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Guidelines to Design Electrolytes for Lithium-ion Batteries: Environmental Impact, Physicochemical and Electrochemical Properties

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Electrolytes for lithium-ion batteries (LiBs) have been put aside for too long because few new solvents have been designed to match electrolyte specifications. Conversely, more attention has been paid to synthesize new electrode materials, and more especially positive electrodes. Particularly, most of the studies dedicated to the investigation of electrolytes for LiBs have been focused on mixing different molecules. Nowadays, the development of high-voltage materials for LiBs stimulates the synthesis of new solvents and new salts more stable against oxidation. Despite the challenges, only few teams are active in this field in developing a rational approach combining physicochemistry, electrochemistry and modelling from the molecular to the macromolecular levels. After assembling a critical collection of physicochemical and electrochemical data from the literature, this paper highlights the main trends between the chemical structure of organic dipolar aprotic solvents and their physicochemical and electrochemical properties in order to provide a guide for the chemists to design new electrolytes for LiBs. This guide also includes indicators to take into account the environmental impact of solvent production by including the life cycle assessment of eight different solvents.

Introduction

The development of new technologies for electrochemical energy storage is one of the main challenges of the next decades. Many hopes now rely on lithium-ion batteries (LiBs) which have invaded the market of laptops and which appear to be the best near-term choice for electric vehicles, and perhaps for network applications (electricity storage from wind turbines or solar cells for example). The performances of the LiBs can be improved either by optimizing the electrolyte, or by developing more efficient electrode materials in terms of energy density and cycling ability or both. Since the first commercialized lithium-ion battery developed by Sony in 1991 composed of graphite as the negative electrode and lithiated cobalt oxide as the positive electrode ($LiCoO_2$),[1,2] researches have been focused on the development of new electrode materials and, to a lesser extent, on the design of electrolytes for LiBs.

Nowadays, graphite electrodes, and more generally carbonaceous materials such as graphite, soft carbon and hard carbon, remain the most used negative electrode materials in LiBs. Few technologies use titanium oxide as a negative electrode ($Li_4Ti_5O_{12}$, known as LTO) while silicon or tin electrodes are considered good alternatives for the future.[3] Conversely, there are more technologies available for positive electrodes. Indeed, many positive electrodes have been disclosed since 1991 in order to improve safety and cycling ability and reduce the cost. For instance, a large amount of research has been focused on developing the cheaper $LiNiO_2$ material because of the cost of cobalt. More sophisticated materials containing three different metals such as $LiNi_{1-x}Co_xO_2$ to obtain better stability than $LiCoO_2$ or $LiNiO_2$ were investigated and commercialized.[4] Later, it was shown that the addition of aluminum in $LiNi_{1-x}Co_xO_2$ leading to the synthesis of $LiNi_{0.70}Co_{0.15}Al_{0.15}O_2$ (commercially known as NCA) allows a significant increase in the cycling ability and the thermal stability.[5] Spinel structures ($LiMn_2O_4$ and $LiNi_xM_{2-x}O_4$ substitutes with M=Ce, Fe, Co, Ni) and olivine structures such as $LiFePO_4$ were developed in the 2000s. The later material is particularly attractive because it is safe and cheap and it exhibits a very good cycling behavior despite possessing a

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moderate energy density. More recently, research has focused on the substitution of iron in $LiFePO_4$ by Mn, Co or Ni because such substitutions are responsible for a significant increase of the operating voltage, i.e. 4.1 V for Mn, 4.8 V for Co and 5.1 V for Ni instead of 3.5 V for Fe (potential given vs. Li^+/Li).[3] However, the lack of electrolytes stable towards oxidation dramatically limits the use of such high potential materials for high-energy applications.

Therefore, it is clear that there is a huge need in the development of new electrolytes exhibiting high anodic stability around 5 V vs. Li^+/Li. Despite the renewal of interest in such electrolytes, only a few teams have been working on the formulation of new electrolytes compatible with the next generation of high-density lithium-ion batteries. Such electrolytes, usually an organic aprotic dipolar solvent or an ionic liquid in the presence of a lithium salt, should exhibit the following specifications for being used in LiBs:

- high ionic conductivity (i.e. at least few mS/cm),
- low viscosity (less than 2 cP),
- high dielectric constant of the solvent (>20),
- good wettability towards separator and electrodes,
- low melting point (T<-20 °C) and high boiling point (T>180 °C),
- high flash point,
- large electrochemical window (>4.5 V vs. Li/Li^+),
- low cost (today the cost of EC/DMC+$LiPF_6$ electrolyte represents 3% of the total cost of LiBs),
- environmentally friendly.

Ionic conductivity and viscosity are related to each other because a decrease of the viscosity of the electrolyte involves an increase of the ionic conductivity. Likewise, organic solvents with high dielectric constants promote salt dissociation, resulting in an increase of the ionic conductivity.[6] The ionic conductivity and the viscosity depend both on the nature of the solvent and the salt, while the dielectric constant depends only on the solvent. The electrochemical window depends on the solvent, the salt and the nature of the electrode because of electrocatalytic reactions.

Usually, the formulation of electrolytes for LiBs involves a mixture of a lithium salt and two or three solvents because all of the previous criteria cannot be reached by using only one solvent. Lithium salts for LiBs must be soluble in dipolar aprotic solvents at a concentration close to 1 M to achieve the maximum ionic conductivity. Such lithium salts should usually have a large anion to ensure a good dissociation in the solvents and to limit ion-pair formation. Furthermore, these salts should be safe, they should exhibit a low environmental impact and a high oxidation potential, especially for high energy applications. Furthermore, they must form a good passivative layer at the negative electrode, especially when graphite is used. In the literature, the most studied salts are lithium perchlorate ($LiClO_4$), lithium hexafluoroarsenate ($LiAsF_6$), lithium tetrafluoroborate ($LiBF_4$), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), lithium triflate (LiTf) and lithium hexafluorophosphate ($LiPF_6$).[7] However, $LiPF_6$ is the most commercialized salt and LiTFSI is more and more used in electrolytes for LiBs despite current collector corrosion issues at high voltage.

Many dipolar organic solvents or ionic liquids in the presence of lithium salts were reported in the literature for their use as electrolytes in LiBs.[7-20] Among these solvents, 7 families of molecules can be highlighted: carbonates, esters, ethers, acetals, sulfoxides, sulfites and sulfones. Alkyl carbonates still remain the most used solvents in LiBs because of their good physicochemical and electrochemical properties. In particular, ethylene carbonate is a must-have in electrolyte formulation for 4V batteries as this solvent allows the formation of the high-quality passivative layer required to avoid graphite exfoliation during charge-discharge cycles.[21] However, alkyl carbonates are not compatible with high-voltage electrodes for 5V batteries and it is mandatory to find new electrolytes exhibiting higher anodic stability than alkylcarbonate for high energy density applications.

This paper provides a critical view on the electrolytes reported in the literature by comparing their physicochemical and electrochemical properties. Many data are gathered in this paper. For the first time, such data have been rigorously homogenized and completed by performing additional experiments in order to furnish a guide for the physicochemists and electrochemists who are interested in the development of new electrolytes. Obviously, the choice of the electrolytes is not only driven by the physicochemical and electrochemical properties because environmental impact must also be taken into account.

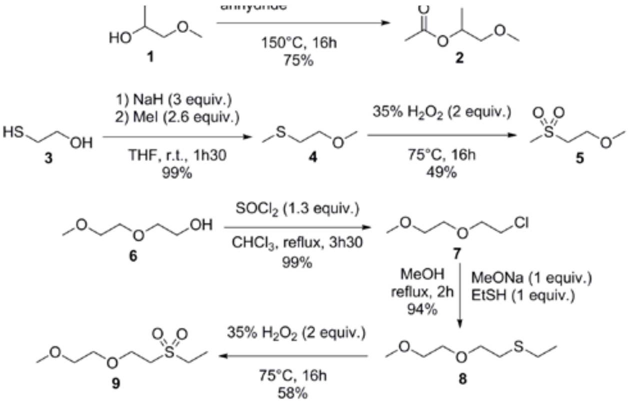
In the present work, the critical analysis of the physicochemical and electrochemical properties of electrolytes is completed by Life Cycle Assessment (LCA) of solvents used in LiBs to guide physicochemists and electrochemists in the design of new electrolytes for LiBs. Finally, some recommendations are made in the choice of the future trends in electrolytes for LiBs.

Experiments

Electrolytes

Because of uncompleted characterization and missing data, many solvents were purchased to achieve complementary analyses and build a homogeneous physicochemical and electrochemical properties database. Compounds were

Figure 1: Syntheses of MPA, MEMS and EMEES



purchased from Sigma-Aldrich, TCI, VWR and Acros Organics with the highest available purity. Three solvents without commercial availability were synthesized (Figure 1).

Methoxypropyl acetate (MPA) **2** was synthesized from 1-methoxypropan-2-ol **1** following the procedure of Nicholas *et al.*.[22] Methoxyethyl methylsulfone (MEMS) **5** was synthesized by alkylating β-mercaptoethanol **3** using sodium hydride and methyl iodide to afford (2-methoxyethyl) (methyl)sulfane **4**, followed by an oxidation of the sulfide to the corresponding sulfone using concentrated hydrogen peroxide.[23,24]

Ethyl methoxyethoxyethyl sulfone (EMEES) **9** was synthesized from diglyme monomethyl ether **6** using a chlorination/ alkylation/oxidation sequence.[24-26] All analytical data for each compound are in good agreement with the those reported in the literature. Complete procedures, NMR and GC-MS spectra are accessible in the ESI. $LiPF_6$ and LiTFSI were purchased from Sigma-Aldrich as battery grade.

All these reagents were opened and stored in an argon filled glove box containing less than 5 ppm of H_2O and O_2.

Physicochemical and electrochemical methods

Thermal characterization was performed by differential scanning calorimetry (DSC) on a Mettler Toledo DSC822e apparatus with single use 40 µL aluminium crucibles previously pierced. Density and viscosity were determined using an Anton Paar DMA 4500M combined densimeter viscometer. Conductivity measurements were performed on a Mettler Toledo FE30 equipped with an Inlab 741-4mm probe. Oxidation potentials were studied by linear and cyclic voltammetry in classical three-electrodes cells using platinum rotating electrode as the working electrode (1000 rpm) and lithium wires as counter and reference electrodes. The same experiments were conducted using only two electrodes in stainless steel Swagelock system, in which the working electrode was platinum or glassy carbon disc, and a lithium disc was used as counter/reference electrode. No major difference was detected on the oxidation potential using either setup. The voltammetry studies were recorded by using Origaflex 500 potentiostat from Origalys Electrochem. All preparations and/or experiments were conducted in an argon-filled glove box containing less than 5 ppm of H_2O and O_2.

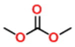
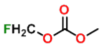
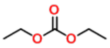
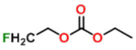
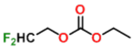
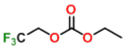
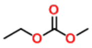
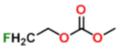
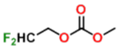
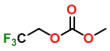
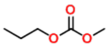
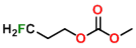
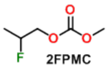
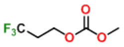
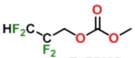
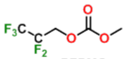
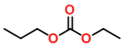
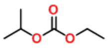
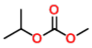
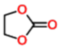
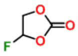
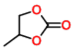
Physicochemical and electrochemical properties

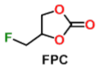
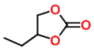
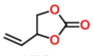
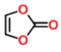
Carbonates

The mixtures of dimethyl carbonate-ethylene carbonate (DMC-EC) or propylene carbonate-dimethyl carbonate-ethylene carbonate (PC-DMC-EC) are the most used solvents in lithium-ion batteries because such mixtures afford very good physicochemical and electrochemical properties in the presence of lithium hexafluorophosphate ($LiPF_6$), which is the most used lithium salt today. Dimethyl carbonate (Table 1-entry 1) is used since it decreases the viscosity of the mixture as DMC viscosity is very low (η=0.59 cP). However, the low dielectric constant (ε_r=3.1) and the exfoliation of graphite electrodes in this mixture limit the use of DMC in LiBs. The addition of propylene carbonate permits an increase in the dielectric constant of the DMC-based mixtures (PC ε_r=64.9, Table 1-entry 22) without affecting dramatically the viscosity despite the high viscosity of PC (η=2.53 cP). Furthermore, the use of PC in DMC-based mixtures allows an increase in the thermal stability because PC exhibits a low melting point and a high boiling point. Unfortunately, PC and DMC cannot be used with graphite in LiBs because these two solvents cannot form a good passivative layer in the presence of lithium salts. To improve the cycling ability at graphite electrode, it is actually mandatory to add ethylene carbonate (Table 1-entry 20). Despite the good anodic stability of these solvents in the presence of $LiPF_6$ at platinum electrode, i.e. 5.2-5.5 V, these solvents cannot be used in 5 V LiBs due to a dramatic decrease of the anodic stability of the electrolytes at the positive electrodes used in LiBs because of electrocatalytic reactions. Therefore, further researches are now focused on the identification of other solvents and salts that could replace them advantageously for 5 V LiBs.

