

Recent Advances toward High Voltage, EC-free Electrolytes for Graphite-based Li-ion Battery

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Abstract:

Lithium-ion batteries are a key technology in today's world and improving their performances requires, in many cases, the use of cathodes operating above the anodic stability of state-of-the-art electrolytes based on ethylene carbonate (EC) mixtures. EC, however, is a crucial component of electrolytes, due to its excellent ability to allow graphite anode operation - also required for high energy density batteries - by stabilizing the electrode/electrolyte interface. In the last years, many alternative electrolytes, aiming at allowing high voltage battery operation, have been proposed. However, often, graphite electrode operation is not well demonstrated in these electrolytes. Thus, we review here the high voltage, EC-free alternative electrolytes, focusing on those allowing the steady operation of graphite anodes. This review covers electrolyte compositions, with the widespread use of additives, the change in main lithium salt, the effect of anion (or Li salt) concentration, but also reports on graphite protection strategies, by coatings or artificial SEI or by use of water-soluble binder for electrode processing as these can also enable the use of graphite in electrolytes with suboptimal intrinsic SEI formation ability.

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Table 1. Acronyms of chemicals

ACRONYM	NAME
<i>ADN</i>	adiponitrile
<i>DEC</i>	diethyl carbonate
<i>DIFEC</i>	difluoro ethylene carbonate
<i>DMC</i>	dimethyl carbonate
<i>DME</i>	dimethoxyethane
<i>DMSO</i>	dimethyl sulfoxide
<i>DS</i>	divinyl sulfone
<i>DTD</i>	1,3,2-dioxathiolane-2,2-dioxide
<i>EA</i>	ethylene acetate
<i>EC</i>	ethylene carbonate
<i>EMC</i>	ethyl methyl carbonate
<i>EMS</i>	ethyl methyl sulfone
<i>ES</i>	ethylene sulfite
<i>ETIPRSO2</i>	ethyl isopropyl sulfone
<i>F-AEC</i>	4-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl]-1,3-dioxolan-2-one
<i>FEC</i>	fluoroethylene carbonate
<i>F-EMC</i>	methyl-2,2,2-trifluoroethyl carbonate
<i>F-EPE</i>	1,1,2,2-Tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether
<i>FMPS</i>	trifluoropropylmethyl sulfone
<i>FMS</i>	methane fluorosulfonyl
<i>GBL</i>	γ -butyrolactone
<i>HDI</i>	hexamethylene diisocyanate
<i>LFP</i>	LiFePO_4
<i>LIBOB</i>	lithium bis(oxalate)borate
<i>LIDFOB</i>	lithium difluoro(oxalate)borate
<i>LIFSI</i>	lithium bis(fluorosulfonyl)imide
<i>LIOTF</i>	lithium trifluoromethane sulfonate
<i>LIPF₆</i>	lithium hexafluorophosphate
<i>LITFSI</i>	lithium bis(trifluoromethanesulfonyl)imide
<i>NCA</i>	$\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$
<i>LNMO</i>	$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$
<i>MA</i>	maleic anhydride
<i>MB</i>	methyl butyrate
<i>MEC</i>	methylene-ethylene carbonate
<i>MEIPRSO2</i>	isopropyl methyl sulfone
<i>MMDS</i>	methylene methanedisulfonate
<i>NMC₁₁₁</i>	$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$
<i>NMC₄₄₂</i>	$\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$
<i>NMC₅₃₂</i>	$\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$
<i>PBF</i>	pyridine boron trifluoride
<i>PC</i>	propylene carbonate
<i>PEO</i>	polyethylene oxide
<i>PES</i>	prop-1-ene-1,3-sultone
<i>PPF</i>	pyridine phosphorus pentafluoride
<i>PS</i>	propylene sulfite
<i>SA</i>	succinic anhydride
<i>SL</i>	sulfolane (also tetramethylene sulfone)
<i>TAP</i>	triallyl phosphate
<i>TEGDME</i>	tertraglyme (tetraethylene glycol dimethyl ether)
<i>TFEC</i>	bis(2,2,2-trifluoroethyl) carbonate)
<i>TFP-PC-E</i>	4-[1,1,2,2-tetrafluoroethoxy)methyl]-1,3-dioxolane-2-one
<i>TRIEGDME</i>	triglyme (triethylene glycol dimethyl ether)
<i>THF</i>	tetrahydrofuran
<i>TTSP</i>	tris(trimethylsilyl) phosphate
<i>TTSPI</i>	tris(trimethylsilyl) phosphite
<i>VC</i>	vinylene carbonate
<i>4-TB</i>	4-(trifluoromethyl) benzonitrile

1. Introduction

According to the U.S. Energy Information Administration's data, the world energy consumption will grow by 300% in 2040 with respect to 1980 [1]. Therefore, reliable, stable and sustainable large-scale renewable energy production systems are required. However, for making an efficient use of the intermittent energy sources (*e.g.*, solar or wind energy), electrical energy storage is required. Among miscellaneous technologies existing or in development in physical, chemical or electrochemical energy storage systems, batteries are good candidates for highly efficient energy storage systems.

The most energy dense rechargeable batteries available, lithium-ion batteries (LIBs) are now the most popular types of rechargeable batteries for portable electronic devices such as laptops and cell phones. In addition, their use is extending to electric vehicles and stationary storage, which motivates intense research efforts. As lithium is the lightest metal and is one of the most electropositive element, it provides the largest specific energy per weight. The concept of lithium metal battery was born when the potential of lithium metal was measured in 1913 [2]. However, it was only in the late 1950's that researchers noticed that Li metal is stable in a series of organic electrolytes [3]. In the 1960's, primary cells with lithium metal were developed [4], quickly followed by the commercialization of primary lithium-manganese oxide (Li/MnO₂) cells [5], which are still used today. In the 1970's, secondary batteries with metallic lithium as anode and Li-insertion compounds as cathodes have drawn intensive attention as candidates for high energy batteries [6–8]. However, the dendritic lithium formation on the anode during cycling, which can result in internal short-circuits, has limited the development of secondary lithium metal batteries using liquid electrolytes. To solve this issue, Armand proposed the innovative concept of lithium 'rocking-chair cells' which consists in substituting the lithium metal anode by an insertion material, the lithium ions being transferred from one side to the other during charge and discharge [9]. Lazzari and Scrosati set up such a cell based on two insertion electrodes [10]. In a practical sense, LIBs did not come into the research mainstream until the improvement of cathode materials by Goodenough *et al.* [11,12] and the successful research and development (R&D) in Japanese companies such as Asahi Chemicals [5], Sony and Sanyo in the 80's [13,14]. A milestone in the development of lithium batteries was the commercialization by

Sony, in 1991, of a ‘rocking-chair’ battery based on a non-graphitic carbon (petroleum coke) anode and LiCoO_2 as cathode, using LiPF_6 in PC/DEC as electrolyte, for camcorders [15]. The name “lithium-ion” battery (LIB) was introduced then and has been used ever since.

