of the SEI layer formed by electrolytes without and with VC revealed that the contents of the F and P elements in VC electrolyte were lower than that of VC-free electrolyte. The F element is arisen from the LiF and PF₅ components, and the P element is derived from PF₅. Therefore, the SEI layer formed in VC-containing electrolyte had lower LiF content which eventuated to the lower SEI film impedance and better performance of Si film electrode [36].

Fluoroethylene carbonate

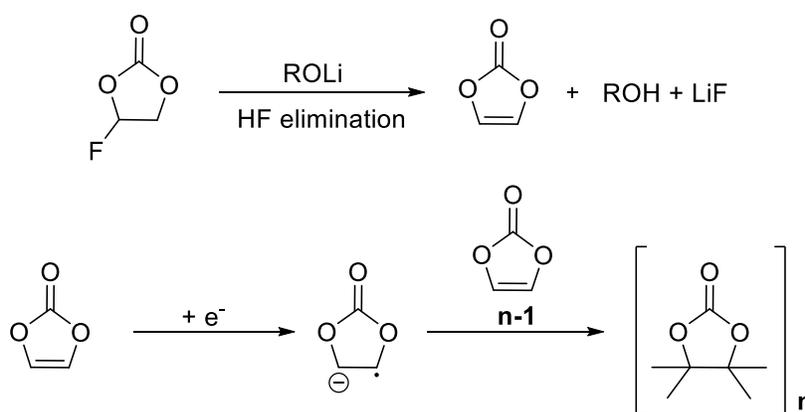
FEC has been found as a versatile additive for LIBs [37]. Also, it can be used for improving the performance of the Si electrode. For the first time, *Choi et al.* [38] found that addition of 3 wt% FEC to the 1.3 M LiPF₆ EC:DEC (3:7, volume ratio) electrolyte significantly improved the discharge capacity retention and CE of Si thin-film electrode. The Si thin-film electrode without and with additive showed the capacity discharge retention of 67.9 and 88.5% respectively after 80 cycles [38]. Compared to other additives, FEC has been known to be the most effective electrolyte additive for Si anode. The cycling performance and SEI composition of Si nano-particle anodes in electrolytes with 5-25 wt% FEC and 3-6 wt% VC have been separately compared. It is found that the Si anodes containing 10-15 wt% FEC show the smallest impedance and also best capacity retention [39].

Addition of fluorine atom to the EC molecule can improve the physical and electrochemical properties such as cathodic and anodic stabilities, liquidous temperature range, and flame retardancy property. FEC possesses a less lowest unoccupied molecular orbital (LUMO) energy level compared to the EC, so FEC readily accepts electrons from the anode, reduces before the reduction of EC, and forms SEI layer. Moreover, it has a lower highest occupied molecular orbital (HOMO) energy level compared to the non-fluorinated carbonate solvents and shows higher resistance towards oxidation. Therefore, these properties make FEC suitable to use as solvent or co-solvent for Si anode [11]. *Chun et al.* [40] depicted that the use of FEC instead of EC as a solvent could promote the electrochemical performance of the Si anodes in ambient and high temperatures. The carbon-coated porous Si anodes in 1.3 M LiPF₆ FEC: ethyl methyl carbonate (EMC) (3:7, volume ratio) achieved the reversible Li extraction capacity of 2200 mAh/g⁻¹ at 30 °C and 1500 mAh/g⁻¹ at 60 °C after 100 cycles which were

higher than that of Si electrodes in 1.3 M LiPF₆ EC:EMC (3:7, volume ratio) electrolyte. The cross-sectional scanning electron microscopy (SEM) images of carbon-coated porous Si anodes in EC-based and FEC-based electrolytes showed 405% and 200% volume expansion after 100 cycles respectively. This exhibits the ability of SEI-derived FEC in suppressing the volume changes of Si anode during cycling [40]. Moreover, a comparative study of four LiPF₆-based electrolyte solutions containing four cyclic carbonates including FEC, EC, propylene carbonate (PC), and 3,4-trans-difluoroethylene carbonate (DFEC) showed that the cycling stability of Si electrodes decreases in the following order that FEC-based electrolyte had the best ability to form passivation layer on the Si electrode: FEC-based>DFEC-based>EC-based>PC-based [41].

