Eliminating voltage delay and stabilizing impedance by electrolyte additives in alkali metal electrochemical cells

The present invention relates to boron-based electrolyte additives for a primary alkali metal electrochemical cell and to a corresponding primary alkali metal electrochemical cell.

A monotonic pulse shape is generally desirable in electrochemical cells. A monotonic pulse shape exists when the voltage curve remains constant under pulse conditions or decreases to the minimum at the end of the pulse, and the minimum voltage of the first pulse in a pulse series is higher than the minimum voltage of the last pulse. The voltage curve of this pulse series is usually rectangular (FIG. 1).

Voltage delay is an undesirable characteristic in the discharge profile of implantable alkali metal cells under current pulse discharge conditions. Voltage delay is caused by the formation of relatively high impedance cover layers on the anode surface, resulting in an increase in the internal resistance of the battery. This effect can only be observed when the batteries are subjected to high pulse current densities and, in the process, the battery voltage drops disproportionately, that is, the voltage at the beginning of the first pulse is lower than at the end of the pulse or when the first pulse is lower than the minimum voltage of the last pulse (FIG. 2).

Voltage delay normally first becomes apparent under pulse loading in alkali metal/metal oxide and alkali metal/mixed metal oxide cells at more than 40% DoD (*depth of discharge*) of their capacity discharge or after extended storage. In certain instances, a high impedance cover layer forms on the anode surface, for example due to dissolution of the cathode active material or due to discharge products in the battery electrolyte, which under certain pulse discharge conditions can result in voltage delay or in non-monotonic behavior.

Electrolyte additives such as phosphates, dicarbonates, nitrites, alkyl phosphates and organic additives including hydroxyl groups (-OH) and carboxyl groups for suppressing or reducing the voltage delay for alkali metal/transition metal oxide (such as Li/SVO) and alkali metal/mixed oxides x and/or transition metal oxide or for Li/SVO cells are known in the prior art.

The aforementioned additives are typically used for alkali metal/transition metal oxide systems, in particular for lithium/silver vanadium oxide (Li/SVO) and lithium/silver vanadium oxide hybrid cathodes (Li/SVO hybrid cathodes), in which increases in impedance and, consequently, voltage delay occur due to high impedance cover layers made of metal deposits such as vanadium, silver and/or metal alloys on the electrode surface. The aforementioned additives, however, are not suitable for alkali metal/carbon monofluoride (Li/CFx) systems, in which the voltage delay occurs due to fluoride lithium deposits on the anode surface.

Organoborate salts are also known in the prior art (for example from US 7740986 B2) as an electrolyte conducting salt or an electrolyte additive for lowering self-discharge and for reducing/eliminating the voltage delay after storage at room and elevated temperatures of the Li/CFx cells. However, compared to the standard electrolyte, the organoborate-based electrolytes show increased battery resistance (see Example 01).

One or more embodiments may provide an electrolyte additive for primary cells, especially containing lithium as the active electrode material, which reduces, and preferably eliminates, voltage delay and reduces battery impedance.

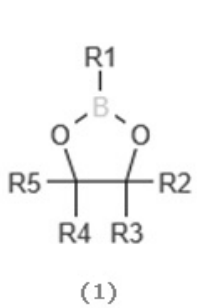
In a first aspect there may be provided a primary cell having the features of claim 1 and in a second aspect there may be provided the use of a boron compound having the features of claim 9. one or more embodiments may be provided in the corresponding dependent claims and in the following description.

According to claim 1, a primary cell is provided, which comprises alkali metal as the active electrode material, particularly as the active anode material, and an electrolyte comprising a boron compound, in particular an organic boron compound.

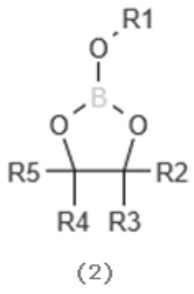
The term "primary cell" is used in its generally known, technical meaning in the context of the present description. It denotes in particular a galvanic cell that, once discharged, can no longer be electrically charged. Primary cells are also referred to as primary battery at times.

The boron compound is in particular a non-ionic compound, that is, preferably not a salt of a boron-containing acid.

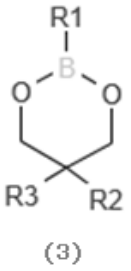
The boron compound may be a compound according to formula (1), (2), (3), (4), (7) or (8):



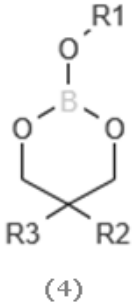
(1) ;



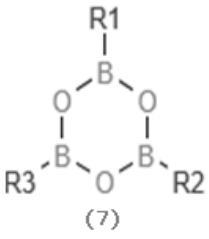
(2) ;



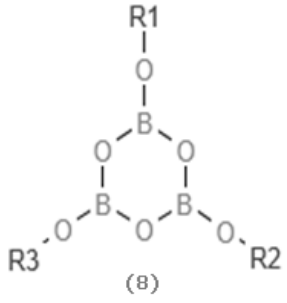
(3) ;



(4) ;



(7) ;



(8) ;

where R1, R2, R3, R4 and R5 independent from one another are selected from the group consisting of hydrogen, alkyl, alkenyl, cycloalkyl, thioether, heterocyclic compounds, aryl and heteroaryl, wherein R1, R2, R3, R4 or R5 is not thiophene.