1.1 The importance of graphite electrode in Li-ion batteries

Compared to other types of carbons, graphite benefits from flat intercalation plateaus close to the potential of Li metal deposition (*ca.* -3 V vs. SHE) and thus provides a higher energy density as well as a higher energy efficiency. However, its layered structure allows for co-intercalation of solvent molecules, which can result in its exfoliation [16]. Its use was possible by an electrolyte consisting of 1-2M of LiPF_6 dissolved in a mixture of EC and DMC [17]. In fact, EC possesses excellent protecting properties toward graphite electrodes, due to the formation of a passivation layer at the graphite/electrolyte interface, upon reduction of electrolyte species, the so-called ‘solid electrolyte interphase’ (SEI) [16,18,19]. Since then, EC-based electrolytes with linear alkyl carbonates as co-solvents (to extend the liquid range and lower the viscosity of the electrolytes) have been mostly used, unless high temperature operation prevents the use of the highly volatile and flammable linear alkyl carbonates [20].

If the SEI allows operating graphite anodes far below the thermodynamic stability limit of the electrolytes, the parasitic reactions occurring at the graphite/electrolyte interface still limit the cycle life of LIBs [21,22], as SEIs deviate from their ideal model (*i.e.* a fast Li^+ single-ion conductor and electronic insulator, impermeable to electrolyte species other than Li^+ , thus effectively preventing electrolyte reduction and self-discharge and ageing). In addition, it should be homogeneous and have good adhesion to the carbonaceous anode surface. Its formation is a critical step performed by battery manufacturers, as consumes capacity and might generate gases (the SEI contains lithium which becomes inactive and gases are evolved upon reduction of conventional solvents), and is crucial for battery lifetime. To improve the SEI performance in terms of consumed capacity and battery ageing, many additives are used in combination with EC in electrolyte formulations.

PC, a close relative to EC, had been a more attractive electrolyte component in early electrolyte formulations (in combination with EC in Li-ion batteries including petroleum coke as anodes [23]) due to its wider liquid range, but mostly failed as a (graphite-based) Li-ion electrolyte solvent because PC co-intercalates between

graphene layers of the graphite anodes rather than forming a SEI, which leads to graphite exfoliation [16]. Although its use is attractive in terms of safety and high temperature operation, as it does not require low viscosity (and flammable) co-solvents for reaching high conductivity, its use is mostly restricted to EC (and additives) containing electrolytes for high temperature electrolyte formulations. However, it is still often used to demonstrate the efficiency of additives with high reduction potential for SEI formation in EC-free electrolytes. Many additives such as ES [24], PS [25], VC [26–29] and FEC [30,31] were tested in PC, as discussed in detail in Xu's reviews on electrolytes [32,33] and in two reviews specifically on additives [34,35]. Nowadays, state-of-the-art electrolytes are based on EC, with LiPF_6 as lithium salt and including additives (*i.e.*, VC, FEC and PES) to enable long term cycling (*e.g.* high coulombic efficiency and good capacity retention) of conventional graphite/layered oxide LIBs operated below 4.3 V [36–38].

1.2 Development of EC-free electrolytes for high voltage applications

In the past decades, continuous attempts have been made to increase further the energy density of LIBs, and cathode materials operating above 4.5 V versus Li/Li^+ have been proposed since the late 1990's, such as LNMO [39] or LiCoPO_4 [40]. Unfortunately, high voltage batteries are still at the research stage, due to the lack of adapted electrolyte. State-of-the-art, EC-based electrolytes (basically 1M LiPF_6 dissolved in the mixture of EC and linear alkyl carbonate) are not suitable for operation above 4.3 V [41–45]. In fact, the main weakness lies in the higher reactivity of EC compared with other components in the electrolyte (*i.e.*, LiPF_6 and linear carbonate such as DMC, EMC or DEC) which was reported experimentally [43,46] and justified theoretically by the structure of the double layer former at the cathode/electrolyte interface [47]. Thus, besides the study of additives for EC-based electrolytes to limit the detrimental reactions with high voltage cathodes [48,49], researchers have been focusing on the development of high voltage electrolytes with EC-free solvents, such as ionic liquids [50], alkyl dinitrile compounds [51], alkyl sulfones [52,53] or fluorinated alkyl carbonates [44,54], which all have shown promising results regarding their compatibility with high voltage cathodes but are mainly tested in cathode/Li half-cell or cathode/LTO full-cell configurations without discussing compatibility of graphite anode. However, poor graphite anode operation limits practical LIB cell performance with those electrolytes and thus we focus here specifically on the research done, mainly since 2010, on designing high voltage, EC-free electrolytes for graphite-based LIBs. Thus, although PC is a popular solvent in the additive literature, as it does

not offer an advantage in terms of anodic stability [55–57], PC-based electrolytes are not reviewed here. The approaches covered include the popular use of additives, changing the main lithium salt, increasing the electrolyte concentration, tuning the binder of the graphite electrode or preparing artificial SEIs. The different classes of solvents discussed in this review as well as the approaches covered are summarized in Figure 1. As can be seen, in the search for practical electrolytes, various approaches are often combined to allow for SEI formation onto graphite, while keeping the ‘high voltage’ capability, linked to the use of alternative solvents or solvent mixtures, the choice of which depends on the final target voltage.

