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Optimization of Cycling Behavior of Lithium Ion Cells at 60°C by Additives for Electrolytes Based on Lithium bis[1,2-oxalato(2-)-O,O´] borate

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We investigated 13 additives well known from literature and studied their effect on the performance of lithium ion cells comprised of electrolytes based on lithium bis[1,2-oxalato(2-)-O,O´] borate. The additives can be attributed to three classes including chemically modified solvents, metal salts, and oligoethers. In contrast to similar studies in literature, where often only a single additive was investigated, the effect of 13 additives was studied under the same conditions at cells cycled up to 500 times at 60°C in a thermostat. The internal resistance of the cells and the charge capacity of cells are reported. Whereas tetra ethylene glycol dimethyl ether showed the best performance, increasing the lifetime of cells by a factor of five and doubling the cell capacity after 500 cycles other additives did show no effect or even deteriorated the cell performance.

Keywords: Lithium-ion battery, cycling, additive, lithium bis[1,2-oxalato(2-)-O,O´] borate

1. INTRODUCTION

The ideal cell for reversible storage of energy combines high performance with long lifetime, safe operation, no environmental concerns, low cost as well as high energy and power density. To optimize a cell for a specific application it is necessary to investigate many parameters that influence each other to some extent. For example, the performance of a battery can be improved by optimization of the electrolyte regarding conductivity, lithium ion diffusion coefficients and its transference numbers. However, the choice of solvents, salts, and additives is not independent, as this choice effects the film formation at electrodes and their permeability for lithium ions.

One of the main objectives in optimizing lithium ion batteries is their lifetime. In contrast to primary batteries, the cycling stability and not so much their self-discharge is the key parameter determining the service life of secondary batteries. The cycling stability of a battery is defined by the number of charging- or discharging cycles until its capacity is reduced to a certain amount of its nominal capacity (typically 50% to 80%) [1]. We use cycling stability and lifetime as synonym and define it as 50% of the initial capacity. At elevated temperatures and high discharge rates pronounced decomposition of the electrolyte and the electrode materials is generally observed, therefore a reduced service life is a result of these conditions [2]. Since the effects, which decrease cycling ability and increase internal resistance are accelerated at elevated temperatures, the optimization should be performed at elevated temperatures as well [3]. We have chosen 60°C for our investigation, which can be interpreted as the worst case over the operation range of the cells.

The cycling stability of lithium ion batteries is mainly determined by the solid electrolyte interphase (SEI) [4], if the electrochemical stability of the salt and the solvent mixture is appropriate [5]. This interphase is formed between the anode and the electrolyte in lithium, lithium ion and other alkaline or alkaline earth based cells [5]. It determines the safety, self-discharge, high current capability and the performance at various temperatures of primary batteries and secondary cells. Additionally it affects the Coulombic efficiency and lifetime of secondary cells. Film formation is also responsible for irreversible capacity loss at the first charging cycle. The goal of the optimization is to customize this interphase to the specific need of the application.

The formation of the solid electrolyte interphase (SEI) was observed first at lithium metal immersed into a solvent. This metal has the most negative standard redox potential which is more negative than the potential of solvated electrons. Therefore lithium dissolves under formation of characteristic blue solutions in various solvents [5]. Because the solvated electrons react with the electrolyte and with the cathode it is necessary to protect the metal with an insoluble protective lithium-ion conductive layer. This is achieved by adding substances to the electrolyte mixture that react with lithium before the electrolyte components do. These additives form a lithium-ion conducting, electronically insulating and insoluble layer for protecting lithium (or the intercalated lithium) from further reaction and dissolution [2]. An overview of the SEI formation of lithium metal is given in literature [2, 3, 6, 7, 10].

In contrast to lithium metal, the SEI is formed at lithium intercalating carbon electrodes during the first charging cycle at potentials between 0.5 to 0.7 V vs. Li/Li^+. The irreversible capacity loss during the first cycle is much more pronounced than in the other cycles due to the formation of this interphase. The composition of the SEI strongly depends on the composition of the solvent mixture, the salt and impurities of the electrolyte. Layers of various lithium salts such as LiF, Li_2O, Li_2CO_3 and elementary boron are formed by decomposition of the salt and impurities such as oxygen and water [5]. Interphases made up of polymers are mostly formed by decomposition of the solvent [5]. These layers dominate the outer part of the SEI [5]. The properties of the SEI are affected by the solvent and the salt. In general films formed by decomposition of solvents are more stable at elevated temperatures [8]. Unlike lithium metal, this interphase does not protect the carbon anode from dissolution but from defoliation caused by intercalation of solvated lithium ions, i.e. co-intercalation of solvent molecules. This co-intercalation is increased by electrolytes containing large amounts of propylene carbonate, because this solvent decomposes at potentials that are lower than the intercalation potential of lithium into graphite [9, 10]. This solvent is preferred for electrolytes used in lithium ion batteries due to its large liquid range and its high donor number. However, propylene carbonate requires a highly sophisticated SEI to protect the graphite from co-intercalation.

A good solid electrolyte interphase is characterized by the following requirements [3, 5]:

- High electronic resistance: reducing self discharge and improving its faradayic efficiency,
- high transference-number of lithium ions tLi+ close to 1: preventing concentration polarization and facilitating lithium intercalation,
- high ionic conductivity: reducing overvoltage and improving internal resistance of the cell
- homogenous morphology and chemical composition: leading to homogenous current distribution,
- good adhesion on the anode surface, and strong mechanic stability and flexibility.