In one embodiment of the primary cell, it is provided that R1, R2, R3, R4 and R5 independent from one another are unsubstituted or are monosubstituted or multiple substituted with at

least one substituent selected from the group consisting of: alkyl, fluoroalkyl, alkoxy, carbonyl, carboxyl, thiol, thio alkoxide, aryl, ether, thioether, nitro, cyano, amino, azido, amidino, hydrazino, hydrazono, carbamoyl, sulfo, sulfamoyl, sulfonylamino, alkylaminosulfonyl, alkyl sulfonyl amino and/or halogen. Preferred substituents comprise halogens, fluoroalkyls and cyano or nitrile groups, wherein R1, R2, R3, R4 or R4 is not thiophene.

In one embodiment of the primary cell, it is provided that the boron compound is a compound according to formula (1), where R1 is an alkyl, in particular a C_1 to C_6 alkyl, in particular methyl, cyclopropyl or cyclohexyl, or an aryl, in particular a phenyl, a benzyl or a naphthyl, which is unsubstituted or substituted with one or more C_1 to C_4 alkyl, –F, -Cl, -Br, -I, -CN, $-CF_3$ or $–OCF_3$, and each of R2 to R4 and R5 independent from one another is a C_1 C_4 alkyl.

In one embodiment of the primary cell, it is provided that the compound according to formula (1) is

- 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane;
- 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-cyclopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(naphthalene-1-ylmethyl)-1,3,2-dioxaborolane;
- 2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(1-naphthyl)-1,3,2-dioxaborolane;
- 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane;
- 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(3,5-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(2-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile;
- 4,4,5,5-tetramethyl-2-[3-(trifluoromethoxy)phenyl]-1,3,2-dioxaborolane;
- 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)aniline;

- 2-[2-(trifluoromethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-[3,5-bis(trifluoromethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; or
- 2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile,

preferably 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane.

In one embodiment of the primary cell, it is provided that the boron compound is a compound according to formula (2), where each of R1 to R4 and R5 independently from one another is a C_1 to C_4 alkyl.

In one embodiment of the primary cell, it is provided that the compound according to formula (2) is

- 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; or
- 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

In one embodiment of the primary cell, it is provided that the boron compound is a compound according to formula (3), where R1 is an alkyl, an alkenyl, in particular an allyl or an aryl, in particular a benzyl, phenyl, or benzoate, which is unsubstituted, or substituted with one or more C_1 to C_4 alkyl, –F, -Cl, -Br, -I, -CN, $-CF_3$ or $–OCF_3$ or a compound according to formula (3), and each of R2 and R3 independent is a C_1 to C_4 alkyl.

In one embodiment of the primary cell, it is provided that the compound according to formula (3) is

- 2-allyl-5,5-dimethyl-1,3,2-dioxaborinane;
- 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane;
- 2,2'-(1,4-phenylene)bis[5,5-dimethyl-1,3,2-dioxaborinane];
- 2-(2-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 2-(1,3,2-dioxaborinane-2-yl)benzonitrile;
- 2-(2-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 4,4'-bis(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)biphenyl;
- ethyl 2-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)benzoate;

- 2-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)-6-(trifluoromethyl)benzonitrile; or
- 4-(trifluoromethyl)-2-(5,5-dinethyl-1,3,2-dioxaborinane-2-yl)benzonitrile.

In one embodiment of the primary cell, it is provided that the boron compound is a compound according to formula (4), where each of R1, R2 and R3 independent from one another is a C_1 to C_4 alkyl.

In one embodiment of the primary cell, it is provided that the compound according to formula (4) is

- 2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane;
- 2-ethoxy-4,4,6-trimethyl-1,3,2-dioxaborinane; or
- 2-methoxy-4,4,6-trimethyl-1,3,2-dioxaborinane.

In one embodiment of the primary cell, it is provided that the boron compound is a compound according to formula (7), where each of R1 to R3 independent from one another is an alkyl, in particular a C_1 to C_4 alkyl, in particular methyl, or an aryl, in particular a phenyl, which is unsubstituted or substituted with one or more –F, -Cl, -Br, -I, -CN, $-CF_3$ or $–OCF_3$.

In one embodiment of the primary cell, it is provided that the compound according to formula (7) is

- trimethylboroxine;
- 2,4,6-triphenylboroxine,
- 2,4,6-tris(4-fluorophenyl)boroxine;
- 2,4,6-tris(3,4,5-trifluorophenyl)boroxine;
- 2,4,6-tris(3,4-difluorophenyl)boroxine; or
- 2,4,6-tris(3,4-dichlorophenyl)boroxine

.