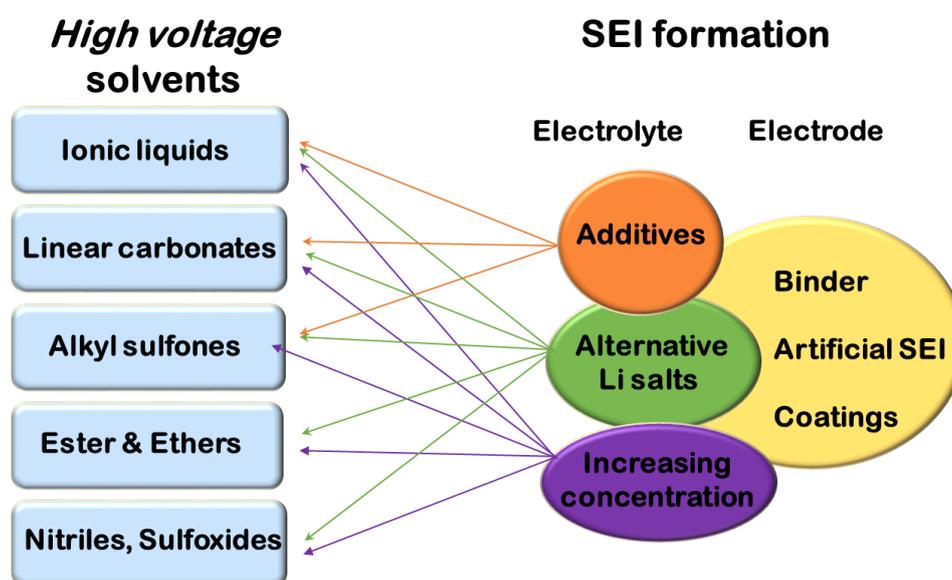


Figure 1: Solvents and approaches used for allowing graphite anode operation in high voltage electrolytes.

2. Additives and Li salts

2.1 EC-free, LiPF₆-based electrolytes

Currently, due to its balanced properties in terms of conductivity [32,33], anodic stability [32,33], aluminum current collector corrosion inhibition at high voltage [58,59], LiPF₆ is the most common lithium salt in electrolytes for LIBs. Therefore, 1M LiPF₆-based electrolytes with EC-free solvents mixtures are discussed here, (*i.e.*, linear alkyl carbonate, fluorinated alkyl carbonates, sulfones and esters). While decomposition products of LiPF₆ (*e.g.*, LiF) are found in the SEI on graphite, it is not, contrary to other lithium salts, known for allowing

SEI formation without EC, whereas other Li salts, such as LiBOB, have been reported to allow graphite operation in PC, by forming a SEI layer upon reduction, prior to PC co-insertion [60,61]. Thus, most of the 1M LiPF₆-based electrolytes using EC-free solvent mixtures need the support of SEI-forming additives. Moreover, even if some electrolytes with alternative salts constitute a good ‘base recipe’ for graphite operation without additive, they can often still benefit from the use of additives, similarly to LiPF₆-based electrolytes. Table 2 gives a general overview of EC-free solvent/additive mixtures allowing graphite electrode continuous cycling as well as the set-up used for graphite cycling.

Table 2. LiPF₆-based, EC-free electrolytes allowing graphite anode cycling

Additive	Additive concentration (wt.%)	Solvent (wt.%)	Experimental conditions	Ref.
VC, FEC, DiFEC	2.5% or 10%	EMC	NMC ₄₂₂ /Graphite 2.8-4.5 V RT, 40 °C, 60 °C	[46]
VC, FEC, DiFEC, MEC	1%, 2%, 3%, 4%, 5%	EMC (≥95%)		[62]
PES	1%, 2%, 3%, 5%, 8%	FEC: TFEC (1:1)		[63]
PES+MMDS	2% PES+0.5% MMDS			[64]
PES, MMDS, SL, MA, DTD, TTSPi, TTSP, PBF, PPF, SA, 4-TB, HDI, TAP	1%	EMC:VC (98:2)		
SA	0.2%, 0.5%, 1%, 2%, 3%	EMC		[65]
VC	10%	SL	Graphite/Li, LFP/Graphite 2.8-4.0 V, RT, 60°, 90°C	[66] [67]
	1%, 2%, 3%, 5%, 8%	SL:EMC (3:7)		(NMC ₄₂₂)/Graphite 2.8-4.4 V
TAP	2%	SL:EMC (3:7)+ 2%VC	LaPO ₄ -coated NMC ₄₄₂ /Graphite 2.8-4.5 V	[49]
MMDS	1%			
TTSPi	1%			
FEC	1%, 2%, 3%, 4%	EMS	Graphite/Li, RT	[69]
	4%	EMS	NMC ₁₁₁ /Graphite	
		EMS:EA (1:1)	3-4.3 V	
		MeiPrSO ₂ :EA (1:1)	RT	
FEC: F-EMC: F-EPE (3:5:2, ratio by volume)			LNMO/Graphite 3.5-4.9 V, RT, 55 °C	[44]
TFP-PC-E	2%	F-AEC:F-EMC:F-EPE (2:6:2, ratio by volume)	LNMO/Graphite 3.5-4.9 V, RT, 55 °C	[70]
FEC:FEMC (1:9, ratio by volume)			(NMC ₅₃₂)/Graphite 2.7-4.7 V, RT	[71]
FEC	2%	SL:DMC (1:1)	Graphite/Li, RT	This work

Dahn's group, in particular, recently investigated different classes of EC-free electrolytes, using linear alkyl carbonates, sulfolane/alkyl-carbonate mixtures and fluorinated alkyl carbonate mixtures as alternative solvents. Specifically, a series of unsaturated alkyl carbonates, fluorinated alkyl carbonates, and sultones, have been used as SEI forming additives in full 4.5 V graphite/NMC₄₄₂ LIBs with EMC as single solvent. Among the additives tested, EC, VC, FEC, PES, DiFEC, MEC, and SA are reported to passivate graphite in EMC. However, VC is able to enable graphite operation at only 2 wt%, while FEC and DiFEC, requires higher amounts [46]. The most efficient additives, VC, FEC, DiFEC have been ranked according to their effect in full cells [62]. The combination of VC and PES seems especially beneficial [63]. A wider group of additives, summarized in Table 2 was reported in EMC and fluorinated alkyl carbonates, including 'high voltage additives' as well and showing an advantage for VC combined with high voltage additives such as PPF or TTFP allowing cells with better capacity retention for long term cycling up to 4.5 V [64].