Further aspects of the SEI and its characterization are found in the reviews of Linden [2], Aurbach [3], Peled [6] and Zhang[35].

Methods for improving the properties of the SEI and the cell can be divided in two categories: Pre-treatment as an ex-situ method prior to use and additives in the electrolyte as an in-situ method. Examples for the first method are: treatment of the electrode material under reductive conditions resulting in a strong decrease of the irreversible capacity [3], controlled oxidation of carbon electrodes [5, 11, 12] for improving the cycling stability, and addition of nano particles of nickel [13] or silver [14, 15] for optimizing the impedance, stability and irreversible capacity of the anode.

The second path uses in-situ methods. Here the electrode is modified by additives which are added to the electrolyte and react with the electrode surface. This reaction commonly occurs in the first cycle of the battery.

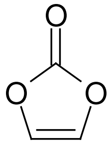
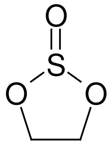
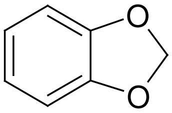
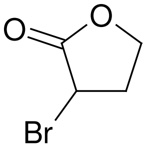
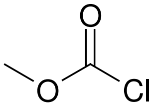
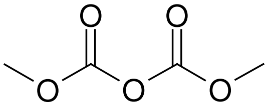
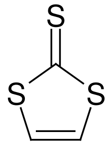
One strategy is to use substances, which are precursors of the SEI. These components react much faster than other components of the electrolyte with lithium, so the SEI is mainly affected by the additives and not by the electrolyte. These additives are commonly typical solvents used in lithium ion batteries derived by functional groups or by the exchange of homologous hetero-atoms to increase reactivity. Examples for these additives are vinylene carbonate, ethylene sulfite, α-bromo-γ-butryrolactone or methyl chloroformate. Dimethyl dicarbonate decomposes to methanol and CO_2 which both contribute to the formation of an SEI built up of LiOMe and Li_2CO_3 [21]. Vinylene trithiocarbonate, which was chosen for its strong structural and reactive relation to vinylene carbonate and ethylene sulfite also belong to this group.

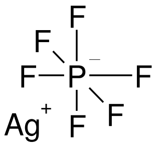
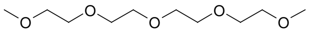
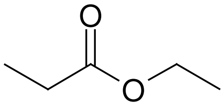
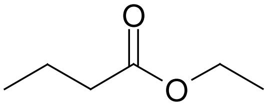
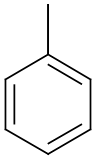
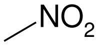
The second group of additives comprises metal salts, which are added to the electrolyte [22]. The metal ion of the salt cannot intercalate into the graphite and therefore forms a film on the electrode. This concept is similar to the pre-treatment method of Honbo [15], but the film is generated in situ and not deposited in high vacuum.

The third group consists of substances such as tetraethylene glycol dimethyl ether whose polyglycol structure is similar to the SEI formed by the polymerization of organic carbonates. Therefore tetraethylene glycol dimethyl ether is recognized as a useful battery additive [8].

An SEI is also formed by esters [32], toluene and nitro methane [2]. Typically one to five mass percent of additives are added to the electrolyte solution [8, 16, 17, 18, 19, 20]. According to literature the additives shown in Table 1 were used in electrolyte solutions containing $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiAsF_6$ and $LiPF_3(CF_2CF_3)$. Up to now, nothing was reported on the use of these additives in batteries with chelatoborate salts, especially not for lithium bis[1,2-oxalato(2-)-O,O´] borate (LiBOB) based electrolytes.

Table 1. Additives for high temperature optimization of LiBOB containing electrolytes. All additives were p.a.-grade, except the additives from Merck (Darmstadt), which were *selectipur*® (battery grade). The water content of the additives was determined by Karl-Fischer-Titration. Literature refers to articles where the additives are used for electrolytes with other lithium salts.

Additive	Structure	ξ_{H2O} / ppm	Supplier	Literature
vinylene carbonate			Acros vacuum destillation prior to use	[8], [16], [17], [18], [19]
ethylene sulfite		138	Fluka	[17], [20]
1,3-benzoldioxole		1130	Fluka	[8]
α-bromo-γ-butyrolactone			Aldrich	[9]
methyl chloroformate		82	Aldrich	[9]
dimethyl dicarbonate		170	Sigma	[21]
vinylene trithiocarbonate			Fluka	

silver hexafluorophosphate			Acros	[22]
tetraethylene glycol dimethyl ether		457	VWR	[16]
propionic acid ethyl ester		157	Merck	[2],[32]
butyric acid, ethyl ester		5	Fluka	[2],[32]
toluene		190	Merck	[2]
Nitro methane		133	Merck	[2]

Literature cited in this article mostly focuses on only one or a few additives. A comprehensive study of the effect of additives is missing. The results from different articles can hardly be compared, because of different electrode materials, salts, solvents and experimental conditions in those investigations.

We want to report on effects caused by numerous additives tested all under the same conditions allowing a direct comparison of the impact of the additives.

2. EXPERIMENTAL PART

To avoid contamination of the solvents by water, all operations, especially preparation of the electrolyte, filling of the battery packs and storage of chemicals, except electrical measurements, were carried out in a glove box (MBraun, Melsungen, type MB150BG, less than 0.2 ppm H_2O and 5 ppm O_2).