The good role of FEC in the improvement of the performance of Si-based LIBs should be explored in the nature and composition of the SEI layer formed by this compound. Many literatures concluded that the SEI layer formed as a result of FEC reduction is predominantly comprising lithium fluoride (LiF) and lithium oxide. According to the proposed mechanism of reduction of FEC by Aurbach (Scheme 1), during the elimination of HF, LiF and VC are formed that VC readily polymerizes *via* its double bond to form polycarbonate species on the Si anode [42, 43].

Yao et al., compared the performance of Si-composite anodes using FEC as the co-solvent (50 wt%) with the electrolyte using FEC as the additive (10 wt%). The studied electrolytes were 1 M LiPF₆ in EC:DEC:FEC (45:45:10, weight ratio), 1 M LiPF₆ in EC:FEC (1:1, weight ratio), and 1 M LiPF₆ in DEC:FEC (1:1, weight ratio). Among the samples, the DEC:FEC electrolyte delivered highest specific capacity and the best capacity retention after 500 cycles, which showed that the FEC in the role of co-solvent exhibits the better performance than that of the additive role [43].



Scheme 1. Possible mechanism of FEC reduction suggested by Aurbach

Boron-containing additives

LiBOB is the most well-known boron-containing compound, which was investigated as an additive and also salt in Si-based LIBs. The Si thin-film electrodes in EC:DEC (3:7, volume ratio) with two different salts of 1.3 M LiPF₆ and 0.7 M LiBOB showed the capacity retentions of 50.8% and 83.5% respectively after 100 cycles. Due to the fact that LiBOB could lessen consumption of lithium ions through trapping of them in the Si electrode which forms a surface layer, the irreversible capacity and cycling performance were improved [24]. Furthermore, Han et al. [44] reported tris(pentafluorophenyl) borane (TPFPB) as a new electrolyte additive for Si thin-film anodes. It was suggested that addition of 5 wt% TPFPB to the 1 M lithium perchlorate (LiClO₄) EC:DEC (1:1, volume ratio) could deliver twofold capacity retention and also higher CE after 100 cycles compared to the electrolyte without additive. The key role of TPFPB in improving the performance of Si thin-film electrode was attributed to formation of a stable SEI layer by TPFPB, suppressing the surface pulverization [44]. Lithium fluoromalonato(difluoro)borate (LiFMDFB) was known as a dual-function additive for Si-based LIBs. LiFMDFB has the potential to form a stable cathode electrolyte interface (CEI) on Li-rich cathodes and it can be paired with a SEI-forming additive such as FEC in a full-cell battery. Si-graphite composite (SGC)/Li_{1.17}Ni_{0.17}Mn_{0.5}Co_{0.17}O₂ full-cell with 1.3 M LiPF₆ in EC:EMC:DMC (3:4:3, volume ratio) containing 5 wt% FEC as SEI additive and 1 wt% LiFMDFB as CEI additive showed an improved capacity retention of 85%, a high CE of 99.5%, and an excellent energy density of 400 Wh/kg⁻¹ after 100 cycles [45].

Other functional additives

In addition to the aforementioned well-known additives, some other functional additives were also investigated to improve the performance of Si-based LIBs. Improving the performance of Si-graphite/Li half-cell and Si-graphite/NMC111 full-cell was fulfilled through the addition of 0.5 wt% LiNO₃, 5-10 wt% methylene ethylene carbonate (MEC), or 10 wt% FEC additives to the 1.2 M LiPF₆ EC:DEC (1:1, weight ratio) standard electrolyte. The cells with an electrolyte containing LiNO₃, MEC, or FEC additives were achieved to the high capacity retention of almost 88%, while the cell with standard electrolyte showed the lower capacity retention of 64% after 100 cycles [13].

The new salt, lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide (LiTDI), was evaluated for nano-Si composite electrodes. The Si electrode with the electrolyte formulation of 0.6 M LiTDI in EC:DMC:FEC:VC (25:50:5:1, volume ratio) could cycle for more than 100 cycles at 1200 mAh/g⁻¹ and a CE of 99%. The characterization analysis of the SEI layer exhibited that in addition to the kinds of carbonates formed by EC and DMC decomposition, a high LiF content and polycarbonates existed in the SEI layer. The LiTDI in combination with FEC and VC additives can be elected as a new and promising salt for Si electrodes in future LIBs [46].