Viscosities of alkyl carbonates, esters and ethers are close in value while sulfoxides, sulfites and sulfones exhibit significantly higher viscosities (*vide infra*). Although, most alkyl carbonates have viscosities ranging from 0.5 cP to 2 cP, it is interesting to highlight that a few alkyl carbonates such as DFEMC (2.6 cP, Table 1-entry 9), TeFPMC (2.6 cP, Table 1-entry 15), FEC (4.1 cP, Table 1, entry 21), FPC (7.64 cP, Table 1-entry 23), etc. are more viscous. The viscosity of cyclic carbonates is higher than that of linear or branched alkyl carbonates because the presence of linear or branched alkyl chains may enable the molecules to arrange and fit themselves in order to facilitate the process of flow.[49] For instance, cyclisation of EMC (Table 1-entry 7) to form PC (Table 1, entry 22) leads to an increase of the viscosity from 0.65 cP to 2.53 cP at 25 °C. Furthermore, the addition of fluorine atoms is responsible for an increase of the viscosity for both linear alkyl carbonates and cyclic carbonates. However, increasing the number of fluorine atoms does not imply necessarily a linear increase of the viscosity. For instance, the addition of one fluorine atom in the alkyl chain of EMC leads to an increase in the viscosity from 0.65 cP for EMC (Table 1-entry 7) to 1.36 cP for MFEMC (Table 1-entry 8). Likewise, the addition of one more fluorine atom in the alkyl chain of MFEMC increases the viscosity from 1.36 cP to 2.60 cP (DFEMC, Table 1-entry 9). Conversely, a decrease in viscosity from 2.60 cP to 1 cP is observed by adding one more fluorine atom in the alkyl chains of DFEMC to form TFEMC (Table 1-entry 10). Similarly, viscosities of MPC, FPMC, TrFPMC, TeFPMC and PFPMC (Table 1-entries 11, 12, 14-16) do not vary monotonically when the number of fluorine atoms increases in the chemical structure of alkyl carbonates. However, it is difficult to predict the variation of the viscosity as a function of the number of fluorine atoms in the chemical structure of the alkyl carbonate as it depends on several parameters including the magnitude of the Van der Waals interactions (mainly related to the dipole moment) and the ability of the molecules to arrange and fit themselves so as to facilitate the process of flow, which depends on the shape of the molecules and their rigidity. The viscosity of alkyl carbonates can be decreased by reducing the rigidity of the

Table 1: Physicochemical and electrochemical data of carbonates

Entry	Structure	mp	bp	η	ε_r	μ	ρ (V_m)	κ	E_{ox} vs Li^+/Li	References
1	 DMC	4.6	91	0.59 (20°C)	3.1	0.76	1.06 (84.98)	6.0	5.5 ^{a} (Pt 5 mV/s)	[27],[28]
2	 MFDMC		108	0.95	9.0		1.24 (98.47)	4.2	6.2 (Pt 5mV/s)	[29],[30]
3	 DEC	-74.3	126	0.75	2.8	0.96	0.97 (121.78)	2.4	5.2^a (Pt 5mV/s)	[28],[31],[32]
4	 EFEC		134	1.40	6.5		1.12 (121,54)	2.4	6.4 (Pt 5mV/s)	[32],[33]
5	 EDFEC			2.69	9.3		1.29 (119.47)	1.7	5.7 (Pt 5mV/s)	[34]
6	 ETFEC			0.92	7.1		1.33 (129.40)	1.0	6.2 (Pt 5mV/s)	[34]
7	 EMC	-53	110	0.65	2.9	0.89	1.01 (103.08)	3.5	6.1 (GC* 10mV/s)	[31],[35]
8	 MFEMC			1.36	7.3		1.19 (102.61)	3.0	6.1 (Pt 5mV/s)	[34]
9	 DFEMC			2.60	9.5			2.3	6.4 (Pt)	[36]
10	 TFEMC	-44	90	1.00	9.6	2.67	1.37 (115.39)	1.5	6.8 (Pt)	[36],[37]
11	 MPC	-49	130	1.08	3.0	4.84	0.98 (120.54)	2.5	6.4 (Pt 5mV/s)	[11]
12	 FPMC			1.75	7.0		1.20 (113.43)	2.5	6.3 (Pt 5mV/s)	[38]
13	 2FPMC			1.90	7.6			1.9	6.4 (Pt 5mV/s)	[32]
14	 TrFPMC			1.75	7.5		1.32 (130.38)	1.5	6.4 (Pt 5mV/s)	[38]
15	 TeFPMC			2.60	9.0		1.35 (140.81)	0.5	6.5 (Pt 5mV/s)	[38]
16	 PFPMC			1.40	6.5		1.43 (145.51)	0.5	6.6 (Pt 5mV/s)	[38]
17	 EPC	-81	148	1.13	3.0	5.25	0.95 (139.12)	1.8	5.1 ($LiCoO_2$ 50μV/s)	[11]
18	 EiPC	-132	135	0.98	3.0		0.94 (140.60)	1.7	5.5 ($LiCoO_2$ 50μV/s)	[11]
19	 MiPC	-76	117	0.86	3.0	4.92	0.97 (121.78)	1.8	5.3 ($LiCoO_2$ 50μV/s) 5.1^a (Pt 5mV/s)	[11],[28]
20	 EC	36.4	248	1,90^b	89.8^b	4.61	1.32^b (66.71)	8.3	6.7 (GC 10mV/s) 5.5 (Pt 0.1mV/s)	[31],[39],[40],[41]
21	 FEC	17.3	210	4.1	78.4	4.70	1.50 (70.70)	5.0	6.6 (Pt)	[36],[42]
22	 PC	-48.8	242	2.53	64.9	4.81	1.20 (85.08)	5.6 6.0^a	6.0 (GC 10mV/s) 5.2^a (Pt 5mV/s)	[28],[31],[39],[40],[41]

23	 FPC		210	7.64	190.0			1.8	6.5 (Pt 5mV/s)	[43],[44]
24	 BC	-53	240	3.12	53.0		1.14 (101.86)	3.2^{a}	4.8^{c} 4.3^{d} (Pt 5 mV/s)	[28],[31],[41],[45]
25	 VEC			2.71^{a}	45.0		1.19 (95.88)	4.3	4.6^{c} 4.2^{d} (Pt 5 mV/s)	[28],[41]
26	 VC	22	162	1.54^{a}	126.0	4.45	1.35 1.35^{a} (63.74)	13.2^{a}	3.9^{c} 5.0 (Pt 10mV/s) 4.7^{a} (Pt 5mV/s)	[28],[31],[41],[46],[47]

mp: melting point in °C; bp: boiling point in °C; η: dynamic viscosity in cP at 25 °C (except if another temperature is given in the Table); ε_r: dielectric constant at 25 °C (except if another temperature is given in the Table); μ: dipole moment in D; ρ: density at 25 °C (except if another temperature is given in the Table); V_m: molar volume in $cm^3.mol^{-1}$ at 25 °C (except if another temperature is given in the Table); κ: ionic conductivity of 1M $LiPF_6$ in $mS.cm^{-1}$ at 25 °C (except if another temperature is given in the Table); E_{ox}(electrode, scan rate): oxidation potential vs. Li/Li^+ in V at room temperature determined in 1 M $LiPF_6$ except for (*) for which E_{ox} was determined in 1.2 M $LiPF_6$; a) This work, b) at 40°C, c) Theoretical data from literature.

molecules with the addition of free-rotational groups in the chemical structure as illustrated in entries 17 and 18 in Table 1 where the replacement of a linear chain by a branched chain decreases the viscosity. Van der Waals interactions, hydrogen bonding and molecular shape influence more or less the melting and boiling points. If the molecules contributing to the lattice are rigid, compact and symmetrical, they tend to "fit" the best and tend to maximize interactions, which results in higher melting points as it takes more energy to separate the molecules. For instance, the melting point of the symmetrical EC (Table 1- entry 20) is much higher than that of PC (Table 1-entry 22) which is not symmetrical. Similar observations are illustrated by comparing the melting points of EPC and EiPC (Table 1-entries 17 and 18). Although it is difficult to give a general rule about the effect of the presence of fluorine atoms on the melting points because of a lack of data in Table 1, it seems that the addition of fluorine atoms in alkyl carbonates may increase slightly the melting point (Table 1, entries 7 and 10). It is probably because of an increase of the Van der Waals interactions as the presence of electronegative atoms usually increases the dipole moment. Likewise, boiling points of alkyl carbonates are linked with the size and the shape of the molecules. The bigger the molecule is, the higher the Van der Waals interactions are and the higher the boiling point is. Furthermore, it seems that the presence of fluorine atoms decreases slightly the boiling point but it is difficult to give a general trend because of the lack of data in Table 1 (only entries 23 and 24). The presence of branching in the chemical structure is responsible for a decrease of the boiling point because the more rod-like the molecules are, the easier they will be able to line up and bond (Table 1, entries 17 and 18).

The dielectric constant of a solvent gives information about the capability of solvent molecules to dissociate salts. The higher the dielectric constant is, the easier the salt is dissociated in the solvent. Table 1 shows that linear or branched alkyl carbonates exhibit lower dielectric constants than cyclic carbonates. Indeed, dielectric constants of linear or branched alkyl carbonates do not exceed 10 while dielectric constants of cyclic carbonates are greater than 40. It means that the mobility of cyclic carbonates is less affected by an external electric field than the mobility of linear or branched alkyl carbonates likely due to the higher viscosity of cyclic carbonates and because dipole-dipole interactions are higher for cyclic carbonates (see dipole moment values of cyclic carbonates and linear or branched alkyl carbonates in Table 1). Furthermore, it is interesting to note that the presence of fluorine atoms in linear or branched alkyl carbonates does not affect significantly the dielectric constant. It is difficult to give a general trend as an increase of the dielectric constant occurs when a fluorine atom is added to PC (ε_r=64.9 for PC and 190 for FPC, Table 1-entries 22 and 23) while a decrease of the dielectric constant is observed when EC is replaced by FEC (ε_r=89.8 for EC and 78.4) for FEC, Table 1, entries 20 and 21).

Ionic conductivity of a salt in a solvent mainly depends on the viscosity and the dielectric constant of the solvent. It is obvious that low ionic conductivity is observed in highly viscous solvents as ionic mobility is low in such media. Furthermore, ionic conductivity is low in solvents exhibiting low dielectric constants as salts are poorly dissociated in such media and, consequently, contact ion-pairs formation is favoured. It is certain that ionic conductivity of electrolytes depends both on the nature of the solvent and the salt. Lithium salts with small anions such as PF_6^- are more mobile but they are also more easily subject to ionic association. Conversely, lithium salts containing anions with moderate size such as $TFSI^-$ [bis(trifluoromethane)-sulfonimide] are better dissociated but their ionic mobility is lower. Table 1 shows that the ionic conductivity of $LiPF_6$ (1M) in linear and branched alkyl carbonates varies between 0.5 $mS.cm^{-1}$ and 6 $mS.cm^{-1}$. However, most values of ionic conductivity are around 2 $mS.cm^{-1}$. The high ionic conductivity of 1M $LiPF_6$ in DMC (6 $mS.cm^{-1}$, Table 1-entry 1) can be explained by the very low viscosity of DMC. The slightly lower ionic conductivity of $LiPF_6$ in MFDMC (4.2 $mS.cm^{-1}$, Table 1-entry 2) is likely due to the slightly higher viscosity of this solvent caused by the presence of fluorine atoms. Conversely, the high ionic conductivity of $LiPF_6$ in cyclic carbonates can be explained by the moderate viscosity of cyclic carbonate and their high dielectric constants (greater than 40), which favours salt dissociation. In particular, it is interesting to highlight the very high ionic conductivity of $LiPF_6$ in VC (Table 1-entry 26), i.e. 13.2 $mS.cm^{-1}$. Such a value is not so surprising because this solvent exhibits a very high dielectric constant (ε_r=126) and a moderate viscosity (η=1.54 cP).

Oxidation potentials depend on the nature of the solvent, the salt and the electrode. Oxidation potentials reported in Table 1 can be compared as most of these data were determined in the presence of the same salt (1M $LiPF_6$) and with the same working electrode (mainly platinum electrode). In a few cases, oxidation potentials were also determined at a glassy carbon electrode or a lithium metal oxide electrode. Comparison of the oxidation potentials obtained at platinum and glassy carbon electrodes provides interesting information about the electrocatalytic phenomena occurring during electrolyte oxidation. For the sake of illustration, entries 20 and 22 show the electrocatalytic effect. Indeed, the oxidation potential decreases from 6.7 V to 5.5 V for EC and from 6.0 V to 5.2 V for PC, respectively, when glassy carbon is replaced by a platinum electrode (electrocatalytic reactions are favoured on platinum electrode). Furthermore, entry 19 shows that the electrocatalytic effect is less important for MiPC on platinum than $LiCoO_2$. Table 1 also shows that the anodic stability of carbonates varies between 5.2 V and 6.8 V. The highest oxidation potential is obtained by TFEMC at a platinum electrode (6.8 V, Table 1-entry 10) while the lowest one is obtained for VC (4.7 V, Table 1-entry 26). Cyclic carbonates seem to be a little bit less stable towards oxidation than linear or branched alkyl carbonates. The ramification and the length of the alkyl chains do not change significantly the anodic stability of the molecules. It appears that the presence of fluorine atoms in the carbonates seems to improve slightly the resistance against oxidation. For instance, the oxidation potential at a platinum electrode increases from 5.5 V to 6.6 V when EC is replaced by FEC (Table 1-entries 20 and 21) or from 6.4 V to 6.6 V when PFPMC is used instead of MPC (Table 1-entries 11 and 16). Although many studies in the literature report oxidation potentials at platinum and glassy carbon electrodes, it is clear that the knowledge of oxidation potential at active materials used in LiBs such as $LiCoO_2$ would be very informative. Unfortunately, there are only few papers providing such data. EPC, EiPC and MiPC (Table 1-entries 17-19) show good anodic stability in the presence of $LiPF_6$ even at $LiCoO_2$ electrodes, i.e. 5.1, 5.5 and 5.3 V vs. Li/Li^+, respectively.