For cycling experiments 25 cm^2 single laminate cells from Gaia Akkumulatorenwerke (Nordhausen) were used. Electrodes contained $Li_{(1-x-y-z)}Ni_xCo_yM_zO_2$ as active cathode material and MCMB (**mi**cro**c**arbon **m**icro **b**eads) as anode material. Carbon black for electronic conductivity and PVdF binder for adhesion were added for a dry-blend. The electrodes were manufactured by a proprietary extrusion process. The electrodes were laminated on current collector foils, which were copper for the negative side and aluminum for the positive side, respectively. Both electrodes were electronically separated by a Celguard® polyolefin foil. The reversible capacities, of the anode and cathode material were 1.63 mAh/cm^2 and 1.79 mAh/cm^2, respectively, resulting in a total cell capacity of 40 mAh for standard cells.

The cells were filled with about 0.5 cm^3 of electrolyte, which was prepared prior to its use from stock solutions inside the glove box. The compositions of these solutions are given in Table 2. Four mass percent of an additive given in Table 1 were added to each electrolyte and the electrolyte was filled into the battery. The cells were finished with a soft-pack aluminum coated plastic foil.

Table 2. Stock solutions of electrolytes for experiments without additives. The temperature limit is the lowest temperature at which the electrolytes can be applied. At this temperature a strong decrease of specific conductivity of the electrolyte is observed, which is caused by precipitation of the salt.

Solution	ξ_{EC} /%	ξ_{PC} / %	ξ_{DEC} / %	ξ_{DMC} / %	ξ_{EMC} / %	ξ_{EP} / %	m_{LiBOB} / mol/kg	Temperature Limit / °C
1	66,7	33,3	--	--	--	--	0,50	-0,30
2	66,7	33,3	--	--	--	--	0,70	0,19
3	66,7	33,3	--	--	--	--	0,90	*
4	66,7	23,3	10,0	--	--	--	0,50	4,55
5	66,7	23,3	10,0	--	--	--	0,70	-2,23 to 8,38
6	66,7	23,3	10,0	--	--	--	0,90	*
7	66,7	13,3	20,0	--	--	--	0,50	12,89
8	66,7	13,3	20,0	--	--	--	0,70	*
9	66,7	13,3	20,0	--	--	--	0,90	*
10	66,7	0,33	30,0	--	--	--	0,50	14,48
11	66,7	0,33	30,0	--	--	--	0,70	*
12	66,7	0,33	30,0	--	--	--	0,90	*
13	20,3	3,50	--	1,40	--	74,8	0,86	<-30
14	20,3	7,16	--	0,24	15,7	56,6	0,76	<-30
15	23,3	10,0	--	--	--	66,7	0,90	<-30
16	33,3	--	--	--	--	66,7	1,00	*

* The amount of salt was insoluble at 25 °C.

Battery grade lithium bis[1,2-oxalato(2-)-O,O´]borate (LiBOB) was obtained from Chemetall (Frankfurt). Ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC) and ethyl propionate (EP) were obtained from Merck, (Darmstadt), quality *selectipur*® (battery grade). The water content of each solvent, determined by Karl Fischer titration, was less than 30 ppm. Additives, their water contents, purities and suppliers are shown in Table 1. Unless otherwise noted, the additives were used as received from new bottles opened inside the glove box. The water content of solvents and additives included in Table 1 was determined with a Mitsubishi Chemical Ind. Ltd. (Tokyo) moisture meter, type CA-02 or with a DL-18 Mettler Toledo (Greifensee) automatic titrator. Water content of LiBOB was 262 ppm, determined by ^{1}H-NMR spectroscopy [23].

Masses were determined with an analytical balance, type AB 204 Mettler Toledo (Greifensee), within the glove box. Because of pressure fluctuations, only a reduced accuracy of about ± 1 mg was achieved. Glassware was dried for at least 24 h at 140 °C at ambient pressure, or at 10^{-1} mbar at 65°C. The battery packs were dried for at least one week at 10^{-1} mbar at 65°C.

During cycling experiments cells were sealed in dry packs closed by a stainless steel clamping frame and were thermally equilibrated in a silicon oil bath at (60.0 ± 0.2) °C with a RK 20 thermostat from Lauda (Lauda-Königshofen).

The cells were cycled with a home built galvanostatic cycling equipment. Details will be published elsewhere [24]. In the first cycle (formation) a constant current of 4 mA (1/10 C) was applied. The charging and the discharging current for the following cycles was 40 mA (1 C). The cells were charged 500 times up to a cell voltage of 4.2 V and discharged until a cell voltage of 3.0 V was reached. For constant currents I the charge Q can be determined by equation (1).

$$Q = I \cdot t \tag{1}$$

The sign of charging currents is positive, while the sign of discharge currents is negative. The relative capacity C_{REL} of a charging or of a discharging cycle Q_i^- was calculated according equation (2) with Q_1^- the capacity of the first discharge which also defined the nominal capacity.

$$C_{REL} = \frac{Q_i^-}{Q_1^-} \cdot 100\% \tag{2}$$

The internal resistance of the cells was determined from the voltage drop, ΔU, resulting from the change of current from charging, I_{CH}, to discharging I_{DC}, yielding R_{CH}, or from discharging to charging yielding R_{DC}, respectively.

$$R_{CH/DC} = \frac{|\Delta U|}{I_{CH} + |I_{DC}|} \tag{3}$$

The low temperature limit of the electrolytes shown in Table 2 was determined by thermal analysis with simultaneous conductivity measurement [25].