Fluorination tends to decrease the energy of the highest occupied molecular orbital (HOMO) and increase that of the unoccupied molecular orbital (LUMO) energy, thus leads to higher stability in oxidation, as compared with non-fluorinated solvents [54] (or lithium salts [72]) counterparts and a higher reduction potential. In particular, FEC, the fluorinated version of EC, is reduced at higher potentials than EC, which can be advantageous for the formation of the SEI prior to the degradation of other electrolyte species. Fluorinated solvents have been investigated for various purposes as Li-ion electrolytes (e.g., flame retardants and SEI additives), but their use as high voltage solvents is relatively new [44,54], even if their good behaviour versus graphite electrodes and their properties as aluminium corrosion inhibitors was already known [73]. They usually lead to electrolytes with lower conductivity than their non-fluorinated counterparts [71,74]. However, with the right formulation (i.e. including a SEI forming compound, such as FEC and a linear fluorinated alkyl carbonate, such as FEMC), cycling of high voltage graphite/LNMO cells [44,70] or graphite/NMC cells up to 4.7 V [71] was achieved.

Alkyl sulfones also possess higher anodic stability than carbonates in presence of Li salts [52,53,75–79]. Angell's group, in particular, introduced linear sulfones, as high voltage electrolyte solvents. Most of them, however, do not allow graphite operation, unless additives, such as VC [75] or FMS [52] is used. SL, a cyclic sulfone, has been used in electrochemical studies since 1971 [80]. Although Angell reported on a slightly lower

anodic stability for SL compared with that of its linear relatives [77], SL, as a by-product of the oil industry (thus mass produced), is a suitable candidate for 5 V LIB. In fact, recent reports on high voltage cathodes have renewed the interest in this solvent [53]. Moreover, SL has also been reported to allow operation of graphite electrodes, either as a single solvent for high temperature application, in presence of a high amount of VC as additive [66,67], or at room temperature, mixed with linear alkyl carbonates [81]. In this case, the carboxymethyl cellulose (CMC) binder used for the graphite electrode seems to play a significant role in SEI building [81]. It is, in fact, known that, binders having functional groups such as CMC [82] or LiPAA [83], when used as binders, can form ester bounds on carbon upon drying and then participate into the SEI formation, together with the electrolyte. As a result, it suppresses, in some cases, the need for additive, while additives are useful in general and allow improved performance [49,68].

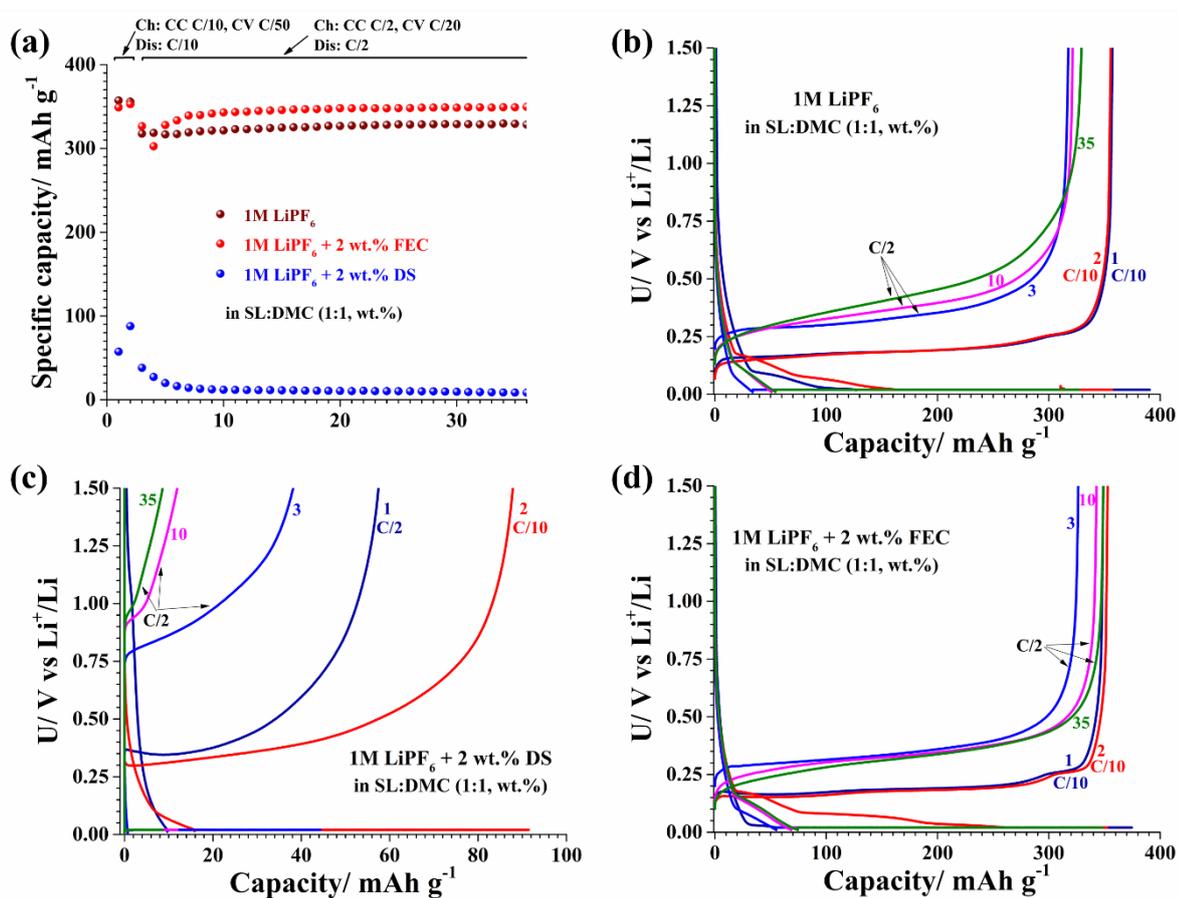


Figure 2. Cycling performance of graphite electrodes (96/2/2 (graphite (SLP30, Timcal)/CMC/SBR), total mass loading: 7.5 mg cm⁻²) in 1M LiPF₆ SL:DMC (1:1, wt.) with and without additive (a) Discharge capacity vs. cycle number (b), (c) and (d) Selected voltage profiles for each electrolyte (as indicated on the graph).