Obviously, oxidation potential is not the only relevant electrochemical property to select an electrolyte for LiBs. Therefore, electrode capacities at the initial and final cycles as well as coulombic efficiency defined as follows are also reported in Table 2:

$$\%E = \frac{C_{\text{charge}}}{C_{\text{discharge}}} \quad (1)$$

C $_{\text{charge}}$ and C $_{\text{discharge}}$ denote the charge capacity and the discharge capacity at the last cycle.

This Table shows that alkyl carbonates can be cycled at various positive electrodes without significant fading (percentage of capacity loss per charge-discharge cycle) and with good coulombic efficiency in half-cell when a cut-off voltage of 4.2 V is applied with $LiCoO_2$ as positive electrode. A very good cycling ability in half-cell was achieved even at a cut-off voltage of 5 V when EC-DMC is tested at $LiNi_{0.5}Mn_{1.5}O_4$ electrode provided that 1% tris-(trimethylsilyl)-borate (TMSB) is added in order to form a protective film at the positive electrode (Table 2-entry 1). Indeed, the cell without TMSB suffered capacity loss and had capacity retention of 84.4% while 95.3% of capacity retention was achieved after 200 cycles in the presence of 1.0 wt.% TMSB in EC/DMC. Conversely, entry 6 in Table 2 shows that conventional carbonate electrolytes without additives such as EC-EMC+$LiPF_6$ can be long-term cycled up to at least 5.2 V (capacity retention=90% after 500 cycles at the 1C rate) by using a positive electrode material such as Cr-doped $LiCr_{0.05}Ni_{0.45}Mn_{1.5}O_4$ likely because electrocatalytic reactions are less preponderant onto such electrodes.

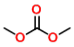
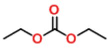
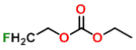
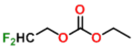
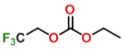
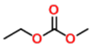
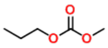
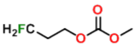
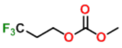
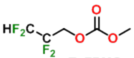
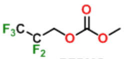
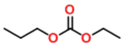
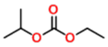
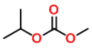
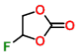
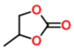
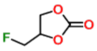
Esters

The comparison of Tables 1 and 3 shows that esters are less viscous than carbonates. Linear esters exhibit viscosities lower than 1.2 cP while the viscosities of cyclic esters are greater than 1.7 cP. The difference in viscosity between esters and carbonates may be explained by stronger Van der Waals interactions in carbonates as this family of molecules exhibits higher dipole moment values. The viscosity does not change monotonically with the number of fluorine atoms. For instance, the addition of one fluorine atom in EA leads to an increase of the viscosity from 0.45 cP to 0.9 cP (Table 3-entries 1 and 2) whereas a decrease of the viscosity from 0.9 cP to 0.65 cP is observed when one more fluorine atom is added to form EDFA (Table 3-entry 3). It is also interesting to note that the position of the fluorine atoms influences the viscosity as well (Table 3-entries 2 and 4).

Melting and boiling points of esters are of the same order as carbonates. It seems that the addition of fluorine atoms in esters is responsible for an increase of the melting point as it has been observed with carbonates (Table 3-entries 1 and 4 and entries 14 and 15). Conversely, the boiling points of esters do not decrease as in the case of carbonates when fluorine atoms are added. An increase of the boiling points when fluorine atoms are added would mean that the interactions between fluorinated ester molecules are greater than those of unfluorinated ones. It is difficult to explain why the boiling points of carbonates and esters vary in the opposite way in the presence of fluorine atoms in the alkyl chains. The lack of data does not allow any expectation of a general trend to explain the variation of the melting and boiling points when fluorine atoms are added in the chemical structure of esters.

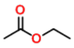
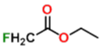
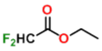
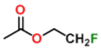
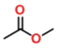
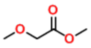
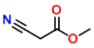
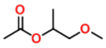
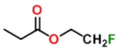
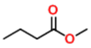
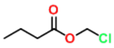
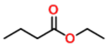
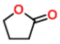
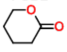
The dielectric constants of linear or branched alkyl esters are lower than those of cyclic esters. Table 3 shows that dielectric constants of esters do not exceed 7, while cyclic esters exhibit dielectric constant higher than 30. The addition of fluorine atoms and their position in the chemical structure slightly change the dielectric constants values. For instance, a change of the position of the fluorine atom in 2FEP and E2FP or the addition of one fluorine atom to form EFA from EA leads to an increase of the dielectric constants from 7 to 11.5 (Table 3-entries 9 and 10) and from 6 to 15 (Table 3-entries 1 and 2), respectively. The same trend is observed for cyclic esters as a significant increase of the dielectric constant is observed when one fluorine atom is added into the chemical structure of GBL (ε_r=39 and 72.6 for GBL and FGBL, respectively, Table 3-entries

Table 2: Charge capacity at electrodes used in LiBs in the presence of carbonates as solvent ($mAh.g^{-1}$) and corresponding coulombic efficiency (%) defined in Eq. (1).

Entry	Structure	Solvent	Electrodes and experimental conditions	Capacity after formation cycles	Capacity last cycle	Number of cycles	Coulombic efficiency	References
1	 DMC	EC/DMC+TMSB* 1/2 (v/v) $LiPF_6$ 1M	$Li/LiNi_{0.5}Mn_{1.5}O_4$ Charge 5V CC Discharge 3V CC	129	115	200	96	[48]
2	 DEC	EC/DEC 1/1 (mol) $LiPF_6$ 1M	$Li/LiCoO_2$ Charge 0.5C CC 4.2V CV Discharge 0.5C CC 3V			50	95	[33]
3	 EFEC	EC/EFEC 1/1 (mol) $LiPF_6$ 1M	$Li/LiCoO_2$ Charge 0.5C CC 4.2V CV Discharge 0.5C CC 3V			50	97	[33]
4	 EDFEC	EC/EDFEC 1/1 (mol) $LiPF_6$ 1M	$Li/LiCoO_2$ 0.2C			50	98	[34]
5	 ETFEC	EC/ETFEC 1/1 (mol) $LiPF_6$ 1M	$Li/LiCoO_2$ 0.2C			50	96	[34]
6	 EMC	EC/EMC 3/7 (v/v) $LiPF_6$ 1M	$Li/LiCr_{0.05}Ni_{0.45}Mn_{1.5}O_4$ C/10 2 cycles then 1C 5.3V	147	125	500	90	[40]
7	 MPC	PC/MPC 1/1 (mol) $LiPF_6$ 1M	$Li/LiCoO_2$ Charge 0.2C CCCV 4.2V 5h Discharge 0.2 CC 3V	130	128	50	99	[38]
8	 FPMC	PC/FPMC 1/1 (mol) $LiPF_6$ 1M	$Li/LiCoO_2$ Charge 0.2C CCCV 4.2V 5h Discharge 0.2 CC 3V	132	128	50		[38]
9	 TrFPMC	PC/TrFPMC 1/1 (mol) $LiPF_6$ 1M	$Li/LiCoO_2$ Charge 0.2C CCCV 4.2V 5h Discharge 0.2 CC 3V	129	125	50		[38]
10	 TeFPMC	PC/TeFPMC 1/1 (mol) $LiPF_6$ 1M	$Li/LiCoO_2$ Charge 0.2C CCCV 4.2V 5h Discharge 0.2 CC 3V	130	126	50		[38]
11	 PFPMC	PC/PFPMC 1/1 (mol) $LiPF_6$ 1M	$Li/LiCoO_2$ Charge 0.2C CCCV 4.2V 5h Discharge 0.2 CC 3V	132	130	50		[38]
12	 EPC	EC/EPC 1/1 (mol) $LiPF_6$ 1M	Charge C/30 3V-4.2V	149	145	5	98	[11]
13	 EiPC	EC/EiPC 1/1 (mol) $LiPF_6$ 1M	Charge C/30 3V-4.2V	141	139	5	99	[11]
14	 MiPC	MiPC $LiPF_6$ 1M	Charge C/30 3V-4.2V	117	111	5	99	[11]
15	 FEC	FEC/ EC/PC 1/3.5/3.5 (v/v/v) $LiPF_6$ 1M				200	99	[36]
16	 PC	PC $LiPF_6$ 1M	$Li/LiCoO_2$ Charge 0.2C CCCV 4.2V 5h Discharge 0.2 CC 3V	130	110	50		[38]
17	 FPC	FPC/EMC 3/7 (mol) $LiPF_6$ 1M	$C/LiCoO_2$ Charge 0.5C CC 4.2V CV Discharge 0.5C CC 3V	122	110	50	97	[43]

* TMSB [tris-(trimethylsilyl)borate] is an additive used for forming a protective film on cathodes.

Table 3: Physicochemical and electrochemical data of esters.

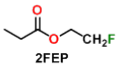
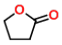
Entry	Structure	mp	bp	η	ε_r	μ	ρ (V_m)	κ	E_{ox} vs Li^+/Li	References
1	 EA	-84	77	0.45	6.0	1.83	0.90 (97.90)	11.5	5.4 (Pt 5mV/s)	[31],[50],[51]
2	 EFA		117	0.90	15.0		1.09 (97.34)	10.0	5.6 (Pt 5mV/s)	[51],[52]
3	 EDFA		99	0.65^e			1.18 (105.16)	6.1^a	4.5^a (Pt 5mV/s)	[28],[53],[54]
4	 2FEA	1	119	1.00	8.0		1.09 (97.34)	8.3	5.8 (Pt 5mV/s)	[51],[55]
5	 MA	-98.2	57	0.37	6.7	1.70	0.93 (79.66)	14.8^a	5.2^a (Pt 5mV/s)	[28],[56],[57],[58]
6	 MMOA		130	0.82^b			1.05 (99.15)	10.4^a	5.1^a (Pt 5 mV/s)	[28],[53],[54]
7	 MCA	-13	205	3.82^b	28.0^b		1.12 (88.47)	4.7^a	6.5^a (Pt 5mV/s)	[28],[53],[54]
8	 MPA			1.07	7.6^c		0.96 (137.67)	5.0^a	3.7^a (Pt 5mV/s)	[28],[54],[59]
9	 2FEP			1.12	7.0		1.06 (113.32)	5.5	6.2 (Pt 5mV/s)	[60]
10	 E2FP		129^d	0.82	11.5		1.02 (117.76)	8.0	5.8 (Pt 5mV/s)	[60],[61]
11	 MB	-84	102	0.60	5.5^e	1.71	0.90 (113.48)	4.2^a	4.6^a (Pt 5mV/s)	[28],[31],[62]
12	 ClMB		148		9.5^c		1.09 (125.32)	1.6^a	5.0^a (Pt, 5mV/s)	[28],[54],[63]
13	 EB	-93	120	0.71	5.1	1.74	0.88 (132.00)	2.7^a	4.3^a (Pt 5mV/s)	[28],[31],[64]
14	 GBL	-43.5	204	1.73	39.0	4.23	1.20 (71.74)	11.9 3.3^a	4.6 ($LiMn_2O_4$, 1mV/s) 5.5^a (Pt 5mV/s)	[10],[28],[31],[65]
15	 FGBL	26.5	210^d	3.35	72.6		1.30 (80.06)	4.9	6.8 (GC* 5mV/s)	[34],[66]
16	 DVL	-31	208	2.00	34.0	4.29	1.06 (94.45)	4.3^a	4.1^a (Pt 5 mV/s)	[28],[31],[67]

mp: melting point in °C; bp: boiling point in °C; η: dynamic viscosity in cP at 25 °C (except if another temperature is given in the Table); ε_r: dielectric constant at 25 °C (except if another temperature is given in the Table); μ: dipole moment in D; ρ: density at 25 °C (except if another temperature is given in the Table); V_m: molar volume in $cm^3.mol^{-1}$ at 25 °C (except if another temperature is given in the Table); κ: ionic conductivity of 1M $LiPF_6$ in $mS.cm^{-1}$ at 25 °C (except if another temperature is given in the Table); E_{ox} (electrode, scan rate): oxidation potential vs. Li/Li^+ in V at room temperature determined in 1 M $LiPF_6$ except for (*) for which E_{ox} was determined in 1 M $LiBF_4$; a) This work, b) at 40 °C, c) at 30°C, d) Extrapolated by nomograph, e) at 20 °C.

14 and 15). Furthermore, comparison of the dielectric constants of MA and MCA as well as MB and ClMB shows that the presence of nitrile or chloride group in the chemical structure of esters seems to increase the dielectric constant (Table 3-entries 5 and 7 as well as 11 and 12). However, there is no additional data in the literature to generalize these observations. In the presence of $LiPF_6$, ionic conductivities of esters are generally greater than those of carbonates, likely because ester viscosity is generally lower than that of carbonates. The tendency to form contact ion pairs may be similar in esters and carbonates as both families of molecules exhibit similar values of dielectric constants. The presence of fluorine atoms and their position in the chemical structure affect the ionic conductivity in relation to the variation of the dielectric constant and the viscosity. It is clear that the low values of ionic conductivity of $LiPF_6$ in cyclic esters come from the high viscosity. Finally, ionic conductivities in esters are not the limiting property for the use of esters in electrolytes for LiBs as their values are high enough.