3. RESULTS

In Table 3 the results of cycling experiments of electrolytes without additives are given. In this table Lifetime and $R_{50\%}$ is defined when the cells reaches 50% of the initial capacity. C_{500} and R_{500} are the relative capacity of the cell and its internal resistance after 500 cycles.

The results in Table 3 show that electrolytes containing only carbonates have longer lifetimes than electrolytes containing esters as solvent components. The cause for this behavior might be a less pronounced ability of esters to form a suitable SEI [26].

Table 3. Stability of lithium ion cells comprising various electrolyte solutions without additives at 60°C.

Solution	Composition	Lifetime / cycles	$R_{50\%}$ / Ω	C_{500} / %	R_{500} / Ω
1	EC/PC	56	--	19,9	--
2	EC/PC	122	1,7/2,4	15,9	4,3/4,98
5	EC/PC/DEC	65	3,6/4,9	--*	--*
13	EC/PC/DMC/EP	31	2,9/3,3	0,5	12,1/13,4
14	EC/PC/DMC/EMC/EP	69	3,3/4,8	2,0	9,2/10,1
15	EC/PC/EP	41	--**	5,4	--**

* The experiment was stopped after 191 Cycles, therefore no prediction of the capacity and resistance after 500 cycles can be made.

** At the time the experiment was conducted, the determination of the resistance was not implemented in the software of the battery test system.

The carbonate-based mixtures contain a high content of ethylene carbonate (EC), which was at least twice as large compared to other solvent mixtures. EC is well known for its good SEI formation. From the observation, that pure carbonate solutions gave a prolonged lifetime compared to solutions based on high ester contents, it cannot be concluded whether the addition of esters or the small content of ethyl carbonate is responsible for the shorter lifetime of cells containing esters. The content of EC should be sufficient for building a SEI, since Aurbach and Gofer found EC reduction dominant even at low EC contents [26]. The capacity and the resistance after 500 cycles are much worse for electrolytes containing esters than for electrolytes based on pure carbonate mixtures as solvent blend. For example, the resistance of cells containing esters is more than doubled at the end of cycling.

Table 4. Effect of additives to the lifetime, remaining capacity and internal resistance of lithium ion batteries at 60°C.

Class	Additive	Life time	$R_{50\%}$ / Ω	C_{500} / %	R_{500} / Ω
1	tetraethylene glycol dimethyl ether	264	2,6/3,9	38	2,9/4,4
	propionic acid ethyl ester	246	2,4/4,2	36	2,8/4,5
	methyl chloroformate	204	5,4/7,6	32	6,2/8,2
	butyric acid ethyl ester	187	2,4/4,3	28	3,0/5,1
2	toluene	141	2,3/4,2	29,1	2,9/5,1
	silver hexafluorophosphate	141	1,8/3,1	21	2,7/4,2
	vinylene carbonate	123	3,2/4,0	18	4,2/5,2
	ethylene sulfite	122	3,4/4,5	19	5,2/6,6
Ref.	without additive	56	--	20	
3	Nitro methane	46	3,1/5,0	3,8	8,1/8,9
	α-bromo-γ-butyrolactone	33	4,8/7,5	14	7,3/10,4
	1,3-benzoldioxole	32	3,2/5,7	17	6,3/8,8
	dimethyl dicarbonate	28	2,8/5,9	15	4,5/9,0
	vinylene trithiocarbonate	11	4,7/6,3	0,2	26/26

Although lifetime (see Table 3) of solution 1 is shorter than that of solution 2, it was selected for the further optimization, since the cell showed a higher remaining capacity after 500 cycles. The effect of the additives on the two solutions might be identical, since the two electrolyte solutions only differ in content of salt.

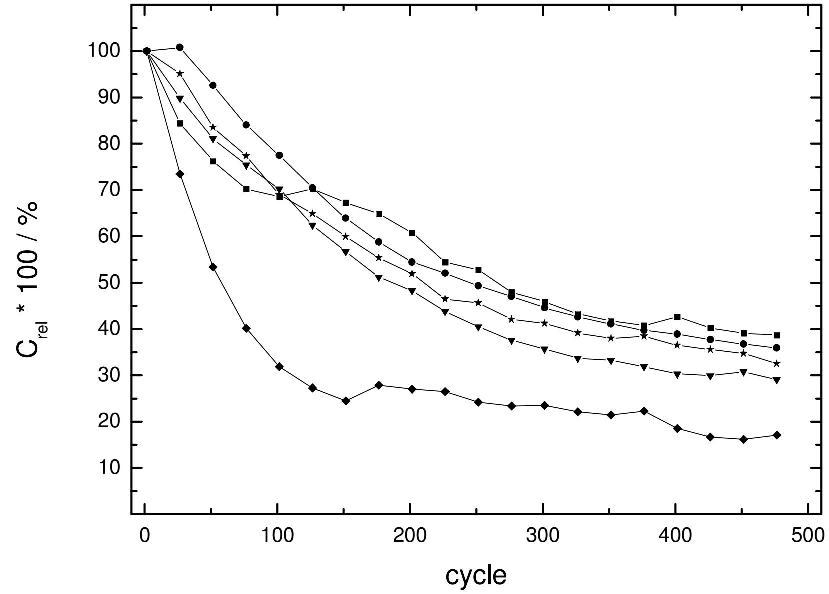


Figure 1. The effect of tetraethylene glycol dimethyl ether ■, propionic acid ethyl ester ●, methyl chlorformate ★ and butyric acid ethyl ester ▼on the capacity of cells based on LiBOB containing electrolytes at 60°C. For comparison the cycling stability of electrolytes without additives ◆ is also shown.