In one embodiment of the primary cell, it is provided that the boron compound is a compound according to formula (8), where each of R1 to R3 independent from one another is a C_1 to C_4 alkyl.

In one embodiment of the primary cell, it is provided that the compound according to formula (8) is 2,4,6-trimethoxyboroxine.

In one embodiment of the primary cell, it is provided that the boron compound is present in the electrolyte in a concentration in the range of 0.001 $mol*l^{-1}$ to 0.5 $mol*l^{-1}$.

In one embodiment of the primary cell, it is provided that the alkali metal, serving as the active electrode material, is lithium, and the primary cell is a lithium battery.

In one embodiment of the primary cell, it is provided that the electrolyte is a non-aqueous electrolyte.

In one embodiment of the primary cell, it is provided that the non-aqueous electrolyte

- comprises a first solvent, which is selected from the group consisting of an ester, an ether, a dialkyl carbonate and a mixture thereof, in particular tetrahydrofuran, methyl acetate, diglyme (bis(2-methoxyethyl)ether), triglyme (tris(2-methoxyethyl)ether), tetraglyme (tetra(2-methoxyethyl)ether), 1,2-dimethoxyethane, 1,2-diethoxyethane, 1-ethoxy, 2-methoxyethane, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, ethyl methyl carbonate, methyl propyl carbonate, ethyl propyl carbonate or a mixture thereof, and
- comprises a second solvent, which is selected from the group consisting of a cyclic carbonate, a cyclic ester, a cyclic amide and a mixture thereof, in particular propylene carbonate, ethylene carbonate, butylene carbonate, γ-butyrolactone, N-methylpyrrolidinone or a mixture thereof, or a polar non-aqueous solvent such as acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, or a mixture thereof.

In one embodiment of the primary cell, it is provided that the electrolyte comprises an anhydrous alkali salt, in particular an anhydrous lithium salt, preferably $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiSbF_6$, $LiClO_4$, $LiAlCl_4$, $LiGaCl_4$, $LiC(SO_2CF_3)_3$, $LiN(SO_2CF_3)_2$, LiSCN, $LiO_3SCF_2CF_3$, $LiC_6F_5SO_3$, LiO_2CF_3, $LiSO_3F$, $LiB(C_6H_5)_4$, $LiCF_3SO_3$ or a mixture thereof.

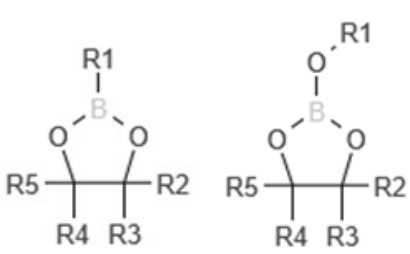
In one embodiment, the primary cell furthermore comprises a carbon monofluoride as the active electrode material, and particularly as the active cathode material. The carbon monofluoride may be present by itself or form hybrid cathodes with metal oxides, preferably of transition metals, for example MnO_2, SVO (silver oxide and vanadium pentoxide), copper silver vanadium oxide, cobalt oxide, nickel oxide, copper oxide, copper sulfide, iron sulfide, iron disulfide, titanium disulfide, or mixtures thereof.

In one embodiment, the primary cell comprises a cathode binder, in particular polytetrafluoroethylene, polyvinylidene fluoride (PVdF), polytetrafluoroethylene (PTFE), polyolefins, preferably thermoplastic elastomers, in particular ethylene propylene diene terpolymers, or mixtures thereof.

In one embodiment, the primary cell comprises carbon, in particular in the form of graphite, graphite powder or carbon black, or aluminum, in particular aluminum powder, titanium, in particular titanium powder, stainless steel, in particular stainless steel powder, or mixtures thereof, as a conducting additive.

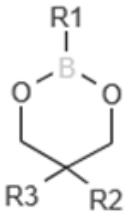
According to claim 9, a boron compound is provided for use as an electrolyte additive of a primary cell comprising an alkali metal as the active electrode material, in particular an organic boron compound.

The boron compound may be a compound according to formula (1), (2), (3), (4), (7) or (8):

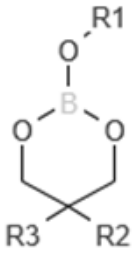


(1)

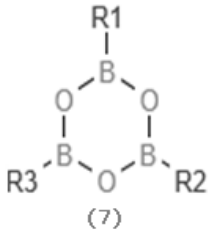
(2) ;



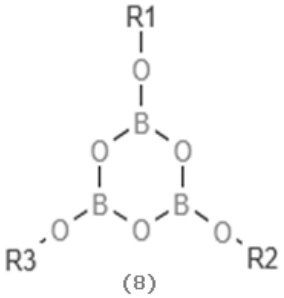
(3) ;



(4) ;



(7) ;



(8) ;

where each of R1, R2, R3, R4 and R6 independent from one another is selected from the group consisting of hydrogen, alkyl, alkenyl, cycloalkyl, thioether, heterocyclic compounds, aryl and heteroaryl, wherein R1, R2, R3, R4 or R5 is not thiophene.