Oxidation potentials are close in value to those obtained with carbonates. The lowest and the highest values of

Table 4: Charge capacity at few electrodes in the presence of esters as solvent (mAh.g^{-1}) and corresponding coulombic efficiency (%) defined in Eq. (1).

Entry	Structure	Solvent	Electrodes and experimental conditions	Capacity after formation cycles	Capacity last cycle	Number of cycles	Coulombic efficiency	References
1	 2FEP	EC/2FEP 1/1 (mol) $LiPF_6$ 1M	Li/$LiCoO_2$ Charge 0.2C CC 4.2V CV Discharge 0.2C 3V	135	112	50		[50]
2	 E2FP	EC/E2FP 1/1 (mol) $LiPF_6$ 1M	Li/$LiCoO_2$ Charge 0.2C CC 4.2V CV Discharge 0.2C 3V	136	112	50		[50]
3	 GBL	GBL $LiBF_4$ 1M	Li/NMC Charge 1C 4.3V Discharge 1C 3V	139	131	50		[68]

oxidation potentials at a platinum electrode, are obtained for MPA (3.7 V vs. Li/Li$^+$, Table 3-entry 8) and MCA (6.5 V vs. Li$^+$/Li, Table 3-entry 7), respectively. Electrocatalytic reactions seem to dramatically influence the anodic stability of esters as a significant decrease of the oxidation potential from 5.5 V to 4.6 V is observed for GBL (Table 3-entry 14) when $LiMn_2O_4$ is used instead of glassy carbon. Data on the cycling ability of esters at $LiCoO_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC) electrodes have been also gathered in Table 4. The fading is low for cyclic and fluorinated esters as it falls between 0.1%/cycle and 0.3%/cycle.

Although it is well-known that ethylene carbonate (EC) is essential to ensure long cycling ability by forming a high-quality passivative film at the graphite electrode, cycling of graphite electrodes in other solvents such as esters without exfoliation is very difficult. Therefore, esters are usually mixed with EC or other additives in order to allow the formation of a good passivative film onto graphite. For instance, the addition of 5% VC (Table 1-entry 26) in ethyl acetate (EA)+ 1M $LiPF_6$ leads to a fading of about 5% after 120 cycles at C/20 and 40 °C in a full-cell containing NMC as positive electrode and graphite as negative electrode.[69]

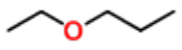
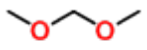
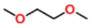
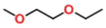
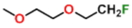
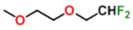
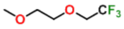
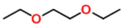
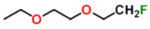
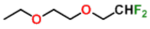
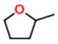
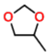
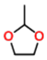
Ethers and acetals

Ethers and acetals exhibit the lowest viscosity among all the solvents used in electrolytes for lithium-ion batteries. Table 5 shows that viscosities do not exceed 1.16 cP even for relatively high molecular weight. Such low viscosity can be explained by weak Van der Waals interactions as the dipole moment remains low (around 1.5 D generally) compared to other solvents such as carbonates for which dipole moments can reach 4 D. Furthermore, the shape of the linear esters may enable the molecules to arrange and fit themselves so as to facilitate the process of flow. No data about the influence of fluorine atoms in the chemical structure on the viscosity of fluorinated ethers or acetals are reported in the literature.

Melting points are also very low compared to the other solvents used in electrolytes for LiBs (generally around -80 to -150 °C). In Table 5, the highest and the lowest melting points are found for DME (-53 °C, entry 3) and 2Me-THF (-137 °C, entry 13). The free rotation of C-O-C bonds in ethers decreases the rigidity and the compactness of the lattice resulting in weaker interactions and, therefore, lower melting points because it takes less energy to dissociate the molecules. The low boiling point of ethers is a limitation for their use in lithium-ion batteries because of safety concerns. Indeed, Table 5 shows that boiling points range between 41 and 125 °C depending on the chemical structure of the ether molecules. Such low boiling points are not surprising because Van der Waals interactions are weak given that dipole moments are low (less than 3 D and more generally around 1.5 D).

Ionic conductivity of salts in solvents depends on several parameters including solvent properties such as the viscosity and the dielectric constant. Usually, the lower the viscosity is, the higher the ionic conductivity of salt is. In the case of ethers, the examination of ionic conductivities of $LiPF_6$ in several ethers shows that the relationship between ionic conductivity, viscosity and dielectric constant is not so obvious. For instance, although THF and 2 Me-THF (Table 5-entries 12 and 13) as well as 1,3-DL, 4Me-1,3-DL and 2Me-1,3-DL (Table 5, entries 14-16) exhibit similar viscosities (0.46 and 0.47 cP for THF and 2Me-THF, 0.59, 0.60 and 0.54 cP for 1,3DL, 4Me-1,3-DL and 2Me-1,3-DL) and similar dielectric constants (7.4 and 6.2 for THF and 2Me-THF, 7.1, 6.8 and 4.4 for 1,3DL, 4Me-1,3-DL and 2Me-1,3-DL), the ionic conductivities of $LiPF_6$ in these solvents are quite different as they vary from 1.7 to 9.1 mS.cm^{-1}. The low values of ionic conductivity observed for 2Me-THF, 4-Me-1,3-DL and 2Me-1,3-DL compared to THF and 1,3-DL in spite of their similar physicochemical properties may be explained by the presence of the methyl group at the α position of the ether function which might make lithium complexation more difficult and might favour the formation of species in solution that do not participate to ionic conductivity such as contact ion-pairs. Table 5 shows that the ionic conductivities of $LiPF_6$ can reach 5-9 mS.cm^{-1} in several linear ethers or in cyclic ethers provided that there is no steric hindrance in the vicinity of the ether function. Moreover, it is interesting to highlight that 11.1 mS.cm^{-1} can be reached by adding DMC into DME in the presence of $LiPF_6$, which is one of the highest ionic conductivities in dipolar aprotic solvents (Table 5-entry 3).

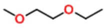
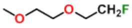
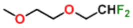
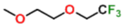
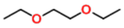
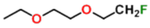
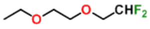
Table 5: Physicochemical and electrochemical data of ethers and acetals

Entry	Structure	mp	bp	η	ε_r	μ (D)	ρ (V_m)	κ	E_{ox} vs Li^+/Li	References
1	 EPE	-126.7	63	0.31[a]		1.16	0.73 (120.75)	4.5 EPE/DMC 1/1[a,d]	5.5[b] 4.2[a,d] EPE/DMC (Pt 5mV/s)	[28],[70],[71],[72]
2	 DMM	-105	41	0.33	2.7	2.41	0.86 (88.49)	1.5[a]	3.5[a] (Pt 5mV/s)	[28],[31]
3	 DME	-58	84	0.46	7.2	1.15	0.86 (104.79)	11.1 DME/DMC 1/1[a,d]	5.0[a,d] DME/DMC (Pt 5mV/s)	[28],[31],[73]
4	 EME		103.5	0.50	6.0		0.85 (122.53)	7.5	4.5 (Pt 5mV/s)	[74],[75]
5	 FEME			1.00	17.0			9.0	5.0 (Pt 5mV/s)	[75]
6	 DFEME			1.10	16.0			4.0	4.8 (Pt 5mV/s)	[75]
7	 TFEME		125[c]	0.80	17.0			2.3	5.0 (Pt 5mV/s)	[75]
8	 DEE	-74	121	0.56	5.1	1.76	0.84 (140.69)	5.8 DEE/DMC 1/1[a,d]	4.5[a,d] DEE/DMC (Pt 5mV/s)	[28],[31],[75],[76]
9	 EFEE			1.15	15.0			7.0	4.9 (Pt 5mV/s)	[75]
10	 EDFEE			1.16	14.5			2.3	4.9 (Pt 5mV/s)	[75]
11	 ETFEE			0.90	15.0			2.2	4.9 (Pt 5mV/s)	[75]
12	 THF	-109	66	0.46	7.4	1.70	0.88 (81.94)	9.1[a]	3.5 [a] (Pt 5mV/s)	[28],[31],[67]
13	 2Me-THF	-137	80	0.47	6.2	1.60	0.85 (101.33)	1.7[a]	3.6 [a] (Pt 5mV/s)	[28],[31],[73]
14	 1,3-DL	-95	78	0.59	7.1	1.25	1.06 (69.89)	5.7[a]	3.4 [a] (Pt 5mV/s)	[28],[31],[67]
15	 4Me-1,3-DL	-125	85	0.60	6.8	1.43	0.98 (89.91)	1.9[a]	3.4 [a] (Pt 5mV/s)	[28],[31]
16	 2Me-1,3-DL		83	0.54	4.4	1.21	0.98 (89.91)	1.6[a]	4.1[a] (Pt 5mV/s)	[28],[31],[77],[78]

mp: melting point in °C; bp: boiling point in °C; η: dynamic viscosity in cP at 25 °C (except of another temperature is given in the Table); ε_r: dielectric constant at 25 °C (except if another temperature is given in the Table); µ: dipole moment in D; ρ: density at 25 °C (except if another temperature is given in the Table); V_m: molar volume in $cm^3.mol^{-1}$ at 25 °C (except if another temperature is given in the Table); κ: ionic conductivity of 1M $LiPF_6$ in $mS.cm^{-1}$ at 25 °C (except if another temperature is given in the Table); E_{ox} (electrode, scan rate): oxidation potential vs. Li/Li^+ in V at room temperature with 1 M $LiPF_6$; a) This work, b) Theoretical data from literature, c) Extrapolated by nomograph, d) mixed with DMC due to insolubility of $LiPF_6$ 1M into these solvents.

Such a high ionic conductivity is also obtained by dissolving 1M $LiPF_6$ in the fluorinated ether FEME (9 $mS.cm^{-1}$, Table 5-entry 5). However, fluorination of ether does not lead systematically to highly conductive electrolytes esters as ionic conductivities of $LiPF_6$ in DFEME or TFEME (Table 5-entries 6 and 7) are equal to 4 and 2.3 $mS.cm^{-1}$ despite their low viscosity and moderate dielectric constant, respectively. Ethers exhibit oxidation potentials lower than carbonates and esters. It is especially the case for cyclic ethers such as the derivatives of THF or DL for which the anodic stability is around 3-4 V vs. Li^+/Li at a platinum electrode. Furthermore, Table 5 shows that oxidation potentials of linear or branched ethers are generally ranged between 4.5 V and 5 V at a platinum electrode except for DMM (3.5 V, Table 5-entry 2) and EPE (5.5 V, Table 5-entry 1). Nonetheless, the anodic stability of ethers is too poor for an application in high-voltage batteries.

Table 6: Charge capacity at few electrodes in the presence of ethers as solvent (mAh.g^{-1}) and corresponding coulombic efficiency (%) defined in Eq. (1).

Entry	Structure	Solvent mixture	Cell and experimental conditions	Capacity after formation cycles	Capacity last cycle	Number of cycles	Coulombic efficiency	References
1	 EME	EC/EME 1/1 (mol) $LiPF_6$ 1M	Li /$LiCoO_2$ 0.2C	135	100	50	99	[75]
2	 FEME	EC/FEME 1/1 (mol) $LiPF_6$ 1M	Li /$LiCoO_2$ 0.2C	135	102	50	99	[75]
3	 DFEME	EC/DFEME 1/1 (mol) $LiPF_6$ 1M	Li /$LiCoO_2$ 0.2C	125	60	50	95	[75]
4	 TFEME	EC/TFEME 1/1 (mol) $LiPF_6$ 1M	Li /$LiCoO_2$ 0.2C	135	120	50	98	[75]
5	 DEE	EC/DEE 1/1 (mol) $LiPF_6$ 1M	Li /$LiCoO_2$ 0.2C	120	105	50	98	[75]
6	 EFEE	EC/EFEE 1/1 (mol) $LiPF_6$ 1M	Li /$LiCoO_2$ 0.2C	130	110	50	98	[75]
7	 EDFEE	EC/EDFEE 1/1 (mol) $LiPF_6$ 1M	Li /$LiCoO_2$ 0.2C	130	110	50	99	[75]
8	 ETFEE	EC/ETFEE 1/1 (mol) $LiPF_6$ 0.5M	Li /$LiCoO_2$ 0.2C	135	110	50	99	[75]

Data on the cycling ability of ethers at $LiCoO_2$ electrodes have been also gathered in the present paper (Table 6). A very good coulombic efficiency close to 99% is obtained with ether electrolytes on $LiCoO_2$ after 50 cycles.

The fluorinated ether 3-(1,1,2,2-tetrafluoroethoxy)-1,1,2,2-tetrafluoropropane (F-EPE) has been studied as a high-voltage solvent for NMC/graphite cells.[79] The use of 20% F-EPE in EC:DEC (1:3, wt. %) leads to the formation of a dense SEI on the graphite electrode, which prevents the direct contact between the graphite surface and the electrolyte during cycling. This is helpful for the reversible intercalation of Li^+ into the graphite electrode while allowing low irreversible capacity loss. Such results show that mixtures of FEC and esters are potentially relevant as new electrolytes for high-voltage applications.