The exceptional performance of Si nanowire (SiNW) electrodes in 1,3-dioxolane (DOL)-based electrolytes including DOL/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and DOL/LiTFSI-LiNO₃ solutions was demonstrated which DOL could be used lonely with LiTFSI or in conjunction with LiNO₃. After 1000 charge-discharge cycles, the SiNW electrodes in DOL/LiTFSI (1 M) and DOL/LiTFSI (1 M)-LiNO₃ (0.1 M) electrolytes delivered a reversible capacity of 1275 and 575 mAh/g⁻¹, whereas the 1 M LiPF₆ in EC:DMC (1:1, volume ratio) as standard electrolyte showed only 20 mAh/g⁻¹ [47].

A 5 V high energy density pouch cell based on SiOC (SiO and carbon compound)/LNMO (LiNi_{0.5}Mn_{1.5}O₄) was assembled and tested containing 1 M LiPF₆ in SL (sulfone):EMC (3:7, weight ratio) electrolyte with 8 wt% FEC additive. Higher anodic stability of SL solvent respect to the EC in the vicinity of high-voltage cathodes like LNMO and the ability of FEC additive to form SEI layer on Si anode caused that the CE of full-cells in SL-based became higher than that of EC-based electrolyte. The CE of full-cells in SL-based and EC-based electrolytes were 90% and 80% respectively [48].

The 1 M LiPF₆ in EC:DEC:EMC (1:1:1, volume ratio) electrolyte containing 1 wt% FEC and also 1 wt% 1,3-propanediolcyclic sulfate (PCS) exhibited an effective electrolyte formulation for SiO_x-C/LNMO full-cells. The full-cells in electrolytes without and with additives showed the discharge capacity retentions of 43.3% and 100.4% respectively after 100 cycles at 0.2 C rate [49]. Table 1 lists available articles in which different additives are reported for Si-based LIBs.

Table 1. Available articles on the using of different additives for Si-based LIBs

Author	Cell architecture	Case-study electrolytes	Achievement	Ref
Ryu et al. (2008)	Si/Li	1.3 M LiPF ₆ in EC:DEC (3:7, volume ratio) containing 5 wt% monomethoxy trimethyl silane, 5 wt% dimethoxy dimethyl silane, or 5 wt% trimethoxy methyl silane additives	Addition of additives possessing alkoxy silane functional groups suppressed the mass accumulation to the Si electrode and improved the cycle life	[34]
Etacheri et al. (2011)	SiNW/Li	1 M LiPF ₆ in EC:DMC (1:1, weight ratio), 1 M LiPF ₆ in DMC+10% FEC, 1 M LiPF ₆ in EC:DMC (1:1, weight ratio)+10% FEC	The reversible capacity for FEC-free, DMC+FEC, and EC+DMC+FEC electrolytes were 343, 1224, and 1159	[42]