Electrolyte and electrode preparation as well as the experimental conditions for the electrochemical testing are the same as reported in [81].

When considering additives for ‘high voltage’ electrolytes, their reactivity at both anode and cathode should be taken into account. VC content, for instance, should be tuned to minimize the oxidation of excess VC at the cathode, if the cathode is to be operated at high voltage. FEC, on the other hand, possesses a higher anodic stability and is often an effective SEI forming additive, in presence of EC or not. In fact, as shown in Figure 2a, in a 1 M LiPF₆ SL:DMC (1:1, wt.) mixture, the addition of 2% FEC improves significantly the delivered capacity during cycling. The voltage profile evolutions (Figure 2d and 2b, respectively with and without FEC) show that without FEC, the discharge plateaus become sloped, as a result of a slower lithium transport, whereas the addition of FEC results in much flatter plateaus, which explains the higher capacity and better capacity retention. This clearly indicates a better SEI stability (the initial coulombic efficiency (ICE) is also improved from 91.5% to 93.1%). This contrasts with the effect of divinyl sulfone (DS) (Figure 2a and 2c). Although DS has been reported as a promising additive in EC-based electrolytes [84,85], it is clearly detrimental to SEI formation and evolution, at least at 2% in this particular EC-free electrolyte, as the irreversible capacity consumed for the SEI formation is too large (ICE = 72.9%), the capacity cycled is low from the first cycle and decreases to zero in few cycles as a result of the high (and continuously increasing) ohmic drop and Li⁺ transport limitation. Thus, even though many additives are known to be effective in EC-based electrolyte, their efficiency need to be reassessed for a use in EC-free electrolyte

2.2 Alternative Li salts

If LiPF₆ is the most popular salt for LIB electrolytes, its sensitivity to moisture, poor thermal stability, and lack of intrinsic SEI forming ability, as well as its poor performance in PEO-based polymer electrolytes, has motivated the development of other Li salts [23]. However, when replacing LiPF₆, the new electrolyte mixture must provide the same advantages such as a high anodic stability and the protection against corrosion of the Al current collectors supporting the cathode. LiTFSI, for instance, is a salt introduced originally for PEO-based electrolytes that offers much better thermal and chemical stability than LiPF₆ as well as high anodic stability. However, its chemical stability is actually an issue as, contrary to LiPF₆, it does not form an AlF₃ passivation layer on

aluminum [86]. Also, it is not reported to participate positively in SEI formation as a single salt at 1M [87]. Thus, if it is sometimes used with low dielectric constant solvent mixtures for reaching good solubility and conductivity, other additives must be used for Al protection, and often for SEI formation. LiFSI is an inorganic salt similar to LiTFSI in terms of structure and conformational flexibility [88], but smaller as the $-CF_3$ substituents are replaced by $-F$ atoms, leading to a lower thermal stability, but higher conductivity, and, in some cases, participates in the formation of the SEI on Li metal [89] or graphite [33,90–92] in EC-free electrolytes. Its properties versus Al current collectors are, however, often problematic, even though halide impurities play a strong role in the corrosion of Al [93,94].

Among Li salts with good SEI forming properties, a non-fluorinated lithium salt, LiBOB, was shown to possess a strong ability to passivate graphite [60]. However, the performances of the electrolytes based on LiBOB as single salt have been inferior to those of conventional electrolytes. Thus, it is often used as an additive, as it can passivate Al current collectors [95], improve the cycling performance of high voltage electrodes [96], and participate in the SEI formation [60,61]. To counterbalance some of its drawbacks (namely, a low solubility and resistive SEI), a half-fluorinated version, LiDFOB was proposed. While LiDFOB also possesses SEI forming properties [97,98], it is not sufficient for graphite operation in PC-based electrolytes without additional additives [99]. Its high reduction potential is, however, useful in presence of low cathodic stability solvents and it can also be used as an additive for SEI formation [100]. Researchers have confirmed that, at 1.7 V and below, in carbonate-based electrolytes [98], the reduction products of LiDFOB (*e.g.* lithium oxalate, other oxalate containing species, and borates [98,101]) dominate the SEI composition [97]. The SEI is thicker (the impedance of the cell is higher as well) as compared with a $LiPF_6$ -containing EC-based electrolyte at low temperature [101] but helps reaching good cycling retention of graphite at room temperature in SL:DMC-electrolyte [92]. In alkyl dinitrile solvent mixtures such as ADN:DMC, 99.9% efficiency has been reached for graphite (in combination with FEC), whereas ADN and alkyl nitriles in general are usually detrimental for SEI formation [102].

3. Effect of lithium salt and anion concentration

3.1 High salt concentration

Table 3. Overview of ‘high concentration’ electrolyte able to operate a graphite anode

Salt	Successful salt concentration	Solvent	Cell configuration	Ref.
LiFSI	[Li(TG)][TFSI] <i>ca.</i> 3 mol L ⁻¹	TG	Graphite/Li, LFP/Graphite	[103]
LiTFSI				[104]
LiTFSI	4.5 M	AN	Graphite/Li	[105]
LiTFSI	3.2 M	DMSO		[106]
LiTFSI	3.0 M	SL		[106]
LiTFSI	3.0 M	THF		[106]
LiFSI	3.6 M	DME		[107]
LiFSI+ LiPF ₆	5 M LiFSI+ 0.5 M LiPF ₆	EA		NMC ₁₁₁ /Graphite and NMC ₄₄₂ /Graphite 2.8-4.7 V
LiFSI	5.5 M	DMC	LNMO/Graphite 2.8-5 V	[108]

Recently, electrolytes with high concentration of Li salt (generally, salt concentration above 3 M) started receiving intensive attention because of various unusual functionalities, such as a wider electrochemical stability window, good SEI forming ability on graphite and Li metal anodes, higher thermal stability, Al dissolution inhibition, and reduced flammability, all beneficial for battery applications. In particular, many EC-free formulations, reported in Table 3 have been proposed and successfully used for graphite cycling. Three recent reviews on concentrated electrolytes detail their possible use for various battery systems, (*i.e.*, LIBs and ‘beyond LIBs’ technologies such as Li-S, Li metal, Li-air, Na-ion and Na-S batteries and aqueous-based LIB [109–111]). EC-free based systems able to allow graphite anode cycling are listed in Table 3. For instance, Yamada’s group reported on steady graphite cycling in a 4.2 mol L⁻¹ AN electrolyte, as shown in Figure 3a.