In one embodiment of the use, it is provided that each of R1, R2, R3, R4 and R5 independent from one another is unsubstituted or is monosubstituted or multiple substituted with at least one substituent selected from the group consisting of: alkyl, fluoroalkyl, alkoxy, carbonyl, carboxyl, thiol, thio alkoxide, aryl, ether, thioether, nitro, cyano, amino, azido, amidino, hydrazino, hydrazono, carbamoyl, sulfo, sulfamoyl, sulfonylamino, alkylaminosulfate, alkylsulfonylamino and/or halogens, wherein R1, R2, R3, R4 or R5 is not thiophene.

In one embodiment of the use, it is provided that the boron compound is a compound according to formula (1), where R1 is an alkyl, in particular a C_1 to C_6 alkyl, in particular methyl, cyclopropyl or cyclohexyl, or an aryl, in particular a phenyl, a benzyl or a naphthyl, which is unsubstituted or substituted with one or more C_1 to C_4 alkyl, –F, -Cl, -Br, -I, -CN, $-CF_3$ or $–OCF_3$, and each of R2 to R4 and R5 independent from one another is a C_1 C_4 alkyl.

In one embodiment of the use, it is provided that the compound according to formula (1) is

- 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane;
- 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-cyclopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(naphthalene-1-ylmethyl)-1,3,2-dioxaborolane;
- 2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;

- 4,4,5,5-tetramethyl-2-(1-naphthyl)-1,3,2-dioxaborolane;
- 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane;
- 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(3,5-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(2-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile;
- 4,4,5,5-tetramethyl-2-[3-(trifluoromethoxy)phenyl]-1,3,2-dioxaborolane;
- 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)aniline;
- 2-[2-(trifluoromethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-[3,5-bis(trifluoromethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; or
- 2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile,

preferably 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane.

In one embodiment of the use, it is provided that the boron compound is a compound according to formula (2), where each of R1 to R4 and R5 independent from one another is a C_1 to C_4 alkyl.

In one embodiment of the use, it is provided that the compound according to formula (2) is

- 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; or
- 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

In one embodiment of the use, it is provided that the boron compound is a compound according to formula (3), where R1 is an alkyl, an alkenyl, in particular an allyl or an aryl, in particular a benzyl, phenyl, or benzoate, which is unsubstituted, or substituted with one or more C_1 to C_4 alkyl, –F, -Cl, -Br, -I, -CN, $-CF_3$ or $–OCF_3$, and each of R2 and R3 independent from one another is a C_1 to C_4 alkyl.

In one embodiment of the use, it is provided that the compound according to formula (3) is

- 2-allyl-5,5-dimethyl-1,3,2-dioxaborinane;

- 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane;
- 2,2'-(1,4-phenylene)bis[5,5-dimethyl-1,3,2-dioxaborinane];
- 2-(2-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 2-(1,3,2-dioxaborinane-2-yl)benzonitrile;
- 2-(2-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 4,4'-bis(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)biphenyl;
- ethyl 2-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)benzoate;
- 2-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)-6-(trifluoromethyl)benzonitrile; or
- 4-(trifluoromethyl)-2-(5,5-dinethyl-1,3,2-dioxaborinane-2-yl)benzonitrile.

In one embodiment of the use, it is provided that the boron compound is a compound according to formula (4), where each of R1, R2 and R3 independent from one another is a C_1 to C_4 alkyl.

In one embodiment of the use, it is provided that the compound according to formula (4) is

- 2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane;
- 2-ethoxy-4,4,6-trimethyl-1,3,2-dioxaborinane; or
- 2-methoxy-4,4,6-trimethyl-1,3,2-dioxaborinane.

In one embodiment of the use, it is provided that the boron compound is a compound according to formula (7), where each of R1 to R3 independent from one another is an alkyl, in particular a C_1 to C_4 alkyl, in particular methyl, or an aryl, in particular a phenyl, which is unsubstituted or substituted with one or more –F, -Cl, -Br, -I, -CN, -CF R3 $–OCF_3$.

In one embodiment of the use, it is provided that the compound according to formula (7) is

- trimethylboroxine;
- 2,4,6-triphenylboroxine,
- 2,4,6-tris(4-fluorophenyl)boroxine;
- 2,4,6-tris(3,4,5-trifluorophenyl)boroxine;
- 2,4,6-tris(3,4-difluorophenyl)boroxine; or
- 2,4,6-tris(3,4-dichlorophenyl)boroxine.

In one embodiment of the use, it is provided that the boron compound is a compound according to formula (8), where each of R1 to R3 independent from one another is a C_1 to C_4 alkyl.

In one embodiment of the use, it is provided that the compound according to formula (8) is 2,4,6-trimethoxyboroxine.

In one embodiment of the use, it is provided that the alkali metal, serving as the active electrode material, is lithium, and the primary cell is a lithium battery.