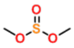
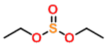
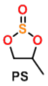
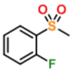
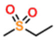
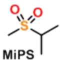
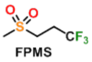
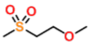
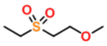
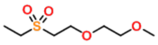
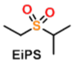
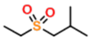
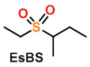
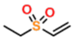
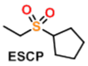
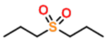
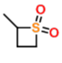
Sulfoxides, sulfites and sulfones

Table 7 gathers the physicochemical properties of sulfoxides, sulfites and sulfones used as electrolytes in LiBs. Generally, sulfur compounds exhibit very high viscosity, which increases sharply with the molecular weight. Among the solvents reported in Table 7, DMSO exhibits the lowest viscosity (1.9 cP, Table 7-entry 1) while EMEES is the most viscous solvent with a viscosity of 12 cP (Table 7-entry 13). As in the case of the other families of solvents used in LiBs, cyclic sulfur compounds are much more viscous than linear or branched ones. Such high viscosity cannot be only related to strong Van der Waals interactions because the dipole moments reported in Table 7 are as high as those observed with carbonates, which are really less viscous. The molecular weight of the sulfur compounds can no longer explain their high viscosity. For instance, viscosities of the carbonates DEC (Table 1-entry 3), MPC (Table 1-entry 11) and EPC (Table 1-entry 17) range from 0.75 cP to 1.13 cP and viscosity of the sulfone MEMS (Table 7-entry 11) is equal to 11.5 cP whereas the molecular weights are of the same order (118 g.mol^{-1} for the cited carbonates against 138 g.mol^{-1} for MEMS). The high viscosity values observed in the case of sulfur compounds may be explained by the degree of freedom of these molecules that makes the process of flow difficult. Anyway, it is clear that such high viscosities represent a huge disadvantage for their use in lithium-ion batteries unless they are mixed with low viscosity solvents.

Another disadvantage for their use as a unique solvent in electrolytes resides in the high melting points of some of them and, more especially, their solid state even at room temperature in certain cases (FS, EMS, FPMS, DPS in Table 7-entries 6, 7, 10, 19, respectively). Melting points of the sulfur compounds gathered in Table 7 are very sensitive to the chemical structure as they vary from -141 °C for DMS (entry 2) to 56 °C for FPMS (entry 10). Very viscous compounds may have vitreous glass transitions. The smallest molecules have the lowest melting points whereas the heaviest ones, i.e. cyclic and fluorinated sulfur compounds, exhibit the highest melting points. In any cases, boiling points are high enough for their use in LiBs. The highest boiling point rise to 328°C for ESCP (Table 7-entry 18) but most of these sulfur compounds have boiling points around 200 °C.

Sulfoxides, sulfites and sulfones have high dielectric constants, which vary from 15 to 58. Such high dielectric

Table 7: Physicochemical and electrochemical data of sulfoxide, sulfites and sulfones.

Entry	Structure	mp	bp	η	ε_r	μ	ρ (V_m)	κ	E_{ox} vs Li^+/Li	References
1	 DMSO	18.5	189	1.90	46.6	3.90	1.09 (71.68)	8.6[a]	4.1[a] (Pt 5mV/s)	[28],[67],[80],[81],[82]
2	 DMS	-141	126	0.87	22.5	2.90	1.20 (91.78)	13.6[a]	4.2[b] ($LiCoO_2$) 4.5[a] (Pt 5mV/s)	[28],[83],[84],[85],[86]
3	 DES	-112	156	0.83	15.6	2.96	1.08 (127.94)	10.2[a]	2.9[b] ($LiCoO_2$) 4.5[a] (Pt 5mV/s)	[28],[53],[85],[86],[87]
4	 ES	-17	174	2.06	39.6	3.74	1.41 (76.67)	9.8[a]	3.4[b] ($LiCoO_2$) 4.6[a] (Pt 5mV/s)	[28],[85],[88],[89],[90]
5	 PS		214[c]					6.3[d]	3.9[b] ($LiCoO_2$) 4.7[a] (Pt 5mV/s)	[28],[85],[91]
6	 FS	48						0.1[e]	5.1[e] (Pt 1mV/s)	[92]
7	 EMS	32	240[c]	5.50[f]	58.0[f]			2.8 2.5[e]	5.5[e] (Pt 20mV/s)	[19],[92],[93]
8	 MiPS		224.8					1.5[e]	5.6[e] (Pt 5mV/s)	[94]
9	 FMS		123			4.02	1.30 (75.45)	2.8[e]	5.5[e] (Pt 5mV/s)	[95],[96],[97]
10	 FPMS	56	180					Unstable[g]	6.7[d]	[98],[99]
11	 MEMS	15	275[c]	11.50[a]			1.21[a] (114.20)	1.2 1.5[a,e]	6.0[d] 5.2[a,e] (Pt 5mV/s)	[19],[28],[99]
12	 EMES	2	286[c]					1.2 1.4[e]	5.6[e] (Pt 1mV/s)	[19]
13	 EMEES		170[a]	12.00[a]			1.15[a] (170.57)	0.2 1.1[e]	5.3[e] (Pt 1mV/s) 4.9[a,e] (Pt 5mV/s)	[19],[28]
14	 EiPS	-8	265	5.60	55.0			2.0 2.2[e]	5.7 ($LiMn_2O_4$ 0.1mV/s) 5.4[a] (Pt 5mV/s) 5.6[e] (Pt 5mV/s)	[28],[93],[98]
15	 EiBS	-15	261	5.50	36.0			2.5[e]	5.6 ($LiMn_2O_4$ 0.1mV/s)	[93],[98]
16	 EsBS	-60	290[c]		48.0			1.5[e]	5.8[f] ($LiMn_2O_4$ 0.1mV/s)	[98]
17	 EVS	<-50	242[c]	10.07			1.15 (104.50)	3.0[e]	4.2[h] (Pt 1mV/s)	[53],[92],[100]
18	 ESCP	38	328[c]					0.8[e]	5.5[e] ($LiCr_{0.015}Mn_{1.985}O_4$)	[101]
19	 DPS	27	266	5.40[i]	32.0[i]	4.44	1.04[i] (144.46)	1.3[e]	5.7[e] (Pt 5mV/s)	[94],[102],[103]
20	 MTS	<-20	270[c]				1.22 (98.50)	2.3[e]	5.6 ($LiMn_2O_4$ 0.1mV/s)	[98],[104]

21	 TMS / SL	27.4	285	10.34^{i}	43.3^{i}	4.81	1.26^{i} (95.37)	2.0^{e}	5.0^{e} (Pt 1mV/s)	[86],[92],[100],[103]
22	 3Me-SL	0.5	276	11.81	29.4		1.18 (113.72)	1.6^{e}	$>5.0^{e}$ (Pt 5mV/s)	[20],[103],[105],[106]

mp: melting point in °C; bp: boiling point in °C; η: dynamic viscosity in cP at 25 °C (except if another temperature is given in the Table); ε_r: dielectric constant at 25 °C (except if another temperature is given in the Table); μ: dipole moment in D; density at 25 °C (except if another temperature is given in the Table);V_m: molar volume in $cm^3.mol^{-1}$ at 25 °C (except if another temperature is given in the Table); κ: ionic conductivity of 1M $LiPF_6$ in $mS.cm^{-1}$ at 25 °C (except if another temperature is given in the Table); E_{ox} (electrode, scan rate): oxidation potential vs. Li/Li^+ in V at room temperature with 1 M $LiPF_6$; a) This work, b) $LiPF_6$ 0.2M, c) Extrapolated by nomograph, d) $LiPF_6$ 1.3M d) Theoretical data from literature, e) in the presence of 1M LiTFSI instead of 1M $LiPF_6$, f) at 35 °C instead of 25 °C, g) Unstable with lithium salts because of the presence of fluorine atoms, which increase the proton acidity, resulting in high reactivity with lithium salts, g) LiTFSI 1.2M i) at 30 °C instead of 25 °C,

constants favour the salt dissociation and, therefore, limit ion-pair formation even at high salt concentrations. The high dissociating power of sulfur compounds explain why $LiPF_6$ and LiTFSI exhibit ionic conductivities of a few $mS.cm^{-1}$ despite their very high viscosity. It is interesting to note that the ionic conductivities of MEMS, EMES, EMEES, and EiPS (Table 7-entries 11-14) are similar in the presence of $LiPF_6$ or LiTFSI while ionic conductivity in dipolar aprotic solvents in the presence of LiTFSI is generally lower than in the presence of $LiPF_6$ because of the lowest ionic mobility of $TFSI^-$. Regarding low-viscosity solvents such as DMSO, DMS and DES (Table 7-entries 1-3), the ionic conductivities of $LiPF_6$ are around 8-14 $mS.cm^{-1}$. Such values of ionic conductivities are the highest ones among those obtained in carbonates, esters and ethers. Therefore, electrolytes containing sulphur compounds as solvent could be used in LiBs thanks to their high ionic conductivity in the presence of lithium salts in spite of their high viscosity provided that no wettability issues and solvent penetration in the porosity of the separator or the electrodes occurs.

Oxidation potentials of sulfur electrolytes reported in Table 7 vary from 2.9 V to 5.8 V, depending on the organic solvent, the salt and the electrode. Theoretical calculations showed that FPMS may exhibit high anodic stability (Table 7-entry 10). Unfortunately, it was impossible to verify the DFT calculations of the oxidation potential of FPMS as this solvent is not stable in the presence of lithium salt, likely due to the presence of fluorine atoms in FPMS, which increases the proton acidity and reactivity towards lithium salts. It must be kept in mind during the selection of electrolytes for high energy density applications that electrocatalytic reactions can diminish considerably the anodic stability. For instance, the oxidation potential of DES in the presence of $LiPF_6$ (Table 7-entry 3) is dramatically reduced from 4.5 V to 2.9 V when oxidation tests are performed at a $LiCoO_2$ electrode usually used in LiBs instead of a platinum electrode. However, the anodic stability of some sulfur compounds are particularly still interesting. For instance, EsBS (Table 7-entry 16) exhibits both interesting physicochemical properties (low melting point, high boiling point, high enough ionic conductivity in the presence of LiTFSI) and high oxidation potential, i.e. 5.8 V vs. Li^+/Li at a $LiMn_2O_4$ electrode. Several solvents seem to be relevant for high voltage applications as reported in Table 7: EiBS, EsBS, EVS, ESCP, DPS, MTS, TMS/SL mixture, 3Me-SL (entries 15-22). Data on the cycling ability of sulfones in various systems (half- cells and full-cells) have also been gathered in the present paper (Table 8). The cycling ability of these electrodes in the solvents reported in Table 8 is good except for EMES and FS in the half-cell $LiCr_{0.015}Mn_{1.985}O_4/Li$ and the full-cell $Li_4Ti_5O_{12}/LiMn_2O_4$, respectively.

Ethylene carbonate is usually used to achieve good cycling at graphite electrodes. A recent study showed that the performance of the graphite electrode in EC-based electrolytes can be significantly improved by adding 0.3% ethylene sulfite (Table 7-entry 4) to inhibit EC decomposition at the first stage and to form a passivation film with more organic compound and better stability than with traditional EC-based electrolyte.[107] The cycling ability of EMES (Table 7- entry 12) in the presence of 1M $LiPF_6$ at a graphite electrode without adding EC has been studied in a half-cell during three charge-discharge cycles.[19] Unfortunately, the charge (and discharge) capacities, i.e. 343.0, (202.8), 251.4, (200.5) and 219.2, (193.0) mAh/g, are well below the theoretical capacity of graphite (372 mAh/g). This rapid decrease of the capacity during charge-discharge cycles may be caused by reaction of the electrolyte with the anode material, which cannot be prevented because of the formation of a low-quality SEI.[108] The difference in cycling ability between non-fluorinated and fluorinated sulfones at the negative electrode is mainly

Table 8: Charge capacity at some electrodes in the presence of sulfones as solvent (mAh.g^{-1}) and corresponding coulombic efficiency (%) defined in Eq. (1).

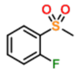
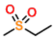
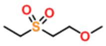
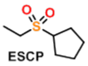
Entry	Structure	Solvent	Electrodes and experimental conditions	Capacity after formation cycles	Capacity last cycle	Number of cycles	Coulombic efficiency	References
1	 FS	FS LiTFSI 1M	$Li_4Ti_5O_{12}/LiMn_2O_4$ C/6 1.5-3V	70	51	100	100	[92]
2	 EMS	EMS LiTFSI 1M	$Li_4Ti_5O_{12}/LiMn_2O_4$ C/3 1.5V-3V	80	79	100	100	[92]
3	 EMES	EMES $LiPF_6$ 1M	$LiCr_{0.015}Mn_{1.985}O_4/Li$ 0.092 mA cm^{-2}	90	60	200	86	[92]
4	 ESCP	ESCP LiTFSI 1M	$LiCr_{0.015}Mn_{1.985}O_4$ C/2	82	77	120	85	[101]
5	 TMS / SL	TMS LiTFSI 1M	$Li_4Ti_5O_{12}/LiMn_2O_4$ C/3 1.5-3V	79	81	100	100	[92]

Table 9: Flash point values (FP) of several organic dipolar aprotic solvents in the presence or in the absence of lithium salts.[109]

Substance	Acronym	FP (°C)
Dimethyl carbonate	DMC	16
Ethyl methyl carbonate	EMC	23.5
Ethylene carbonate	EC	145.5
Ethyl acetate	EA	0.5
Methyl cyano acetate	MCA	43
γ-Butyrolactone	GBL	95.5
Dimethoxyethane	DME	1
Tetrahydrofuran	THF	-21
Dimethylsulfone	MS	143
Sulfolane	TMS/SL	165
EC:DMC (1:1 wt)	/	25
EC:DMC (1:1 wt) + $LiPF_6$ (1M)	/	25.5
EC:DMC (1:1 wt)+ LiTFSI (1M)	/	26

explained by the quality of the SEI. Therefore, in contrast with the stability on the cathode surface, which is invariant for all sulfones, the ability to form an effective SEI is found to be critically sensitive to the sulfone chemical structure. EMS (Table 7-entry 7) and EiPS (Table 7-entry 14) fail to form an effective SEI onto graphite electrode.[98]

Conversely, EiBS (Table 7-entry 15) and EsBS (Table 7-entry 16) show reversible Li-ion intercalation/deintercalation between 0.2 and 0.5 V despite a high resistance of the passivative film onto the graphite electrode. Therefore, the presence of fluorine atom in the chemical structure of sulfones may improve the quality of the passivative layer. As mentioned above, FPMS (Table 7-entry 10) alone is unstable towards $LiPF_6$ but such lack of stability can be avoided by mixing FPMS with EMC. In such a mixture, Li-ion intercalation/deintercalation into and from graphite can be performed thanks to the formation of a very good passivative film. This electrolyte was also studied successfully in a half-cell containing $LiMn_2O_4$ electrode as a positive electrode. A good reversibility was achieved after 20 cycles. Therefore, FPMS can be considered a promising candidate for LiBs.