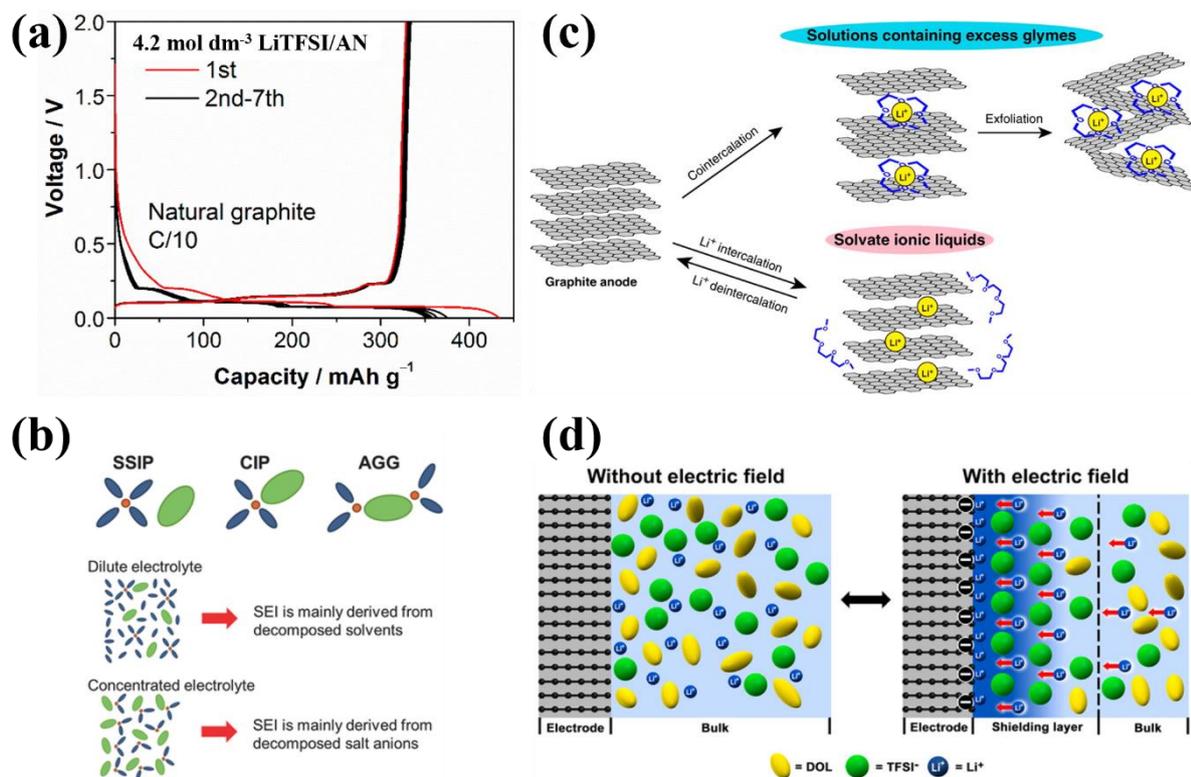


Figure 3. (a) Voltage profile of a graphite electrode in a 4.2 mol L^{-1} LiTFSI/AN electrolyte at C/10. Reproduced with permission from [105]. (b) Representative Li^+ cation solvate species (SSIP, CIP and AGGs) in dilute and concentrated electrolytes and schematic illustration of the electrolyte reduction mechanism at the electrode/electrolyte interface in dilute and concentrated electrolytes. The red dot represents Li^+ , the blue ellipse represents solvent molecular and the green ellipse represents the salt anion. Reproduced with permission from [111] (c) Mechanism of Li ion desolvation at the graphite/glyme-Li salt solvate ionic liquids. Reproduced with permission from [104]. (d) Formation of a transient SEI in a concentrated electrolyte. Reproduced with permission from [112].

Generally, in 1 M solutions, the coordination number of Li^+ with solvent is around 4, and Li^+ solvation is dominated with solvent-separated ion pairs (SSIPs), as illustrated in Figure 3b [111]. In this case, many free solvent molecules exist in the solution [32,111,113]. By choosing salts with low lattice energy (e.g. LiFSI and LiTFSI) and solvents with high solvation ability, very high concentration can be reached, in which the number of solvent molecules per Li^+ is limited. Thus, the molar ratio of solvent/ Li^+ can be less than 4 and even below 2 and no ‘free’ solvent molecule remains: All are involved in the first solvation shell of Li^+ . Contact ion pairs (CIPs) and larger aggregates (AGGs) thus dominate [105–107,114–116]. This induces changes in HOMO and

LUMO of the electrolyte species due to their close interaction and changes in activity (which can, in particular, increase significantly the anodic stability of the solvents). Moreover, unlike dilute systems, in which the SEI on graphite is mainly formed by solvent decomposition products [117], in concentrated electrolytes, the SEI is predominantly formed by the salt anions decomposition [105,106,111,118,119] (Figure 3b), which, in some cases, allows reversible Li^+ de/intercalation from/into graphite. Other parameters that influence Li^+ insertion into graphite can be modified as well. Watanabe and coll. [104] analysed the mechanism of Li^+ desolvation at the interface of graphite anode in glyme-based concentrated systems (also known as ‘solvate ionic liquids’) in terms of voltage shift. Between 1.2 V and 0.4 V vs. Li/Li^+ , the electrochemical intercalation of solvate $[\text{Li}(\text{TG})_x]^+$ cations ($x>1$) in dilute solutions is a lower energy process compared with that of Li^+ desolvation from the $[\text{Li}(\text{TG})_x]^+$ complex. In concentrated solutions (*i.e.* $[\text{Li}(\text{TG})_1][\text{TFSI}]$), however, co-intercalation of $[\text{Li}(\text{TG})_x]^+$ is greatly suppressed as the desolvation process is more favourable, as illustrated in Figure 3c. More recently, Lu *et al.* [112] proposed another anode protection mechanism considering the electrochemical double layer formation on the surface of anode. Upon potential variations, the electrolyte components at the electrode/electrolyte interface (double layer) would reorganize reversibly to form a transient protective surface layers on the anode, as illustrated in Figure 3d, rather than forming a stable SEI upon reduction.