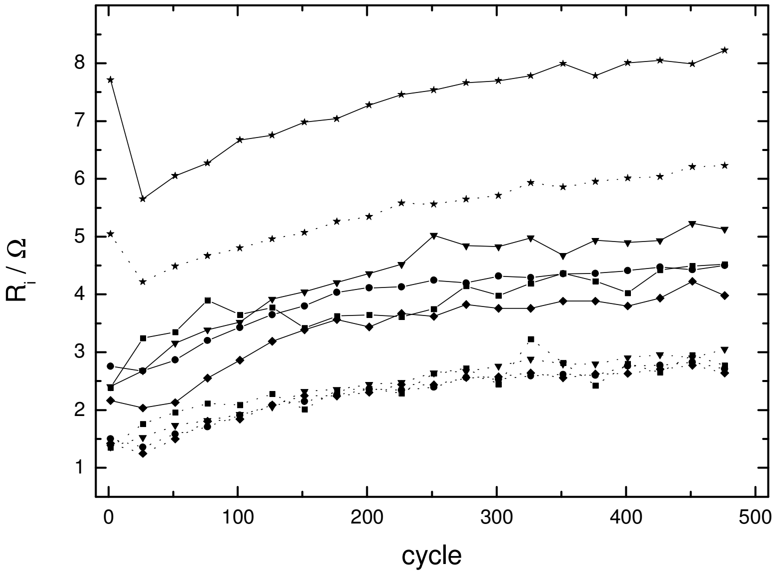


Figure 2. The effect of tetraethylene glycol dimethyl ether ■, propionic acid ethyl ester ●, methyl chlorformate ★ and butyric acid ethyl ester ▼on internal resistance of cells based on LiBOB containing electrolytes at 60°C. For comparison the cycling stability of electrolytes without additives ◆ is also shown. R_{CH} determined from the end of charging is indicated by solid line, R_{DC} measured at the end of discharging by dashed line.

The investigated additives can be divided in three performance classes as shown in Table 4. Additives such as tetraethylene glycol dimethyl ether, propionic acid ethyl ester, methyl chloroformate and butyric acid ethyl ester, cause a remarkable improvement of both the lifetime and the final capacity of the cell. Additives of this group are able to increase the lifetime of the cell by a factor of up to five. In addition, the final capacity is doubled. The change of capacity and internal resistance with prolonged cycling of cells containing these additives is presented in Figures 1 and 2.

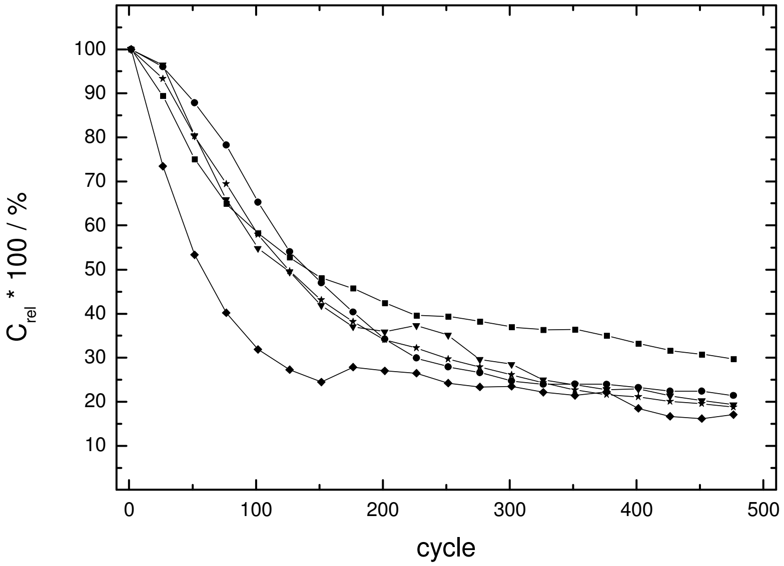


Figure 3. The effect of toluene ■, silver hexafluorophosphate ●, vinylene carbonate ★ and ethylene sulfite ▼on the capacity of cells based on LiBOB containing electrolytes at 60°C. For comparison the cycling stability of electrolytes without additives ◆ is also shown.