Further features and advantages are described hereafter based on the description of the figures of exemplary embodiments. In the drawings:

FIG. 1 shows the pulse curve of an electrochemical cell without voltage delay;

FIG. 2 shows the pulse curve of an electrochemical cell with voltage delay;

FIG. 3 shows the impedance curve of a battery comprising an electrolyte additive known from the prior art (lithium bis(oxalato)borate (LiBOB));

FIG. 4 shows an impedance curve (a), and a pulse discharge and pulse curve at 180 mAh depth of discharge (B) of a battery comprising an electrolyte additive (4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane (TMTFPDDB); and

FIG. 5 shows an impedance curve (a), and a pulse discharge and pulse curve at 180 mAh depth of discharge (B) of a battery comprising a further electrolyte additive (trimethylboroxine (TMB)).

Examples:

Lithium carbon monofluoride cells (Li/CFx) have the highest theoretical specific capacity compared to commercial lithium primary batteries. The overall equation of the discharge is as follows:

$$CFx + xLi \rightarrow C + xLiF$$

LiF is an anionic and electrical insulator, which, on the one hand, adheres to the surface of the cathode pores and, on the other hand, partially dissolves in the electrolyte. At a depth of discharge between the MOL and EOL states, the fluoride concentration in the electrolyte increases, resulting in a high impedance cover layer of lithium fluoride compounds on the anode surface (Table 1). Under certain pulse discharge conditions, this can result in voltage delay or in non-monotonic behaviour.

Table 1: Fluoride content on lithium anode surface at different depths of discharge

Cell no.	DoD [%]	Fluoride [µg]
Cell 1	50	2.05
Cell 2	50	1.95
Cell 3	50	2.15
Cell 4	80	4.40
Cell 5	80	3.90
Cell 6	80	4.15
Cell 7	90	23.45
Cell 8	90	21.00
Cell 9	90	24.65
Cell 10	95	63.10
Cell 11	95	69.75
Cell 12	95	66.60

One or more embodiments may relate, in general, to an electrochemical alkali metal cell and in particular to a lithium/carbon monofluoride or a lithium/carbon monofluoride metal oxide cell, which are suitable for uses with current pulse discharge and without voltage delay. More

precisely, the present invention relates to an electrochemical lithium metal cell comprising a non-aqueous electrolyte, which prevents voltage delay due to an electrolyte additive.

One or more embodiments may relate in particular to dioxaborolane, diboron and boroxine electrolyte additives for alkali metal electrochemical cells comprising carbon monofluoride (CFx) or CFx transition metal oxide hybrid cathodes (such as Li/CFx-MnO2, Li/CFx-SVO, etc.) as the cathode active material. The LiCFx system shows voltage delay under pulse conditions prior to the end-of-life (EOL) state. To suppress the voltage delay and reduce the increase in impedance, in particular dioxaborolane, diboron and boroxine additives are added to the electrolyte.

Advantage(s) may include the formation of a solid electrolyte interface (SEI) film on the negative electrode (for example a lithium metal), which protects the electrode surface, that is, the electrolyte additive on the anode surface is reduced, protecting the same against the formation of a high impedance cover layer, which, in turn, improves the stabilization of the internal resistance of the battery, improves the discharge power, and eliminates the voltage delay (Table 2).

Table 2: Boron content on lithium anode surface at EOL state

Cell no.	Boron [µg]
Cell 13	11.75
Cell 14	10.42

One or more embodiments may relate to the above-described electrochemical alkali metal cell comprising non-aqueous, ionically conductive electrolytes and at least one compound according to general formula (1), (2), (3), (4), (5), (6), (7) and (8).

The electrochemical cell for the execution and comparison examples were produced from the following components:

	Example 1	Example 2	Example 3
Electrolyte additive	LiBOB	TMTFPDDB	TMB

Cathode active material:	CFx
Conducting additives (percentage by weight, %)	Graphite (3%) and carbon black (2%)
Cathode binder (percentage by weight, %)	Polytetrafluoroethylene (3%)
Electrolyte	1M LiClO4 in 1,2-dimethoxyethane, ethylene carbonate and propylene carbonate (4:4:2)
Anode	Lithium

Example 1 (Comparison Example):

FIG. 3 shows the impedance curves of the discharge with 12.7 KOhm and daily pulse loading of 10 mA/156 s, wherein the measurement was carried out in each case with a standard electrolyte (without electrolyte additive) and a standard electrolyte containing 0.075 M lithium bis(oxalato)borate (LiBOB) as the additive. As mentioned at the outset, LiBOB is an electrolyte additive known from the prior art. It is clearly apparent that an increase in the internal resistance of the battery occurs with increasing discharge.

Example 2:

FIG. 4 illustrates the discharge data with 12.7 KOhm and daily pulse loading of 10 mA/156 s, wherein the impedance curve of the battery during the discharge is shown in (a) and the pulse curve at 180 mAh is shown in (b). A standard electrolyte and the standard electrolyte containing 0.075 M of an electrolyte additive, which in this case is 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane (TMTFPDDB), were used. It is clearly apparent that the internal resistance of the battery does not increase across wide discharge ranges due to the electrolyte additive.