3.2 Ionic liquid: Effect of anion concentration on SEI formation

Ionic liquids (ILs) are defined as molten salts with melting points lower than 100 °C [120]. Considering their outstanding properties such as high thermal stability, low-volatility and non-flammability, organic ILs have drawn researchers intensive attention for electrolyte application with various reviews detailing this topic [120–122]. In particular, they have been reported to be well suited vs. Li metal [89,123,124], especially when they include the TFSI and FSI anions. The cycling of graphite is more challenging as the SEI needs to be formed during the first cycle and, in the case of ILs, before the insertion of the cation of the IL, which induces, in general, graphite exfoliation. Successful graphite cycling was reached first using VC with a TFSI-based IL [125]. It was noted afterward that FSI allows the formation of a SEI on graphite without any additive [126]. While not as widespread as alkyl carbonate electrolyte research, a graphite/NMC LIB using IL-based electrolytes was sent on a satellite and operated in space [127]. Although, in the case of ILs, the anion concentration is very high, it is also known that the presence of Li salt influences significantly the passivation of anodes. For instance, while

pure N-methoxyethyl-N-methyl pyrrolidinium TFSI decomposes extensively well above Li metal plating potential, the electrolytes including LiTFSI allow lithium metal plating [128]. Matsui *et al.*, in particular, evaluated the effect of the anion type and salt concentration on the charge-discharge performance of a graphite anode in 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMImFSI) IL-based electrolytes: At 1.46 mol L⁻¹, LiFSI/EMImFSI enables graphite electrode operation at room temperature with sufficient discharge capacity by forming a suitable, low internal resistance SEI [129]. To the best of our knowledge, however, although in the past decade there are few reports on graphite anodes combined with various cathode materials (e.g., LiCoO₂ [116,121], LiFePO₄ [121], NMC [130]) cycled IL-based electrolytes, so far, there is no report showing a LIB cells with graphite anodes using IL electrolytes operating above 4.3 V.

Overall, the same approaches as for conventional electrolyte can be used (additives, the type and concentration of anions) in the future for high voltage IL-based electrolytes with graphite anode.

3.3 ‘Intermediate’ salt concentration

The effect of salt (or anion) concentration is significant at much lower concentrations than in ILs or ‘concentrated electrolytes’. Dahn and coll., for instance, noticed in their investigation of full graphite/NMC cell in EMC-based electrolytes [29] an improvement of performance at 1.5 M, which has been linked to an improvement in Li⁺ desolvation.

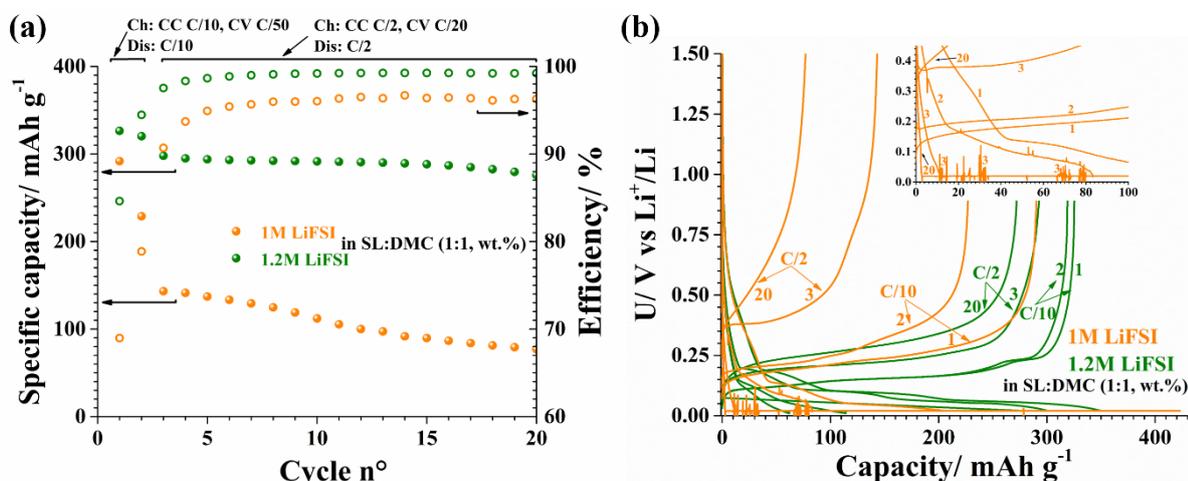


Figure 4. Cycling performance of graphite electrodes 96/2/2 (graphite (SLP30, Timcal)/CMC/SBR), total mass loading: 7.5 mg cm^{-2} in 1M and 1.2M LiFSI, SL: DMC (1:1,wt.) electrolytes. (a) Capacity and efficiency vs. cycle number. (b) Voltage profiles (1st, 2nd, 3rd and 20th cycle). The electrolyte preparation, electrode preparation and electrochemical testing method was the same as reported in [81].