Safety concerns

Physicochemical and electrochemical properties of the solvents are not the sole aspects to take into account when formulating new organic electrolytes for LiBs. Indeed, the thermal properties of electrolytes, and more especially their flammability, may pose a serious safety issue for their use in the consumer and transportation markets. In particular, the flash point (temperature at which enough vapour is produced to enable a first ignition) and the self-extinguishing times (time during which the sample burns) are very good indicators to evaluate potential thermal issues of the electrolytes for LiBs.[109] Flash points (FP) are the most widespread indicators to evaluate safety issues in electrolytes for LiBs. The flash point increases with decreasing the vapour pressure and increasing the boiling point of the compound. Both the vapour pressure and the flash point of solvent mixtures and electrolytes are dominated by the vapour pressure and flash point of the component having the highest volatility. For LiBs electrolytes these are DMC, EMC, DEC and EA. Table 9 gathers flash points of several solvents and electrolytes among many others reported in the paper published by Hess *et al.* (the reader can refer to this paper to have more information about the assessment of safety issues in electrolytes for LiBs).[109] This Table shows that cyclic carbonates are safer than acyclic carbonates with flash points (FP) exceeding 135 °C compared with a value lower than 35 °C for the latter.Moreover, it is interesting to note that the mixtures of acyclic and cyclic carbonates have FP values close to those observed for acyclic carbonates alone. Likewise, low FP values are reported for acyclic esters such as ethyl acetate (EA, 0.5 °C) and methyl cyanoacetate (MCA, 43 °C). Conversely, cyclic esters exhibit high FP and low flammability.[110] Despite their low FP, ethers are generally flammable compounds unless they contain fluorine atoms.[111-113] Finally sulfones exhibit very interesting

Table 10: Solvents used in the main data sources for Life Cycle Inventories

Battery	Solvent	Lithium Salt	Solvent in electrolyte (%mass)	Electrolyte in cell (%mass)	Impact during the production of LiBs		References
					GWP	Highest impact	
LMO-C	PC, EC, DEC, DMC, DME	$LiAsF_6$, $LiPF_6$, $LiBF_6$, LiTFSI, $LiC(SO_2CF_3)3$, LiTf	83.40	13.6-18.0	-	-	[124]
LMO-C	PC	$LiPF_6$	-	-	-	-	[125]
LMO-C	EC	$LiPF_6$	89.35	14.8	7.40%[c]	FDP 10.0%[c]	[122]
LFP-C	DME	LiCl[b]	84.9	19.1	2.36%	-	[119]
LMO-C	EC	$LiPF_6$	89.4	15.1	3.09%	CED 4.8%	[120]
NCA-C	DMC, EC[a]	$LiPF_6$	88.20	26.0	4.83%	E/A 33.0%	[121]
LFP-TiO				19.0	13.90%	GWP	
NMC-C	EC[a]	$LiPF_6$[a]	88	20.1	1.06%	FPD 3.5%	[118]
LFP-C					1.09%	FDP 3.5%	
LMO-C	EC+DMC	$LiPF_6$	85.40	10.3-12.4%	-	-	[126]

CED: Cumulated Energy Demand, E/A: Eutrophication/Acidification, FDP: fossil depletion, a) Modeled as a generic chemical, b) Proxy for the salts described in [124], c) Own calculation using the Ecoinvent 3.2. process battery production, Li-ion, rechargeable, prismatic | U Allocation at the Point of Substitution and the ReCiPe E (midpoint) methodology.

thermal properties as they are generally non-flammable and have very high flash points.[109]

However, it appears of great interest to acquire additional data concerning the flammability and the FP of sulfones containing additional functional groups such as ether or ester.[19] The use of additives such as redox shuttles or flame retarders is a solution for safety issues of LiBs[131, 132]. The redox shuttles are electrolyte additives which can produce reversible oxidation/reduction at a defined voltage slightly higher than the end-of-charge voltage to prevent voltage increasing due to overcharge. Many redox shuttle additives have been reported in the literature for 3V and 4V lithium-ion batteries[131]. Conversely, only few papers reported redox shuttles additives of high voltage up to 4.8 V such as tetraethyl-2,5-di-tert-butyl-1,4-phenylene diphosphate (TEDBPDP)[133]. On the other side, the use of flame-retardant electrolyte additive is the most important and effective methods to solve the safety problems. Currently, the flame-retardant molecules are mainly focused on phosphate class compounds (trimethylphosphate, dimethyl methyl phosphate, etc.) or more recently fluorinated propylene carbonates, which can efficiently block the chain reactions of hydroxyl radicals during the combustion of the organic electrolytes solution[134]. Therefore, the search for new redox shuttle or flame retarder additives which can operate at high voltage, i.e. with high anodic stability, is really a challenge, especially when 5V electrolytes exhibit low flash point as in the case of acetate or esters.

Environmental impact of the production of organic solvents for LiBs

LCA (Life Cycle Assessment) is a method for the identification and quantification of environmental impacts potentially caused by human activities. These activities are usually products or processes. LCA has a holistic perspective, commonly addressing a wide span of impacts through the entire activity, or through the entire lifespan of a product.[114] It consists of three subsequent key stages, followed by the interpretation of the results. The first stage is the definition of the Goal and Scope of the assessment. It includes the selection of the activity to be evaluated, but also the limits of such activity. For example, it will detail whether the study focuses on the manufacturing of a product, or if it also includes its use and end-of-life. The second stage is the construction of the Life Cycle Inventory (LCI), a collection of all the energy and material flows of environmental significance. Finally, in the Life Cycle Impact Assessment stage (LCIA), these flows are translated into potential environmental impacts, such as climate change or ozone layer depletion.

Over more than two decades, LCA has been applied to a number of industrial sectors, including production and use of LiBs. In a literature review on electric mobility, Hawkins *et al.* indicated the electricity used to charge the vehicle was several times more impactful than the production of the battery.[115] On LiBs, a recent review revealed that the performance of the battery had a greater effect on the environmental impact than the materials that constitute the battery.[116] Nevertheless, both conclusions rely heavily on global warming potential (GWP) and energy related impacts because those were the categories

Table 11: Solvents and their production routes

		Route	LCI in Ecoinvent 3.2	LCI in literature	Original LCI
Carbonates	DMC	Shell Omega process		✓	✓
	EC	From ethylene oxide and CO_2	✓		
Esters	EA	Fischer esterification	✓		
		Dehydrogenation pathway			✓
		Avada process			✓
		Butane oxidation	✓		
	GBL	Reppe process	✓		
		Maleic anhydride pathway			✓
Ethers	DME	Cleavage of ethylene oxide in presence of dimethyl ether	✓		
		DOW process			✓
		Shell Omega process			✓
		Hydration/coupling pathway			✓
	THF	Reppe process	✓		
		Hydrogenation of maleic anhydride			✓
		Mitsubishi acetoxylation			✓
Sulfones	SL	Hydrogenation of sulfolene			✓
	EMS	From methanethiol			✓
		From ethanethiol and chloromethane			✓

most widely evaluated. Thus, it is possible the environmental importance of batteries in general and battery materials in particular is higher than currently reported. Such an idea has been supported by at least a recent study suggesting the environmental importance of battery and battery component production depend on the actual use of the battery.[117]

Peters *et al.*[117] noticed a high degree of dependency in the LCA literature on LiBs: more recent studies rely heavily on previous work for the construction of their inventories. The main data sources for most LCI according to Peters et al. can be seen in Table 10, with detailed information regarding the electrolytes used and their impacts.

The eight data sources presented in Table 10 take into account four possible solvents (PC, EC, DME, and DMC) and two salts ($LiPF_6$ and LiCl). There is a good agreement in the composition of the electrolyte between studies, i.e. ≈85% solvent and ≈15% Li salts. They also coincide in identifying the electrolyte as one of the key components of a cell, although its mass ranges between 10 and 26% of the full cell. Half of these studies performed an LCIA, but only one covered a broad range of environmental impacts.[118] According to the results presented in these LCAs, and namely on the results for GWP, it would be possible to conclude that electrolytes are not an environmental hotspot for LiBs production. The share of electrolytes in the impacts from the production of LiBs tends to be significantly lower than their mass contribution. Electrolyte impact varies between 1 and 3%[118-121] and between 5 and 14%[121,122]. It is worth noting that for the last two references, most of the impact is due to the Li salt, despite its relatively small mass. Still, it would be necessary to evaluate additional impact categories to obtain a more complete picture of the environmental importance of electrolytes, and solvents, in LiBs.[115,116]

Goal and Scope

As a first step towards a more comprehensive view of the environmental profile of electrolytes, we conducted an LCA of eight of the most common solvents studied for formulating electrolytes in LiBs (Table 11). We followed a cradle-to-grave perspective: raw material extraction and production were included while use and end-of-life were not. As such, we used 1 kg of solvent produced as a functional unit, the flow to which all others are referred.

Five out of the eight targeted solvents (EC, EA, GBL, DME, and THF) were already included in Ecoinvent, one of the most widely used databases for LCIs.[123] However, only in the case of ethylene acetate (EA) more than one production route is available. Thus, we have built LCIs for additional production routes with the objective of evaluating whether there are differences between them in environmental terms.

As explained below, the constructed inventories rely significantly on information that is not process specific. Thus, our focus is to find potential hot spots and expected differences among solvents, rather than identifying the solvent (or the production route) with the lowest environmental impact.

Life Cycle Inventories

The detailed LCIs and their description are available in the ESI. However, three key assumptions are worth mentioning here:

- As for several solvents and organic chemicals in Ecoinvent, the LCIs developed here rely on generic information for key aspects such as electricity consumption or emissions. We think this is a valid approximation when the objective is to assess a full LiB, which is the application we expect readers will give to these inventories. However, it also means the conclusions of our study should be seen as interim, until LCI based on actual process data become available.
- The conversion rates presented in Ecoinvent were usually 95% or higher. These values are indicative of the overall efficiency of the process, potentially including reagent recirculation, and not as the conversion of a single-step reaction. We also used a conversion of 95% for our LCIs

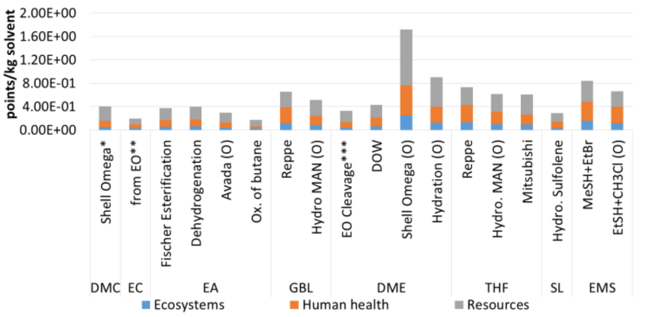
when no information was available in the literature. For those processes whose references reported substantially lower rates (e.g., 69%,[127] 76%,[128] 83%,[129]), two inventories were built: one with the conversion rates reported in the literature, another with a conversion of 95%. The latter are the only ones used for the following results, since it is likely they are more representative of current technology at industrial scale.

- Battery production usually requires materials of the highest purity, e.g., battery-grade lithium. Low-selectivity processes, among others, might not enable to produce high-quality solvents. Alternatively, they might do so at an extra cost, which would entail higher environmental impacts. However, we were not able to find information on the subject for all solvents. Thus, we assumed all processes evaluated produced a solvent suitable for LiBs.

Life Cycle Assessment

General overview

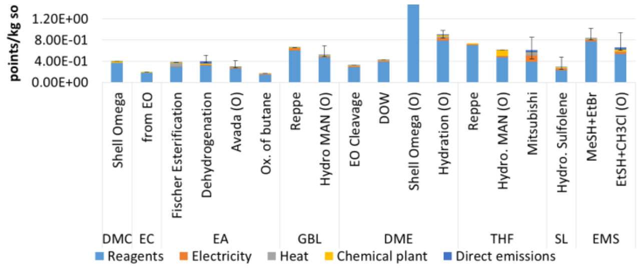
Figure 2: Endpoint Impacts for the production of 1kg of solvent



Single score (Hierarchist) and weighted (Average)

(O) Optimized process; Solvent used in references: * [120], and [125]; ** [119], [121]; and [125;***[118]

Figure 3: Sources of impact for the production of 1kg of solvent



Single score (Hierarchist) and weighted (Average) (O) Optimized process. Error bars indicate the impacts using the smallest and largest electricity and heat use reported in Ecoinvent for solvent production.