Example 3:

FIG. 5 illustrates the discharge data with 12.7 KOhm and daily pulse loading of 10 mA/156 s, wherein the impedance curve of the battery during the discharge is shown in (a) and the

pulse curve at 180 mAh is shown in (b). A standard electrolyte and the standard electrolyte containing 0.075 M of an electrolyte additive, which in this case is trimethylboroxine (TMB), were used. It is also clearly apparent here that the internal resistance of the battery does not increase across wide discharge ranges due to the electrolyte additive.

In one embodiment, through the use of dioxaborolane, diboron and boroxine additives, voltage delay can be eliminated, and the battery impedance can be reduced.

In implantable batteries for cardiac therapies, batteries that showed voltage delays used only a portion of the total capacity (until voltage delay appeared). As a result of the dioxaborolane, diboron and boroxine electrolyte additives, the overall discharge capacity of the implantable batteries can be rendered usable.

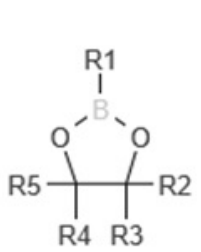
Claims

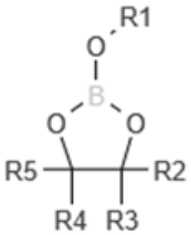
1. A primary cell, comprising:

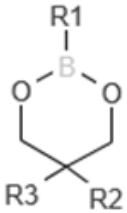
   – an alkali metal as the active electrode material, particularly as the active anode material, and

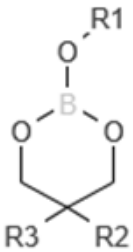
   – an electrolyte comprising a boron compound,

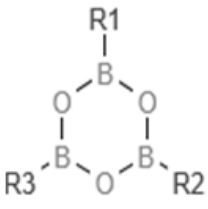
   wherein the boron compound is a compound according to formula (1), (2), (3), (4), (7) or (8)

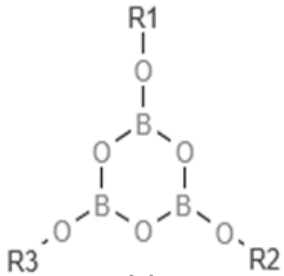


(1) ;


(2) ;


(3) ;


(4) ;


(7) ;


(8)

   wherein

   each of R1, R2, R3, R4 and R5 independent from one another is selected from the group consisting of hydrogen, alkyl, alkenyl, cycloalkyl, thioether, heterocyclic compounds, aryl and heteroaryl, wherein R1, R2, R3, R4 or R5 is not thiophene.

2. The primary cell according to claim 1, wherein each of R1, R2, R3, R4 and R5 independent from one another is unsubstituted or is monosubstituted or multiple substituted with at least one substituent selected from the group consisting of: alkyl, fluoroalkyl, alkoxy, carbonyl, carboxyl, thiol, thio alkoxide, aryl, ether, nitro, cyano,

amino, azido, amidino, hydrazino, hydrazono, carbamoyl, sulfo, sulfamoyl, sulfonylamino, alkylaminosulfonyl, alkylsulfonylamino halogens, and thioether excluding thiophene.

3. The primary cell according to claim 1 or 2, wherein the boron compound is

- a compound according to formula (1), where R1 is an alkyl, particularly a C_1 to C_6 alkyl, particularly methyl, cyclopropyl or cyclohexyl, or an aryl, in particular a phenyl, a benzyl or a naphthyl, which is unsubstituted or substituted with one or more C_1 to C_4 alkyl, –F, -Cl, -Br, -I, -CN, -CF_3 or –OCF_3, and each of R2 to R5 independent from one another is a C_1 C_4 alkyl;
- a compound according to formula (2), where each of R1 to R5 independent from one another is a C_1 to C_4 alkyl;
- a compound according to formula (3), where R1 is an alkyl, an alkenyl, particularly an allyl or an aryl, particularly a benzyl, phenyl, or benzoate, which is unsubstituted, or substituted with a C_1 to C_4 alkyl, –F, -Cl, -Br, -I, -CN, -CF_3 or –OCF_3 or a compound according to formula (3), and each of R2 and R3 independent from one another is a C_1 to C_4 alkyl;
- a compound according to formula (4), where each of R1, R2 and R3, independent from one another is a C_1 to C_4 alkyl;
- a compound according to formula (7), where each of R1 to R3 independent from one another is an alkyl, particularly a C_1 to C_4 alkyl, particularly methyl, or an aryl, particularly a phenyl, which is unsubstituted or substituted with one or more –F, -Cl, -Br, -I, -CN, -CF R3 –OCF_3; or
- a compound according to formula (8), where each of R1 to R3 independent from one another is a C_1 to C_4 alkyl.