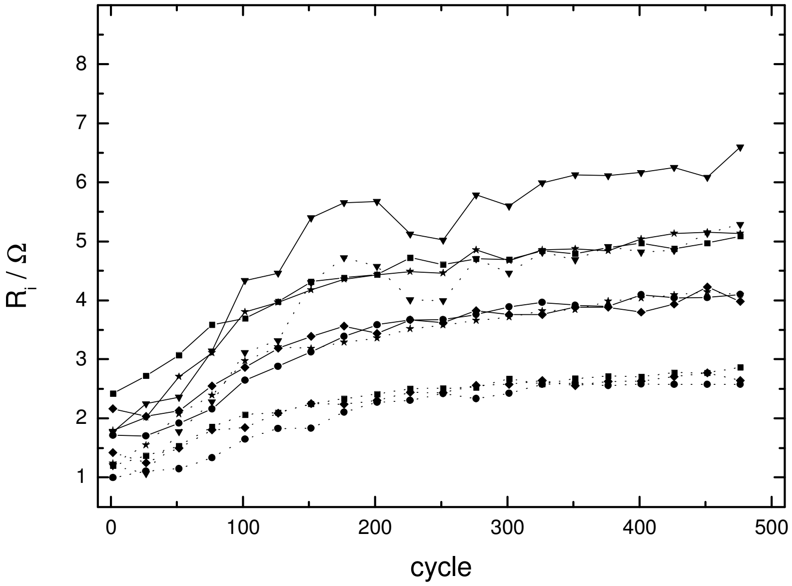


Figure 4. The effect of toluene ■, silver hexafluorophosphate ●, vinylene carbonate ★ and ethylene sulfite ▼on internal resistance on of cells based on LiBOB containing electrolytes at 60°C. For comparison the cycling stability of electrolytes without additives ◆ is also shown. R_{CH} determined from the end of charging is indicated by solid line, R_{DC} measured at the end of discharging by dashed line.

The second class of additives, including toluene, silver hexafluorophosphate, vinylene carbonate and ethylene sulfite also shows an improvement of the characteristics of the cell, but less than those of group one. Figures 3 and 4 show the development of the parameters of cells containing electrolytes with these additives.

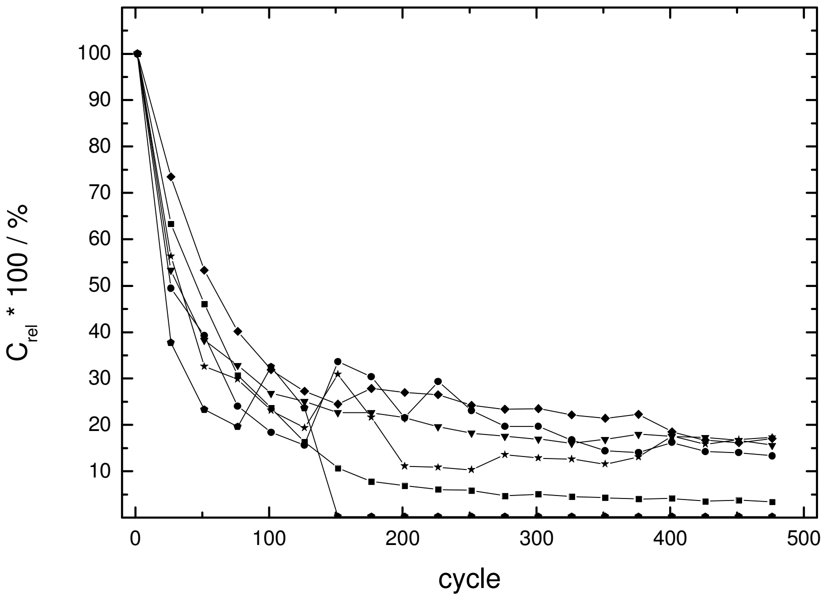


Figure 5. The effect of nitro methane ■, α-bromo-γ-butyrolactone ●, 1,3-benzoldioxole ★, dimethyl dicarbonate ▼ and vinylene trithiocarbonate ⬟ on the capacity of cells based on LiBOB containing electrolytes at 60°C. For comparison the cycling stability of electrolytes without additives ◆ is also shown.

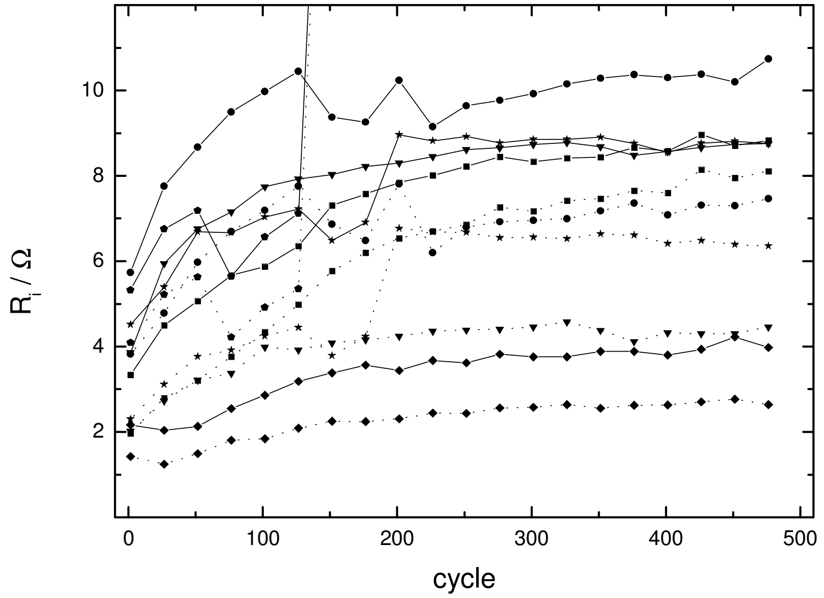


Figure 6. The effect of nitro methane ■, α-bromo-γ-butyrolactone ●, 1,3-benzoldioxole ★, dimethyl dicarbonate ▼ and vinylene trithiocarbonate ⬟ on internal resistance of batteries based on LiBOB containing electrolytes at 60°C. For comparison the cycling stability of electrolytes without additives ◆ is also shown. R_{CH} determined from the end of charging is indicated by solid line, R_{DC} measured at the end of discharging by dashed line.