LCIA was calculated using the ReCiPe method,[130] as it is recommended in the ILCD Handbook.[114] Midpoint impacts were calculated following the Hierarchist (H) perspective, and the endpoint impacts aggregated according to the average weighting (A) for a single score. Figure 2 presents the potential total impact for the production of 1 kg of solvent for the three Endpoint indicators: damage to ecosystems diversity (ED), damage to human health (HH), and damage to resource availability (RA). The latter is the most impactful endpoint category for 16 solvents, while for the remaining two it is HH (GBL Reppe, and EMS EtSH+CH_3Cl).

The contribution of the different midpoint impact categories is detailed in the ESI. GWP is the dominating category for damage to ecosystems, where it is responsible for the majority of the potential impact (84% on average). The remaining impact is mostly due to agricultural and natural land occupation (ALOP and NLOP, 10% and 4% respectively).

GWP is also the largest impactor to human health (63% on average). Human toxicity (HTP) and particulate matter formation (PMFP) also contribute to the total impact in a significant way. They are responsible on average for 13 and 23% of the HH impact, respectively.

Damage to resources availability is completely dominated by the fossil depletion (FDP), responsible for at least 91% of the impact.

Results in Figure 2 indicate there are substantial environmental differences between solvents, and within a solvent, between production routes. Due to differences in the scope, it is not possible to compare directly our results with those from the references cited in Table 10. Nevertheless, it is worth mentioning that they found the electrolyte's contribution to be most significant for GWP and FDP (Table 10), which are the two most impactful midpoint categories in our results. According to Figure 2, the Ecoinvent solvents used in previous studies (DMC, EC, and DME from EO) are among those with lower impact. Thus, it is likely that if other solvents are used, their contribution to the overall impact of the battery production process will increase.

Sources of impact

For most solvents, the majority of the impact is generated not during their production, but during the synthesis of their reagents (Figure 3). Most reagents derive from liquefied petroleum gas or natural gas, making them very impactful in terms of FD: They require fossil fuels as feedstock as well as a source of energy. Energy consumption during the production of reagents is also significant in terms of GWP (see ESI).

Heat and electricity used during the synthesis of solvents however, plays a comparatively small role in defining the environmental profile of the whole production processes. The relative importance of energy use is further assessed with a sensitivity analysis. For those processes where we used generic electricity and heat demands ($3.30\ 10^{-1}$ kWh and 2 MJ heat per kg product respectively), error bars in Figure 3 indicate the impact of using the smallest and largest consumptions reported in Ecoinvent for solvent production ($2.00\ 10^{-4}$ kWh and $3.73\ 10^{-2}$ MJ/kg product, and 7.2510^{-1} kWh and 29.52 MJ/kg respectively). Since we assume energy requirements were on a "per reaction" basis (see ESI), the largest differences are found in those processes with several stages (DME Shell Omega, THF Mitsubishi and sulfones), which already had the highest energy requirements in our LCIs.

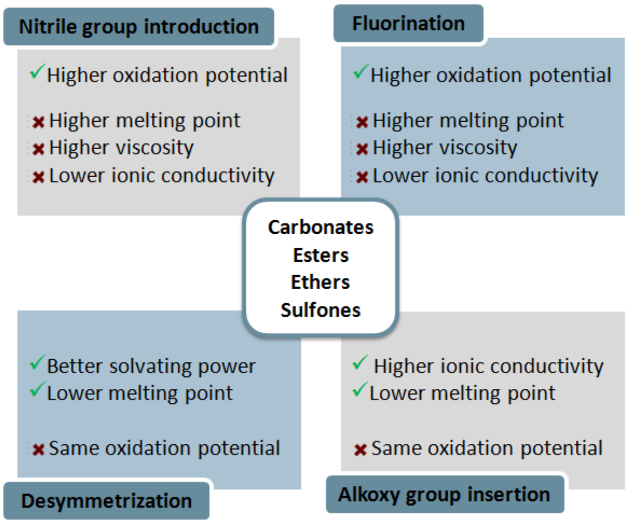


Figure 4: Trends about the Influence of the chemical structure of the solvents on their properties.

While generally desirable, using less energy than initially assumed would result only in moderate impact reductions (maximum of 24% for THF Mitsubishi and a reduction to less than 1% of the initially assumed demand). If energy demands are higher than we assumed, impacts would increase a maximum of 42% for EtSH+CH_3Cl if the heat demand is 18 times higher than our assumption.

The construction of the chemical plant where the solvents are produced and the direct emissions taking place there cause moderately small impacts. Still, direct emissions can cause larger impacts, particularly in terms of GWP, in non-optimized processes (i.e. processes with a low conversion rate), as it can be seen in the ESI.

Limitations and recommendations

The impacts associated with the original processes tend to be higher, but nevertheless comparable to those of processes already available in Ecoinvent. We strongly support the collection of LCI based on process data, but until such inventories become available, we suggest LCA practitioners and battery researchers to use our LCIs.

Although solvents constitute the majority of the electrolyte in mass, previous work found lithium salts to be responsible for most of the impact. Because $LiPF_6$ was the only salt evaluated, and only for a limited number of impact categories, a complete environmental picture of these salts is still missing. Thus, we see the LCA of different lithium salts not only as a follow up of these work, but as a necessary step towards a more detailed description of LiBs.

Conclusions

The design of new electrolytes for lithium-ion batteries (LiBs) is a difficult task because electrolyte properties must match a great number of specifications such as high ionic conductivity, low viscosity, high dielectric constant of the solvent, good wettability towards separator and electrodes, low melting point, high boiling point and high flash point for safety reason while being as cheap as possible and as much as possible environmentally friendly. More recently, a high anodic stability of the electrolyte was required in order to cycle positive electrodes at high-voltage for high-energy applications such as electric vehicles. Therefore, many challenges are coming for developing new electrolytes. Such a development cannot be made blindly. After analysing data from the literature and completing this set of data by new ones to homogenize them, this paper evidenced the following trends between the chemical structure of the solvent and their physicochemical and electrochemical properties for the four main families of solvent used in LiBs, i.e. carbonates, esters, ethers and sulfones (Figure 4).

It appears that the addition of groups exhibiting electron-withdrawing inductive effect improves the anodic stability of the electrolyte at the expense of other physicochemical properties such as the viscosity, the ionic conductivity, and the melting point. Furthermore, the insertion of alkoxy groups in the chemical structure of the solvent is responsible for an improvement of the ionic conductivity and a decrease of the melting point while the loss of symmetry leads to an increase of the solvating power and a decrease of the melting point without significant change in oxidation potential. By taking into account these effects and data previously published, it would be interesting to explore two fields:

-functionalization of sulfones to improve their physicochemical properties, especially their viscosities and their ionic conductivities in the presence of lithium salts.

- development of new esters exhibiting better electrochemical properties.

Last but not least, the choice of the electrolytes must take into consideration the environmental impact of their production though the environmental footprint of the electrolyte in LiBs has so far been considered minor. Nonetheless, LCA conducted in the present paper indicates that some solvents might potentially be more impactful than those already assessed in the literature. There seems to be important differences, not only between solvents but also between production routes for a given solvent. However, LCI based on process data will be required to confirm these hypotheses.

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Notes and references

1 T. Nagaura, K. Tozawa, *Prog. Batteries Sol. Cells*, 1990, **9**, 209.
2 A. Yoshino, K. Sanechika, T. Nakajima, US Pat., 4 668 595, 1987.
3 J. Swiatowska, P. Barboux, in *Lithium Process Chemistry: Resources, Extractions, Batteries and Recycling*, ed. A. Chagnes, J. Swiatowska, Elsevier, Amsterdam, 1st edn, 2015, ch. 4, pp. 125-166.
4 A. Rougier, I. Saadoune, P. Gravereau, P. Willmann, C. Delmas, *Solid State Ion.*, 1996, **90**, 83.
5 M. Guilmard, C. Pouillerie, L. Croguennec, C. Delmas, *Solid State Ion.*, 2003, **160**, 39.
6 A. Chagnes, J. Swiatowska in *Lithium Ion Batteries - New Developments*, ed. Ilias Belharouak , InTech, Vienna, 1st edn, 2012, ch. 6, pp. 145-172.
7 A. Chagnes, in *Lithium Process Chemistry: Resources, Extractions, Batteries and Recycling*, ed. A. Chagnes, J. Swiatowska, Elsevier, Amsterdam, 1st edn, 2015, ch. 5, pp. 167-189.
8 A. Chagnes, B. Carré, D. Lemordant, P. Willmann, *Electrochim. Acta,* 2001, **46** 1783.
9 A. Chagnes, C. Mialkowski, B. Carré, D. Lemordant, V. Agafonov, P. Willmann, *Journal de Physique IV*, 2001, **11**, 10.
10 A. Chagnes, B. Carré, D. Lemordant, P. Willmann, *J. Power Sources*, 2002, **109**, 203.
11 I. Geoffroy, A. Chagnes, B. Carré, D. Lemordant, P. Biensan, S. Herreyre, *J. Power Sources*, 2002, **112**, 191.
12 C. Mialkowski, A. Chagnes, B. Carré, P. Willmann, D. Lemordant, *J. Chem. Thermodyn.*, 2002, **34**, 1845.
13 A. Chagnes, S. Nicolis, B. Carré, P. Willmann, D. Lemordant, *ChemPhysChem*, 2003, **4** 559.
14 A. Chagnes, H. Allouchi, B. Carré, G. Oudou, P. Willmann, D. Lemordant, *J. Appl. Electrochem.*, 2003, **33**, 589.
15 A. Chagnes, B. Carré, P. Willmann, R. Dedryvère, D. Gonbeau, D. Lemordant, *J. Electrochem. Soc.*, 2003, 159, A1255.
16 A. Chagnes, M. Diaw, B. Carré, P. Willmann, D. Lemordant, *J. Power Sources*, 2005, **145**, 82.
17 M. Diaw, A. Chagnes, B. Carré, P. Willmann, D. Lemordant, *J. Power Sources*, 2005, **146**, 682.
18 L. Gzara, A. Chagnes, B. Carré, M. Dhahbi, D. Lemordant, *J. Power Sources*, 2006, **156**, 634.
19 X.-G. Sun, C. A. Angell, *Electrochem. Commun.*, 2005, **7**, 261.
20 A. Hofmann, M. Schulz, S. Indris, R. Heinzmann, T. Hanemann, *Electrochim. Acta*, 2014, **147**, 704.
21 A. Chagnes, in *Lithium Process Chemistry: Resources, Extractions, Batteries and Recycling*, ed. A. Chagnes, J. Swiatowska, Elsevier, Amsterdam, 1st edn, 2015, ch. 2, pp. 41-80.
22 W. J. Bailey, L. Nicholas, *J. Org. Chem.*, 1956, **21**, 648.
23 T. Takeda, H. Furukawa, M. Fujimori, K. Suzuki, T. Fujiwara, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1863.
24 M. Jereb, *Green Chem.*, 2012, **14**, 3047.
25 V. Gudipati, D. P. Curran, C. S. Wilcox, *J. Org. Chem.*, 2006, **71**, 3599.
26 H. C. Brown, M. Zaidlewicz, P. V. Dalvi, G. K. Biswas, *J. Org. Chem.,* 2001**, 66***,* 4795.
27 D. J. Schroeder, A. A. Hubaud, J. T. Vaughey, *Mat. Res. Bull.*, 2014, **49**, 614.
28 This work.
29 M. Takehara, S. Watanabe, N. Nanbu, M. Ue, Y. Sasaki, *Chem. Lett.*, 2004, **33**, 338.
30 N. Nanbu, S. Watanabe, M. Takehara, M. Ue, Y. Sasaki, *J. Electroanal. Chem.*, 2009, **625**, 7.
31 K. Xu, *Chem. Rev.*, 2004, **104**, 4303.
32 N. Nanbu, T. Nachi, M. Takehara, M. Ue, Y. Sasaki, *Electrochemistry*, 2012, **80**, 771.
33 M. Takehara, S. Watanabe, N. Nanbu, M. Ue, Y. Sasaki, *Chem. Lett.*, 2008, **37**, 368.
34 Y. Sasaki, *Electrochemistry*, 2008, **76**, 2.
35 O. Borodin, W. Behl, R. T. Jow, *J. Phys. Chem. C*, 2013, **117**, 8661.
36 M. Ue, Y. Sasaki, Y. Tanaka, M. Morita, in *Electrolytes for Lithium and lithium Ions batteries*, ed. R. T. Jow, K. Xu, O. Borodin, M. Ue, Springer, New York, 1st edn, 2014, ch. 4, pp. 93-255.
37 R. Naejus, C. Damas, D. Lemordant, R. Coudert, P. Willmann, *J. Chem. Thermodyn.,* 2002, **34**, 795.
38 Y. Sasaki, H. Satake, N. Tsukimori, N. Nanbu, M. Takehara, M. Ue, *Electrochemistry*, 2010, **78**, 467.
39 K. Abea, Y. Ushigoe, H. Yoshitake, M. Yoshio, *J. Power Sources*, 2006, **153**, 328.
40 W. Xu, X. Chen, F. Ding, J. Xiao, D. Wang, A. Pan, J. Zheng, X. S. Li, A. B. Padmaperuma, J.-G. Zhang, *J. Power Sources,* 2012, **213**, 304.
41 R. S. Assary, L. A. Curtiss, P. C. Redfern, Z. Zhang, K. Amine, *J. Phys. Chem. C*, 2011, **115**, 12216.
42 M. Kobayashi, T. Inoguchi, T. Iida, T. Tanioka, H. Kumase, Y. Fukai, *J. Fluor. Chem.*, 2003, **120**, 105.
43 N. Nanbu, K. Takimoto, M. Takehara, M. Ue, Y. Sasaki, *Electrochem. Commun.*, 2008, **10**, 783.
44 X. J. Wanga, H. S. Lee, H. Li, X. Q. Yang, X. J. Huang, *Electrochem. Commun.*, 2010, **12**, 386.
45 J. Kumelan, D. Tuma, S. P. Verevkin, G. Maurer, *J. Chem. Eng. Data*, 2008, **53**, 2844.
46 M. S. Newman, R. W. Addor, *J. Am. Chem. Soc.,* 1955, **77**, 3789.
47 A. H. Saadi, W. H. Lee, *J. Chem. Soc. B*, 1966, 5.
48 H. Rong, M. Xu, B. Xie, X. Liao, W. Huang, L. Xing, W. Li, *Electrochimica Acta*, 2014, **147**, 31.
49 D. S. Viswanath, T. K. Ghosh, D. H. L. Prasad, N. V. K. Dutt, K. Y. Rani, *Viscosity of Liquids: Theory, Estimation, Experiment, and Data*, Springer, Dordrecht, 2007.
50 N. Nanbu, Y. Suzuki, K. Ohtsuki, T. Meguro, M. Takehara, M. Ue, Y. Sasaki, *Electrochemistry*, 2010, **78**, 446.
51 P. K. Kancharla, T. Kato, D. Crich, *J. Am. Chem. Soc.*, 2014, **136**, 5472.
52 J. Leroy, J. Bensoam, C. Wakselman, F. Mathey, *Tetrahedron*, 1980, **36**, 1931.
53 Sigma-Aldrich.
54 E. Perricone, M. Chamas, J.-C. Leprêtre, P. Judeinstein, P. Azais, E. Raymundo-Pinero, F. Béguin, F. Alloin, *J. Power Sources*, 2013, **239**, 217.
55 D. Limat, Y. Guggisberg, M. Schlosser, *Liebigs Ann*, 1995, 849.
56 P. J. McElroy, A. T. Gellen, S. S. Kolahi, *J. Chem. Eng. Data*, 1990, **35**, 38.
57 M. A. Postigo, A. B. Mariano, A. F. Jara, N. Zurakoski, *J. Chem. Eng. Data*, 2009, **54**, 1575.
58 E. Y. Tyunina, M. D. Chekunova, *J. Mol. Liq.*, 2013, **187**, 332.
59 J.-T. Chen, W.-C. Chang, *J. Chem. Eng. Data*, 2005, **50**, 1753.
60 N. Nanbu, K. Ohtsuki, H. Mutsuga, Y. Suzuki, M. Takehara, M. Ue, Y. Sasaki, *Electrochemistry*, 2012, **80**, 746.
61 A. Thenappan, D. J. Burton, *J. Org. Chem.*, 1990, **55**, 2311.
62 C. Laurence, P. Nicolet, M. T. Dalati, J.-L. M. Abboud, R. Notario, *J. Phys. Chem.*, 1994, **98**, 5807.
63 C. Charnock, B. Brudeli, J. Klaveness, *Eur. J. Pharm. Sci.*, 2004, **21**, 589.
64 J. B. Romans, C. R. Singleterry, *J. Chem. Eng. Data*, 1961, **6**, 56.
65 J. Huang, X. Liu, X. Kang, Z. Yu, T. Xu, W. Qiu, *J. Power Sources*, 2009, **189**, 458.
66 H. Machleidt, *Liebigs Ann Chem.*, 1964, **676**, 66.
67 S.-I. Tobishima, T. Okada, *Electrochim. Acta*, 1985, **30**, 1715.
68 J. Kasnatscheew, R. W. Schmitz, R. Wagner, M. Winter, R. Schmitz, *J. Electrochem. Soc.*, 2013, **160**, A1369.