4. The primary cell according to any one of the preceding claims, wherein the boron compound is

- 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane;
- 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-cyclopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;

- 4,4,5,5-tetramethyl-2-(naphthalene-1-ylmethyl)-1,3,2-dioxaborolane;
- 2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(1-naphthyl)-1,3,2-dioxaborolane;
- 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane;
- 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(3,5-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(2-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile;
- 4,4,5,5-tetramethyl-2-[3-(trifluoromethoxy)phenyl]-1,3,2-dioxaborolane;
- 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)aniline;
- 2-[2-(trifluoromethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-[3,5-bis(trifluoromethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile,
- 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
- 2-allyl-5,5-dimethyl-1,3,2-dioxaborinane;
- 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane;
- 2,2'-(1,4-phenylene)bis[5,5-dimethyl-1,3,2-dioxaborinane];
- 2-(2-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 2-(1,3,2-dioxaborinane-2-yl)benzonitrile;
- 2-(2-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 4,4'-bis(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)biphenyl;
- ethyl 2-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)benzoate;
- 2-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)-6-(trifluoromethyl)benzonitrile;
- 4-(trifluoromethyl)-2-(5,5-dinethyl-1,3,2-dioxaborinane-2-yl)benzonitrile,
- 2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane;

- 2-ethoxy-4,4,6-trimethyl-1,3,2-dioxaborinane;
- 2-methoxy-4,4,6-trimethyl-1,3,2-dioxaborinane;
- trimethylboroxine;
- 2,4,6-triphenylboroxine,
- 2,4,6-tris(4-fluorophenyl)boroxine;
- 2,4,6-tris(3,4,5-trifluorophenyl)boroxine;
- 2,4,6-tris(3.4-fluorophenyl)boroxine;
- 2,4,6-tris(3,4-dichlorophenyl)boroxine, or
- 2,4,6-trimethoxyboroxine.

5. The primary cell according to any one of the preceding claims, wherein the boron compound is present in the electrolyte in a concentration in the range of 0.001 mol/L to 0.5 mol/L.

6. The primary cell according to any one of the preceding claims, wherein the alkali metal is lithium, and the primary cell is a lithium battery.

7. The primary cell according to any one of the preceding claims, wherein the electrolyte is a non-aqueous electrolyte.

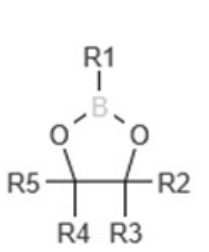
8. The primary cell according to claim 7, wherein the non-aqueous electrolyte

- comprises a first solvent, which is selected from the group consisting of an ester, an ether, a dialkyl carbonate, tetrahydrofuran, methyl acetate, diglyme, triglyme, tetraglyme, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1-ethoxy, 2-methoxyethane, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, ethyl methyl carbonate, methyl propyl carbonate, ethyl propyl carbonate and a mixture thereof, and
- comprises a second solvent, which is selected from the group consisting of a cyclic carbonate, a cyclic ester, a cyclic amide, propylene carbonate, ethylene carbonate, butylene carbonate, γ-butyrolactone, N-methylpyrrolidinone, a polar non-aqueous solvent, acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, and a mixture thereof.

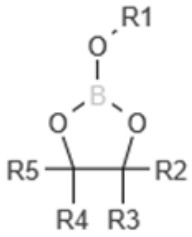
9. The primary cell according to any one of the preceding claims, wherein the electrolyte is selected from the group consisting of an anhydrous alkali salt, an anhydrous lithium salt, $LiClO_4$, LiPF6, LiBF4, $LiAsF_6$, $LiSbF_6$, $LiClO_4$, $LiAlCl_4$, $LiGaCl_4$, $LiC(SO_2CF_3)_3$, $LiN(SO_2CF_3)_2$, LiSCN, $LiO_3SCF_2CF_3$, $LiC_6F_5SO_3$, LiO_2CF_3, $LiSO_3F$, $LiB(C_6H_5)_4$, $LiCF_3SO_3$ and a mixture thereof.

10. The primary cell according to any one of the preceding claims, further comprising a carbon monofluoride as the active electrode material, or as the active cathode material.

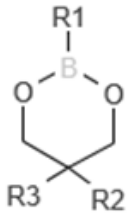
11. Use of a boron compound as the electrolyte additive of a primary cell comprising an alkali metal as the active electrode material, wherein the boron compound is a compound according to formula (1), (2), (3), (4), (7) or (8)



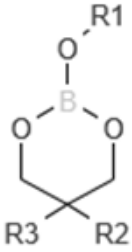
(1) ;



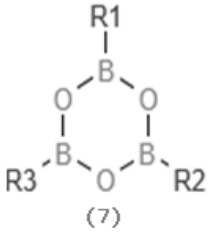
(2) ;



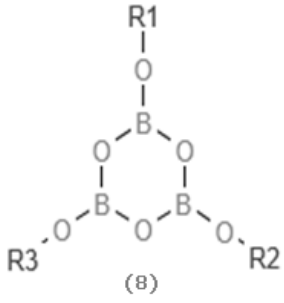
(3) ;



(4) ;



(7) ;



(8)

wherein

each of R1, R2, R3, R4 and R5 independent from one another is selected from the group consisting of hydrogen, alkyl, alkene, cycloalkyl, thioether, heterocyclic compounds, aryl and heteroaryl, wherein R1, R2, R3, R4 or R5 is not thiophene.