			mAh/g ⁻¹ respectively after 30 cycles
<i>Nakai et al.</i> (2011)	Si thin-film/Li	1 M LiPF ₆ in EC:DEC (1:1, volume ratio), 1 M LiPF ₆ in FEC:DEC (1:1, volume ratio)	The half-cells in EC and FEC-based electrolytes showed 2.8 Ah/g ⁻¹ after 30 cycles and 3.25 Ah/g ⁻¹ after 50 cycles respectively [50]
<i>Lin et al.</i> (2011)	Si nano particles (SiNP)/Li	1 M LiPF ₆ in EC:DMC (1:1, volume ratio), 1 M LiPF ₆ in FEC:DMC (1:1, volume ratio), 1 M LiPF ₆ in FEC:EC:DMC (1:1:2, volume ratio)	The reversible capacity for FEC-free, 50% FEC, and 25% FEC electrolytes were 1157, 2573, 2165 mAh/g ⁻¹ after 100 cycles [51]
<i>Elazari et al.</i> (2012)	Si thin-film/TiS ₂ composite	1 M LiPF ₆ in FEC:DMC (1:4, weight ratio)	The full-cell delivered an approximately charge and discharge capacities of 180 mAh/g ⁻¹ after 300 cycles at 0.2 C rate [52]
<i>Fridman et al.</i> (2013)	Si thin-film/LiNMO	1 M LiPF ₆ in FEC:DMC (1:4, weight ratio)	The full-cell showed the capacity retention of 92.2% after 200 cycles, 88.5% after 300 cycles and 74.2% after 500 cycles at 0.5 C rate [53]
<i>Fridman et al.</i> (2013)	Si thin-film/ xLi ₂ MnO ₃ ·(1-x) LiNi _y Mn _z Co _{1-y-z} O ₂	1 M LiPF ₆ in FEC:DMC (1:4, weight ratio)	The full-cell showed a discharge capacity of 195 mAh/g ⁻¹ and cycling efficiency of 99.5% after 200 cycles at C/8 rate [54]
<i>Eom et al.</i> (2013)	SGC/Ni _{0.8} Co _{0.15} Al _{0.05} O ₂ (NCA)	1 M LiPF ₆ in EC:DEC (1:1, weight ratio) containing 10 wt% FEC	The discharge capacity obtained for full-cells without and with FEC were ~106 and ~112 mAh/g ⁻¹ [55]

<i>Bordes et al.</i> (2014)	SGC/ NCA	1 M LiPF ₆ in EC:DEC (1:1, weight ratio) containing 5-20 wt% FEC	respectively after 50 cycles at 0.5 C The optimized content of FEC was 5 wt% which showed the highest capacity and the most stable cyclability	[56]
<i>Young et al.</i> (2015)	Binder-free Si/Li	1.2 M LiPF ₆ in EC, 1.2 M LiPF ₆ in FEC, 1.2 M LiPF ₆ in EC:FEC (85:15, weight ratio)	The FEC-based electrolytes showed higher capacity retention after 5 cycles compared to the EC-based electrolyte	[57]
<i>Xu et al.</i> (2015)	SiNP/Li	1 M LiPF ₆ in EC:DEC (50:50, weight ratio), 1 M LiPF ₆ in EC:DEC:FEC (45:45:10, weight ratio)	The capacity loss for FEC-free and FEC-based electrolytes were 30% and 5% after 80 cycles respectively	[58]
<i>Hy et al.</i> (2015)	Si/Li	1 M LiPF ₆ in EC:DEC (1:1, volume ratio) containing 2 wt% VC	The Si anode with the Al ₂ O ₃ coating and VC additive had a capacity of 630 mAh/g ⁻¹ after 200 cycles, while the anode without coating and additive showed only 400 mAh/g ⁻¹ after 50 cycles	[59]
<i>Uchida et al.</i> (2015)	Si/NMC111	1 M LiPF ₆ in EC:DMC (1:1, volume ratio) containing 10 wt% FEC	The full-cell with additive achieved a CE of 99.6% after 100 cycles	[22]
<i>Nguyen et al.</i> (2016)	Si-graphite/ NMC532	1 M LiPF ₆ in EC:EMC (3:7, volume ratio), 1 M LiPF ₆ in FEC:DEC (1:1, volume ratio), 1 M LiPF ₆ in FEC:DEC (1:1, volume ratio) with 3 wt% VC, 1 M	Among the electrolytes, the full cell with blended additives of VC and FEMC showed the best performance with the	[60]