The third class of additives consisting of nitromethane, α-bromo-γ-butyrolactone, 1,3-benzodioxole, dimethyl dicarbonate, and vinylene trithiocarbonate does not improve the long-term stability, and lifetime of the cell is lowered in comparison to the electrolyte without an additive. A strong decay of capacity of cells containing these additives versus cycling is shown in Figures 5 and 6.

4. DISCUSSION

Tetraethylene glycol dimethyl ether (TEGME) was found to be the best additive. An improvement of a factor of nearly five in lifetime can be achieved. With this additive the capacity after 500 cycles is also doubled compared to an electrolyte without additive. The positive effect of this additive is due to its molecular structure that is similar to that of a suitable SEI so it provides good adhesion and thermal stability [29].

According to Herstedt [8], TEGME shows a too large irreversible capacity loss at graphite based batteries with $LiBF_4$ electrolytes. In contrast to this, irreversible capacity loss is reduced by this additive for cells using MCMB as anode material and LiBOB as salt.

Different studies done by Laik [30] and Herstedt[8] show that TEGME forms Li-alkoxides during electrochemical cycling of the batteries. Proposed reactions for these formations are [31]:

$$\mathrm{ROR'} + \mathrm{e}^{-} + \mathrm{Li}^{+} \rightarrow (\mathrm{R'OR}^{-\bullet})\mathrm{Li}^{+} \tag{4}$$

$$\mathrm{R}^{\bullet}\mathrm{OR\text{-}Li}^{\bullet} \rightarrow \mathrm{ROLi} + \mathrm{R}'^{\bullet} \text{ or } \mathrm{R'OLi} + \mathrm{R}^{\bullet} \tag{5}$$

$$\mathrm{R}^{\bullet}+\mathrm{H}^{\bullet} \leftrightarrow \mathrm{RH} \text{ or } 2\mathrm{R}^{\bullet} \rightarrow \mathrm{R\text{-}R} \text{ or } \mathrm{R}^{\bullet} + \mathrm{Li}^{\bullet} \leftrightarrow \mathrm{R\text{-}Li} \tag{6}$$

A PES spectra study reveals Li-alkoxides as the main TEGME reaction products on graphite [8].

Since this additive is a member of the family of polyethylene oxides, this class of substances should be studied further for finding better candidates. An improvement may also be achieved by variation of the number of ethylene oxide groups or by deriving the end groups.

According to Herstedt [8], TEGME shows an additional beneficial effect as electrolyte additive, because it enables the reversible Li^+ ion intercalation in graphite while PC based electrolytes are present [28].

Esters

By addition of esters improvements nearly as good as with TEGME were achieved. Instead of the typical use as co-solvents for optimizing the conductivity of the electrolytes [2],[27],[32], esters were used here for lifetime improvement. According to Smart [32], the SEI forming capabilities of esters grow with increasing chain lengths of the alcohol or the acid group of the ester. In contrast to this statement, our experiments show a larger improvement of the lifetime by the addition of propionic acid ethyl ester than by butyric acid ethyl ester. The acid- or the alcohol group of these esters can be changed and a broad variety of potential candidates can be estimated. A comparative study is required to investigate the influence of ester length and the combination of functional groups on the cycling behavior as well as the internal resistance.

We found the concentration of the additive having some impact on the result: The addition of small amounts of propionic acid ethyl ester and butyric acid ethyl ester strongly increased both life time and final capacity, whereas a large amount reduced the lifetime of the cell. Therefore the amount of esters should be selected carefully, if they are used in high amounts for improving conductivity.

Methyl chloroformate and α-bromo-γ-butyrolactone

The reactivity of esters can be enhanced by substitution with halogen atoms. A typical example for such an active ester is methyl chloroformate. The improvement achieved by this additive is in between the range to that of the non halogenated propionic acid ethyl ester and butyric acid ethyl ester. The mechanism of SEI formation with an activated ester is obviously similar to that of non substituted esters. In contrast to methyl chloroformate, the addition of α-bromo-γ-butyrolactone reduces the lifetime of the battery in comparison to the battery without additive. Naji et al. report similar performance of these additives at graphite $LiBF_4$ / PC electrolytes [9]. Because we find a completely different performance of these additives with our MCMB/LiBOB system, a different kind of SEI forming mechanism for these additives at MCMB is proposed. If halogenated additives are added to electrolytes, halogen ions are released to the electrolyte by reactions during cycling. Especially in the case of chloride this always entails the danger of corrosion of the aluminum current conductors. So these additives may improve cycling stability but can reduce the storage and long term lifetime of the battery.

Toluene

This additive forms an SEI by electrochemical polymerization [33],[34] leading to an improvement of the cycling stability. The addition of this additive has the effect of reduced gassing [33, 34]. It is an interesting observation that toluene shows some effect during normal cycling at our system. Aromatic additives are claimed to protect batteries at abnormal high potentials [33, 34]. The class of aromatic hydrocarbons provides a huge number of substances which are worth for further investigation.