69 R. Petibon, J. Harlow, D. B. Le, J. R. Dahn, *Electrochim. Acta*, 2015, **154**, 227.
70 M. Obama, Y. Oodera, N. Kohama, T. Yanase, Y. Saito, K. Kusano, *J. Chem. Eng. Data*, 1985, **30**, 1.
71 R. A. Spurr, H. Zeitlin, *J. Am. Chem. Soc.*, 1950, **72**, 4832.
72 L. H. Slaugh, *J. Am. Chem. Soc.*, 1961, **83**, 2734.
73 F. Ossola, G. Pistoia, R. Seeber, P. Ugo, *Electrochim. Acta*, 1988, **33**, 47.
74 K. Kusano, *J. Chem. Eng. Data*, 1978, **23**, 139.
75 Y. Sasaki, G. Shimazaki, N. Nanbu, M. Takehara, M. Ue, *ECS Trans.*, 2009, **16**, 23.
76 H. D. Purohit, R. J. Sengwa, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2030.
77 M. Kilpatrick, *J. Am. Chem. Soc.*, 1963, **85**, 1036.
78 W. G. Lloyd, B. J. Luberoff, *J. Org. Chem.*, 1969, **34**, 3949.
79 C. Wang, S. Tang, X. Zuo, X. Xiao, J. Liu, J. Nan, *J. Electrochem. Soc.*, 2015, **162**, A1997.
80 D. Martin, A. Weise, H.-J. Niclas, *Angew. Chem. Int. Ed.*, 1967, **6**, 318.
81 S. Miyanaga, K. Tamura, S. Murakami, *J. Chem. Thermodyn.*, 1992, **24**, 291.
82 N. Mozhzhukhina, L. P. Méndez De Leo, E. J. Calvo, *J. Phys. Chem. C*, 2013, **117**, 18375.
83 D. N. Bennion, W. H. Tiedemann, *J. Chem. Eng. Data*, 1971, **16**, 368.
84 E. Plichta, M. Salomon, S. Slane, M. Uchiyama, *J. Solution Chem.*, 1986, **15**, 663.
85 B. T. Yu, W. H. Qiu, F. S. Li, L. Cheng, *J. Power Sources*, 2006, **158**, 1373.
86 S. Li, W. Zhao, Z. Zhou, X. Cui, Z. Shang, H. Liu, D. Zhang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 4920.
87 W. J. Svirbely, J. J. Lander, *J. Am. Chem. Soc.*, 1948, **70**, 4121.
88 J. G. Pritchard, P. C. Lauterbur, *J. Am. Chem. Soc.*, 1961, **83**, 2105.
89 A. Simon, G. Heintz, *Chem. Ber.*, 1962, **95**, 2333.
90 P. G. Sears, W. C. O'Brien, *J. Chem. Eng. Data*, 1968, **13**, 112.
91 M. S. Berridge, M. P. Franceschini, E. Rosenfeld, T. J. Tewson, *J. Org. Chem.*, 1990, **55**, 1211.
92 A. Abouimrane, I. Belharouak, K. Amine, *Electrochem. Commun.*, 2009, **11**, 1073.
93 K. Chiba, T. Ueda, Y. Yamaguchi, Y. Oki, F. Shimodate, K. Naoi, *J. Electrochem. Soc.*, 2011, **158**, A872.
94 S. Yoon, Y.-H. Lee, K.-H. Shin, S. B. Cho, W. J. Chung, *Electrochim. Acta*, 2014, **145**, 170.
95 I. Merke, N. Heineking, M. Berdan, H. Hartwig, J. Demaison, *J. Mol. Struct.*, 2000, **517–518**, 351.
96 P. Švec, A. Eisner, L. Kolářová, T. Weidlich, V. Pejchal, A. Růžička, *Tetrahedron Lett.*, 2008, **49**, 6320.
97 S.-Y. Lee, K. Ueno, C. A. Angell, *J. Phys. Chem. C*, 2012, **116**, 23915.
98 K. Xu, C. A. Angell, *J. Electrochem. Soc.*, 2002, **149**, A920.
99 Y. Wang, L. Xing, W. Li, D. Bedrov, *J. Phys. Chem. Lett.*, 2013, **4**, 3992.
100 F. Bardé, Y. Chen, L. Johnson, S. Schaltin, J. Fransaer, P. G. Bruce, *J. Phys. Chem. C*, 2014, **118**, 18892.
101 X.-G. Sun, C. A. Angell, *Solid State Ion.*, 2004, **175**, 257.
102 T. W. Bates, K. J. Ivin, G. Williams, *T. Faraday Soc.*, 1967, **63**, 1976.
103 J. F. Casteel, P. G. Sears, *J. Chem. Eng. Data*, 1974, **19**, 196.
104 N. P. Volynskii, S. E. Shevchenko, *Petrol. Chem.*, 2007, **47**, 109.
105 E. V. Whitehead, R. A. Dean, F. A. Fidler, *J. Am. Chem. Soc.*, 1951, **73**, 3632.
106 B. S. Rawat, I. B. Gulati, K. L. Mallik, *J. Appl. Chem. Biotechnol.*, 1976, **26**, 247.
107 A. Li, P. Du, Z. Chen, R. Zhao, W. Huang, L. Zou, D. Huang, H. Chen, *Ionics*, 2015, **21**, 2431.
108 W. Xu, A. J. Shusterman, M. Videa, V. Velikov, R. Marzke, C. A. Angell, *J. Electrochem. Soc.*, 2003, **150**, E74.
109 S. Hess, M. Wohlfahrt-Mehrens, M. Wachtler, *J. Electrochem. Soc.*, 2015, **162**, A3084.
110 J. Kalhoff, G. G. Eshetu, D. Bresser, S. Passerini, *ChemSusChem*, 2015, **8**, 2154.
111 D. Kong, D. J. am Ende, S. J. Brenek, N. P. Weston, *J. Hazardous Mat.*, 2003, **102**, 155.
112 Q. Zhong, M. He, X. Guo, Y. Zhang, *J. Chem. Eng. Data*, 2009, **54**, 1666.
113 J. Arai, *J. App. Electrochem.*, 2002, **32**, 1071.
114 European Commission - Joint Research Centre - Institute for Environment and Sustainability, *ILCD Handbook: General Guide for Life Cycle Assessment - Detailed Guidance*, ed. Publications Office of the European Union, Luxemburg, 1st ed., 2010.
115 T. R. Hawkins, O. M. Gausen, A. H. Strømman, *Int. J. Life Cycle Assess.,* 2012, **17**, 997.
116 C. Bauer, J. Hofer, H.-J. Althaus, A. Del Duce and A. Simons, *Applied Energy*, 2015, **157**, 871.
117 J.F. Peters, M. Baumann, B. Zimmermann, J. Braun, M. Weil, *Renew. Sustain. Energy Rev.,* 2017, **67**, 491.
118 G. Majeau-Bettez, T. R. Hawkins, A. H. Strømman, *Environ. Sci. Technol.*, 2011, **45**, 4548.
119 M. Zackrisson, L. Avellán, J. Orlenius, *J. Clean. Prod.*, 2010, **18**, 1519.
120 D. A. Notter, M. Gauch, R. Widmer, P. Wäger, A. Stamp, R. Zah, H.-J. Althaus, *Environ. Sci. Technol.*, 2010, **44**, 6550.
121 C. Bauer, Ökobilanz von Lithium-Ionen Batterien – Analyse der Herstellung von Energiespeichern für den Einsatz in Batteriefahrzeugen, Studie im Auftrag von Volkswagen AG Paul Scherrer Institut, Labor für Energiesystem-Analysen, Villigen, Switzerland, 2010.
122 R. Hischier, M. Classen, M. Lehmann, W. Scharnhorst, Life cycle inventories of Electric and Electronic Equipment: Production, Use and Disposal, Swiss Centre for Life Cycle Inventories, Dübendorf, 2007.
123 Swiss Centre for Life Cycle Inventories, Ecoinvent 3.2, http://www.ecoinvent.org/, (accessed December 2015).
124 L. Gaines, R. Cuenca, Costs of Lithium-Ion Batteries for Vehicles, Center for Transportation Research, Energy Systems Division Argonne National Laboratory, Argonne, IL, 2000.
125 C. J. Rydh, B. A. Sandén, *Energy Convers. Manag.*, 2005, **46**, 1957.
126 J. B. Dunn, L. Gaines, M. Barnes, M. Wang, J. Sullivan, Material and energy flows in the materials production, assembly, and end-of-life stages of the automotive lithium-ion battery life cycle, Argonne National Laboratory (ANL), 2012.
127 H. F. Jr. McShane, W. W. Gilbert, US Pat., 2772291 A, 1956.
128 C. Baimbridge, P. Bolomey, J. D. Love, US Pat., 20040044253 A1, 2004.
129 H. O. Folkins, E. L. Miller, *Ind. Eng. Chem. Process Des. Dev.*, 1962, **1**, 271.
130 M. Goedkoop, R. Heijungs, M. A. J. Huijbregts, A. De Schryver, J. Struijs, R. van Zelm, ReCiPe 2008: A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level, Ministry of Housing, Spatial Planning and Environment (VROM), The Hague, The Netherlands, 2013.
131 J. Wen, Y. Yu, C. Chen, *Mater. Express*, 2012, **2ß (3)**, 197.
132 A. M. Haregewoin, A. S. Wotango and B. J. Hwang, *Energy Environ. Sci.*, 2016, DOI: 10.1039/C6EE00123H.
133 L. Zhang, Z. Zhang, H. Wu, K. Amine, Energy Environ. Sci. 2011, **4**, 2858.
134 S. S. Zhang, *J. Power Sources* 20016, **162**, 1379.