		LiPF ₆ in FEC:DEC (1:1, volume ratio) with 3 wt% VC and 5 wt% methyl (2,2,2-trifluoroethyl) (FEMC) carbonate	discharge capacity retention of 83% after 100 cycles
Fears et al. (2015)	Si/Li	1.2 M LiPF ₆ in EC:DMC (3:7, volume ratio), 0.1 M LiTFSI in dimethyl perfluoroglutarate (PF5M ₂)	The Si/Li half-cell in PF5M ₂ as a fluorine-rich electrolyte solvent showed higher delithiation capacity retention compared to the EC-based electrolyte after 25 cycles [61]
Xu et al. (2015)	Si/Li	1 M LiPF ₆ in EC:DMC (1:1, volume ratio) + 10% FEC additive, 1 M LiPF ₆ in EC:DMC (1:1, volume ratio) + 1% lithium difluorophosphate (LiPO ₂ F ₂) and 2% <i>N,N</i> -dimethyltrifluoroacetamide (DMTFA) additives	At 60 °C, the half-cell with LiPO ₂ F ₂ and DMTFA additives showed almost no capacity loss after 100 cycles but a capacity retention of 73.3% was achieved for FEC-based electrolyte [62]
Schroder et al. (2015)	Si thin-film/Li	1 M LiPF ₆ in EC:DEC (1:1, weight ratio), 1 M LiPF ₆ in EC:DEC:FEC (45:45:10, weight ratio)	The electrode cycled in EC-based and FEC-based electrolytes showed 1252 and 3000 mAh/g ⁻¹ capacity respectively after 100 cycles [63]

Conclusions

The engagement of functional electrolyte additives to resolve the volume expansion and pulverization problems in Si anode have captured more attentions in recent years. This review aimed at presenting a comprehensive study of well-known additives used in Si-based LIBs. Among these additives, the FEC has been known to be the most effective additive for Si anodes. Addition of a low amount of FEC additive to the electrolyte can suppress the volume expansion of Si and promote the

performance of Si-based LIBs. Incorporation of fluorine atom to the EC chemical structure improves the physical and electrochemical properties of this conventional solvent, and in addition to the role of FEC as an additive, this compound can be used as solvent or co-solvent in Si-based LIBs to diminish the destructive effects of volume expansion and pulverization phenomena.

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Abbreviations

<i>Si</i>	<i>Silicon</i>
<i>LIBs</i>	<i>Lithium-ion batteries</i>
<i>SEI</i>	<i>Solid electrolyte interface</i>
<i>FEC</i>	<i>Fluoroethylene carbonate</i>
<i>EVs</i>	<i>Electric vehicles</i>
<i>SA</i>	<i>Succinic anhydride</i>
<i>LiBOB</i>	<i>Lithium bis(oxalato)borate</i>
<i>VC</i>	<i>Vinylene carbonate</i>
<i>PFPS</i>	<i>Pentafluorophenyl isocyanate</i>
<i>EC</i>	<i>Ethylene carbonate</i>
<i>DEC</i>	<i>Diethyl carbonate</i>
<i>LiPF₆</i>	<i>Lithium hexafluorophosphate</i>
<i>CE</i>	<i>Coulombic efficiency</i>
<i>DMAA</i>	<i>Dimethylacrylamide</i>
<i>DMC</i>	<i>Dimethyl carbonate</i>
<i>TMMS</i>	<i>Trimethoxy methyl silane</i>
<i>VTMS</i>	<i>Vinyl tris(2-methoxyethoxy) silane</i>
<i>EMC</i>	<i>Ethyl methyl carbonate</i>
<i>LUMO</i>	<i>Lowest unoccupied molecular orbital</i>
<i>SS</i>	<i>Stainless steel</i>
<i>HOMO</i>	<i>Highest occupied molecular orbital</i>
<i>-Si-O-Si-</i>	<i>Silicon oxide</i>
<i>-Si-OH</i>	<i>Silanol</i>
<i>SEM</i>	<i>Scanning electron microscopy</i>
<i>LiClO₄</i>	<i>Lithium perchlorate</i>

<i>TPFPB</i>	<i>Tris(pentafluorophenyl) borane</i>
<i>LiFMDFB</i>	<i>Lithium fluoromalonato(difluoro)borate</i>
<i>LiF</i>	<i>Lithium fluoride</i>
<i>DFEC</i>	<i>3,4-Trans-difluoroethylene carbonate</i>
<i>SGC</i>	<i>Si-Graphite composite</i>
<i>MEC</i>	<i>Methylene ethylene carbonate</i>
<i>SiNW</i>	<i>Si nanowire</i>
<i>PCS</i>	<i>1,3-Propanediolcyclic sulfate</i>
<i>LiTFSI</i>	<i>Lithium bis(trifluoromethanesulfonyl)imide</i>
<i>LiTDI</i>	<i>Lithium 4,5-dicyano-2-(trifluoromethyl)imidazolidide</i>

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