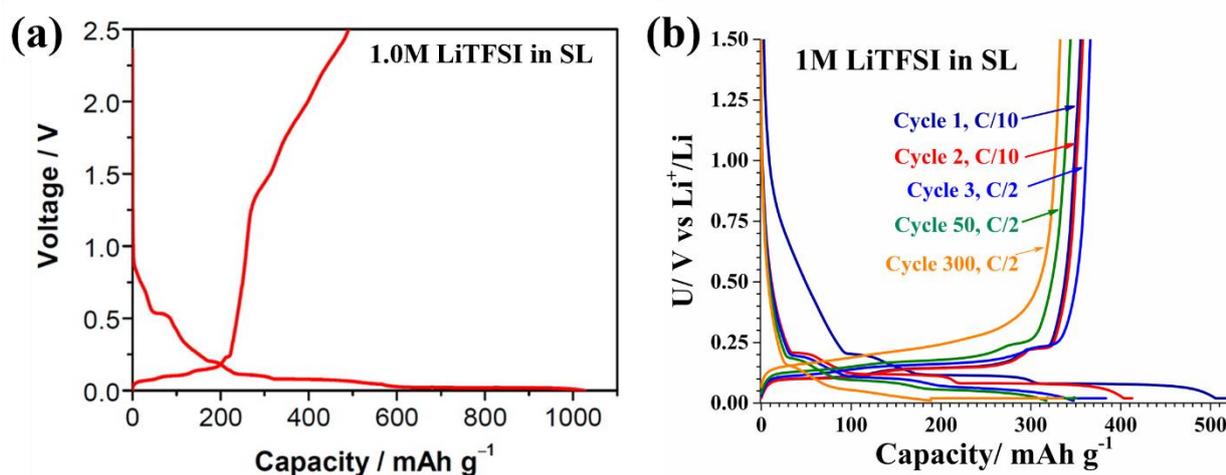
A remarkable effect of the salt concentration is also seen in the case of LiFSI in SL:DMC electrolytes. Compared with a 1M electrolyte, the 1.2M electrolyte allows significant improvement of the cycling performance, with rather stable capacities and efficiencies close to 100% in the first 20 cycles, as shown in Figure 4 (a), whereas the 1M electrolyte induces high ohmic drop and slow Li⁺ transport as well as irregular voltage profiles (Figure 4 (b)).

4. Electrode modification

4.1 Protective layers and artificial SEIs

The SEI formation of graphite anode in EC-free electrolytes is clearly influenced by all the electrolyte components and their concentrations. However, the effect of an inactive component is also of paramount importance: The electrode binder, whose original role is only to bind the electrode particles together and ensure adhesion to the current collector, which is crucial for LIB processing and long-term cycling, also plays a role in SEI formation. In fact, two classes of binders are used to assemble composite LIB electrodes: PVDF (or PVDF-HFP), usually processed in N-methyl pyrrolidone and water processable binders (either soluble, such as carboxymethyl cellulose (CMC) or particulate (styrene butadiene-rubber (SBR) latexes). Among them, water soluble binders (CMC, LiPAA, Alginates), include –OH and –COOH groups, which interact and can even covalently bond to the carbonaceous surfaces, by reacting with graphite surface groups. It results in a covering of the graphite surface by the binder, which creates a scaffold that participates in the SEI formation. According to earlier reports, it is known that carboxymethyl cellulose (CMC) plays an important role in SEI formation on carbon composite anode including alloying [82,131–133], conversion [134] or conversion/alloying materials [135]. Furthermore, in our recent study of 1M LiPF₆ SL:DMC systems, the use of CMC as binder for graphite electrode, has been recognized as the key reason for allowing graphite cycling without any additives [81]. In

fact, although 1M LiTFSI in SL fails in allowing cycling of PVDF-based graphite electrodes due to the reduction of SL below 0.5 V [106] (Figure 5a), it is not the case with a CMC-based graphite electrode (Figure 5b). Despite that the first cycle efficiency is still too low for the LIB application, CMC enables stable long term cycling, with no detrimental effect on the cathode performance. Other water soluble binders such as PAA [136] or alginates [137] can also be considered to use for graphite anode due to their favorable SEI forming properties, so far



shown in EC-based electrolytes.

Figure 5. Charge–discharge curves of graphite/Li half cell with 1.0 mol L⁻¹ LiTFSI in SL electrolyte. (a) with a PVDF-based graphite electrode, reproduced with permission from [106] (b) using a 90/5/5 (graphite (SLP30, Timcal)/SuperP/CMC), total mass loading: 2 mg cm⁻².

4.2 Graphite surface pretreatment

The surface pretreatment of graphite via carbon coating [138,139], polymer-blend coating [140,141], and metal coating [142] is known to influence the surface properties and reduce the irreversible capacity consumption upon SEI formation and change the reaction chemistry. The coating becomes part of the SEI and the concept of artificial SEI was proposed by E. Peled and is detailed in a recent review on SEI [19]. Early reports have shown that the exfoliation of graphite can be prevented and the Li-ion intercalation be improved in PC-based electrolyte systems (either as single solvent or mixed with EC), using carbon or organic compounds [138,143]. To the best of our knowledge, there is no report on artificial SEI or surface modification purely intended for EC-free electrolytes with graphite anode so far. Given their much higher theoretical capacity (vs. graphite) and more challenging operation, researchers are now paying more and more attention to the formation of artificial SEI of

Li metal or Si-Graphite composite anodes [144–147]. While research is still at an early stage and most of the developed processes cannot be scaled up easily, this approach, in principle, could allow using electrolytes with no ‘intrinsic’ SEI forming capability. In fact, Wang’s group recently reported a 4.0 V class aqueous LIBs of both high energy density and high safety, using an “inhomogeneous additive” approach (basically using a protecting hydrophobic layer as SEI precursor and water repellent to stabilize graphite or Li metal anodes [148]). Meanwhile, simulation results suggest the possibility of EMC-based electrolyte for better cycling result with an artificial SEI layer (PEO-graphite) [149].

5. Conclusion

The SEI formation on graphite depends on many factors, among which, the reactivity of the individual electrolytes species, including Li salt and additives, the change in reactivity following their interaction within the electrolytes, their concentration, the surface groups on the graphite electrode, possible graphite pretreatment and binder influence. Therefore, results on graphite electrodes are often difficult to compare, as they depend at the same time, on the materials used, but also on their processing into electrodes. To date, however, several electrolytes have outperformed EC-mixtures for graphite/high voltage cathode, including linear alkyl carbonate, fluorinated alkyl carbonate and SL mixtures in terms of efficiency and cycling stability. Cost and rate performance are two other parameters, not discussed here, which often prevent alternative electrolyte to rival EC mixtures, as removing the high dielectric constant solvent EC often leads to inferior conductivities and most alternative lithium salts are more costly than LiPF₆. Finally, the use of alternative binders and protective layers is becoming more popular (carbon coated graphite is now used in commercial Li-ion batteries) and might allow reaching even higher performance for graphite-based Li-ion batteries with high voltage electrolytes that are not optimal intrinsically for graphite cycling.

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