$AgPF_6$

In contrast to the other additives forming an organic film on the anode material, $AgPF_6$ forms a metallic film comprised of Ag [22]. This film prevents the co-intercalation and decomposition of PC in MCMB according to Wu [22]. To avoid the HF formation by the PF_6^- anion silver bis[1,2-oxalato(2-)-O,O´] borate (AgBOB) may be used instead. Because of the completely different mode of action a combination with other additives is very promising.

VC

Vinylene carbonate, a widely studied additive in literature [35], yields only an intermediate improvement of the cycling stability. By reductive polymerization of the carbon-carbon double bound, an improved SEI is formed by poly-alkyl-Li-carbonate species [16],[19] and [35] which also may contain C=C double bounds [19].

In contrast to the $LiBF_4$ / graphite system investigated by Herstedt [8] where vinylene carbonate gave better results than TEGME, it is less good in LiBOB/MCMB systems. This observation is similar to effects by 1,3-benzodioxole which is superior in Herstedt's battery but not in ours.

Ethylene Sulfite and vinylene trithiocarbonate

Another reductive additive improving the cycling stability of LiBOB systems is ethylene sulfite. Similar to $AgPF_6$, the reduction products of this additive are adsorbed at the active sites of the carbon [35]. Other sulfur containing additives similar to ethylene sulfite are propylene sulfite [36, 37] and aryl sulfites [36]. Similar to the sulfites which are derivatives of the carbonates used as battery electrolytes, SO_2, CS_2 and polysulfide are used as battery additives [35]. According to Zhang [35], the effectiveness of these additives seems to increase with the content of sulfur in the molecule while their amount in the electrolyte must be strictly limited, because of their anodic instability. Therefore this class of substances can act as a redox shuttle increasing the self discharge [35].

Vinylene trithiocarbonate, a substance not used as a battery additive up to now, was checked due to its structural similarity to battery electrolytes. Unfortunately the cycling behavior of batteries is deteriorated by the addition of this additive while vinylene carbonate and ethylene sulfite give a slight improvement. Perhaps the SEI formed by this substance is too stable and a reduction of the amount of additive may cause an improvement of stability.

Nitro methane

In contrast to the other additives shown above, the addition of nitro methane reduces the cycling stability. Although this substance [2] is mentioned in literature as a battery additive only little information is given about its mode of operation.

1,3-benzodioxole

The addition of 1,3-benzodioxole also deteriorates the cycling behavior in comparison to batteries without any additive. Similar to vinylene carbonate, 1,3-benzodioxole acts as an SEI precursor [8],[38]. Because these substances are reduced at higher potential in comparison to solvent or salt [8], they should dominate the SEI formation. In contrast to the findings of Herstedt [8], 1,3-benzodioxole performs less than TEGME if LiBOB is used as salt and MCMB as anode active material instead of $LiBF_4$ and graphite. This result is very astonishing, because according to Herstedt

[8], the SEI formed by 1,3-benzodioxole is composed of Li-alkoxides which are equal to the reaction products of the SEI formation by TEGME. Herstedt [8] also finds lower content of LiF inside the SEI formed by 1,3-benzodioxole in contrast to that formed by TEGME. Our batteries contain no fluorine, so the composition of the SEI may be completely different, if LiBOB is used as salt. Maybe the reduction products of LiBOB are in some kind incompatible with products formed by 1,3-benzodioxole.

Dimethyl dicarbonate

Dimethyl dicarbonate was proposed by Levi et al [21] as a battery additive for $LiPF_6$ EC/DMC electrolytes with graphite anode active material. They found a substantial increase in cycling performance [21]. This SEI contains more ROLi and $ROCO_2Li$ than that of batteries without any additives reducing the impact of trace HF [21].

Because our batteries do not contain any fluorine, the protection from HF is not necessary. We assume that the films formed by dimethyl dicarbonate are not very compatible with films formed by LiBOB so cycling stability is reduced. Perhaps a decrease of the amount of dimethyl dicarbonate might enhance the cycling behavior of the LiBOB based battery.

5. CONCLUSIONS

The cycling lifetime of lithium-ion-batteries containing LiBOB as salt can be improved substantially by the addition of additives. In this study thirteen additives were tested under the same conditions so the effect of different additives can be compared. In contrast to the systems described in literature, typically $LiBF_4$/graphite systems, the improvements were different if the same additives were applied to our LiBOB/MCMB systems: TEGME gave superior results in our system while it performed less in $LiBF_4$/graphite systems. VC or α-bromo-γ-butyrolactone behaved just vice versa. We believe that the composition of a favorable SEI on MCMB with LiBOB differs from that on graphite with $LiBF_4$. This should be especially the case if LiBOB is used as salt, because the part of the SEI formed by this salt does not contain any LiF but instead some polyborates.

The amount of additive added to the batteries should be optimized to achieve even better cycling stability. Another step of optimization would be the addition of more than one additive to an electrolyte. Due to their completely different mode of action, a combination of tetraethylene glycol dimethyl ether or esters like propionic acid ethyl ester with silver salts would be very promising. To find the best composition of these multiple additive mixtures the simplex method or other design of experiments (DoE) methods may be applied also. An example of this method for optimization of conductivity can be found in Refs. [23], [39]. By deriving the additives shown in this article a lot of new candidates for improving battery performance may be generated.

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