12. Use of a boron compound as an electrolyte additive of a primary cell comprising an alkali metal as the active electrode material according to claim 11, wherein each of R1,

R2, R3, R4 and R5 independent from one another is unsubstituted or is monosubstituted or multiple substituted with at least one substituent selected from the group consisting of: alkyl, fluoroalkyl, alkoxy, carbonyl, carboxyl, thiol, thio alkoxide, aromatic compound, ether, thioether, nitro, cyano, amino, azido, amidino, hydrazino, hydrazono, carbamoyl, sulfo, sulfamoyl, sulfonylamino, alkylaminosulfonyl, alkylsulfonylamino and halogens, wherein R1, R2, R3, R4 or R5 is not thiophene.

13. Use of a boron compound as an electrolyte additive of a primary cell comprising an alkali metal as the active electrode material according to claim 11 or 12, wherein the boron compound is

- a compound according to formula (1), where R1 is an alkyl, particularly a C_1 to C_6 alkyl, particularly methyl, cyclopropyl or cyclohexyl, or an aryl, particularly a phenyl, a benzyl or a naphthyl, which is unsubstituted or substituted with one or more C_1 to C_4 alkyl, –F, -Cl, -Br, -I, -CN, $-CF_3$ or $–OCF_3$, and each of R2 to R5 independent from one another is a C_1 C_4 alkyl;
- a compound according to formula (2), where each of R1 to R5 independent from one another is a C_1 to C_4 alkyl;
- a compound according to formula (3), where R1 is an alkyl, an alkenyl, particularly an allyl or an aryl, particularly a benzyl, phenyl, or benzoate, which is unsubstituted, or substituted with one or more C_1 to C_4 alkyl, –F, -Cl, -Br, -I, -CN, $-CF_3$ or –OCF, and each of R2 and R3 independent from one another is a C_1 to C_4 alkyl;
- a compound according to formula (4), where each of R1, R2 and R3independentfrom one another is a C_1 to C_4 alkyl.;
- a compound according to formula (7), where each of R1 to R3 independent from one another is an alkyl, in particular a C_1 to C_4 alkyl, particularly methyl, or an aryl, particularly a phenyl, which is unsubstituted or substituted with one or more –F, -Cl, -Br, -I, -CN, -CF R3 $–OCF_3$; or
- a compound according to formula (8), where each of R1 to R3 independent from one another is a C_1 to C_4 alkyl.

14. Use of a boron compound as an electrolyte additive of a primary cell comprising an alkali metal as the active electrode material according to any one of claims 11 to 13, wherein the boron compound is

- 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane;
- 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-cyclopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(naphthalene-1-ylmethyl)-1,3,2-dioxaborolane;
- 2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(1-naphthyl)-1,3,2-dioxaborolane;
- 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane;
- 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(3,5-dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-(2-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile;
- 4,4,5,5-tetramethyl-2-[3-(trifluoromethoxy)phenyl]-1,3,2-dioxaborolane;
- 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)aniline;
- 2-[2-(trifluoromethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-[3,5-bis(trifluoromethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzonitrile,
- 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane;
- 2-allyl-5,5-dimethyl-1,3,2-dioxaborinane;
- 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane;
- 2,2'-(1,4-phenylene)bis[5,5-dimethyl-1,3,2-dioxaborinane];
- 2-(2-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 2-(1,3,2-dioxaborinane-2-yl)benzonitrile;

- 2-(2-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane;
- 4,4'-bis(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)biphenyl;
- ethyl 2-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)benzoate;
- 2-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)-6-(trifluoromethyl)benzonitrile;
- 4-(trifluoromethyl)-2-(5,5-dinethyl-1,3,2-dioxaborinane-2-yl)benzonitrile,
- 2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane;
- 2-ethoxy-4,4,6-trimethyl-1,3,2-dioxaborinane;
- 2-methoxy-4,4,6-trimethyl-1,3,2-dioxaborinane;
- trimethylboroxine;
- 2,4,6-triphenylboroxine,
- 2,4,6-tris(4-fluorophenyl)boroxine;
- 2,4,6-tris(3,4,5-trifluorophenyl)boroxine;
- 2,4,6-tris(3.4-fluorophenyl)boroxine;
- 2,4,6-tris(3,4-dichlorophenyl)boroxine, or
- 2,4,6-trimethoxyboroxine.

15. Use of a boron compound as an electrolyte additive of a primary cell comprising an alkali metal as the active electrode material according to any one of claims 11 to 14, wherein the primary cell is a lithium battery.