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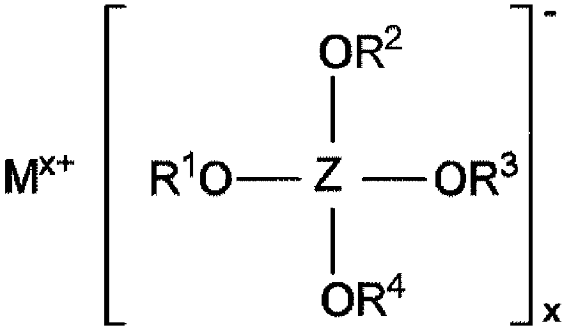
(54) Titre : ELECTROLYTE A BASE DE SO_2 POUR PILE RECHARGEABLE, ET PILE RECHARGEABLE

(54) Title: SO_2-BASED ELECTROLYTE FOR A RECHARGEABLE BATTERY CELL, AND RECHARGEABLE BATTERY CELL



$$M^{x+}\left[\begin{array}{c} OR^2 \\ | \\ R^1O - Z - OR^3 \\ | \\ OR^4 \end{array}\right]^-_x$$

formula (I)

(57) Abrégé/Abstract:
The invention relates to an SO_2-based electrolyte for a rechargeable battery cell containing at least one first conducting salt of the formula (I)

(see formula I)

wherein M is a metal chosen from the group consisting of alkali metals, alkaline earth metals, metals of group 12 of the periodic table of the elements and aluminum; x is an integer from 1 to 3; substituents R^1, R^2, R^3 und R^4 are independently chosen from the group consisting of C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkyl, C_6-C_{14} aryl and C_5-C_{14} heteroaryl; and Z is aluminum or boron. Furthermore, the invention relates to a rechargeable battery cell (2) containing an electrolyte according to at least one of the aforementioned claims, an active metal, at least one positive electrode (4), at least one negative electrode (5) and a housing (1).

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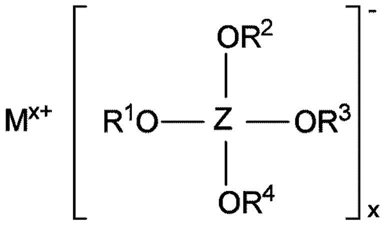
Abstract

The invention relates to an SO_2-based electrolyte for a rechargeable battery cell containing at least one first conducting salt of the formula (I)



$$M^{x+}\left[\; R^1O-\overset{\displaystyle OR^2}{\underset{\displaystyle OR^4}{\overset{|}{\underset{|}{Z}}}}-OR^3 \;\right]^{-}_{x}$$

formula (I)

wherein M is a metal chosen from the group consisting of alkali metals, alkaline earth metals, metals of group 12 of the periodic table of the elements and aluminum; x is an integer from 1 to 3; substituents R^1, R^2, R^3 und R^4 are independently chosen from the group consisting of C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkyl, C_6-C_{14} aryl and C_5-C_{14} heteroaryl; and Z is aluminum or boron. Furthermore, the invention relates to a rechargeable battery cell (2) containing an electrolyte according to at least one of the aforementioned claims, an active metal, at least one positive electrode (4), at least one negative electrode (5) and a housing (1).

SO_2-based electrolyte for a rechargeable battery cell, and a rechargeable battery cell

Description

The invention relates to an SO_2-based electrolyte for a rechargeable battery cell, and a rechargeable battery cell.

Rechargeable battery cells are of great importance in many technical fields. They are often used for applications, which require only small rechargeable battery cells with relatively low current intensities, for example for the operation of cell phones. However, there is also a great need for larger rechargeable battery cells for high-energy applications, with mass storage of energy in the form of battery cells being of particular importance for the electric drive of vehicles.

High energy density is an important requirement for these types of rechargeable battery cells. This means that the rechargeable battery cell should contain as much electrical energy as possible per unit weight and volume. Lithium as an active metal has proven to be particularly advantageous for this purpose. The active metal of a rechargeable battery cell is the metal whose ions within the electrolyte migrate to the negative or positive electrode during cell charging or discharging. This is where they participate in electrochemical processes, which lead directly or indirectly to the release of electrons into the external circuit or to the absorption of electrons from the external circuit. Rechargeable battery cells containing lithium as an active metal are also referred to as lithium ion cells. The energy density of these lithium ion cells can be increased either by expanding the specific capacitance of the electrodes or by increasing the cell voltage.

Both the positive and negative electrodes of lithium ion cells are designed as insertion electrodes.

The term “insertion electrode” in the sense of this invention refers to electrodes which have a crystalline structure that ions of the active material can be stored in and removed from during operation of the lithium ion cell. This means that the electrode processes can take place not only on the surface of the electrodes, but also within the crystalline structure. The negative electrode of lithium ion cells has a carbon coating, which is applied to a conducting element made of copper. The conducting element provides the electronically conductive connection required between the carbon coating and the external circuit. The positive electrode is made of lithium cobalt oxide ($LiCoO_2$), which is applied to a conducting element made of aluminum. Both electrodes typically have a thickness of less than 100 µm and are therefore very thin. When charging the lithium ion cell, the ions of the active metal are removed from the positive electrode and stored in the negative electrode. The reverse process takes place when the lithium ion cell is discharged.

The electrolyte is an important functional element of any rechargeable battery cell. It usually contains a solvent or blend of solvents and at least one conducting salt. Solid electrolytes or ionic liquids, for example, contain no solvent. They contain a conducting salt only. The electrolyte is in contact with the positive and negative electrodes of the battery cell. At least one ion of the conducting salt (anion or cation) is so mobile in the electrolyte that a charge transport between the electrodes, required for the functioning of the rechargeable battery cell, can take place through ionic conduction. The electrolyte is being oxidatively electrochemically decomposed at a certain upper cell voltage of the rechargeable battery cell. This process often leads to an irreversible destruction of the electrolyte components, and thus to a failure of the rechargeable battery cell. Reductive processes can also decompose the electrolyte when falling below a certain cell voltage. In order to avoid these processes, the positive and negative electrodes are selected in a way that ensures that the cell voltage is below or above the decomposition voltage of the electrolyte. The electrolyte thus determines the voltage window, i.e. the range within which the rechargeable battery cell can be operated reversibly.

State-of-the-art lithium ion cells known contain an electrolyte consisting of an organic solvent or solvent blend and a conducting salt dissolved therein. The conducting salt is a lithium salt such as lithium hexafluorophosphate ($LiPF_6$). The solvent blend can, for example, contain ethylene carbonate. Due to the organic solvent or solvent blend, these kinds of lithium ion cells are also referred to as organic lithium ion cells. It has long been known that unintentional overcharging of organic lithium ion cells leads to the irreversible decomposition of electrolyte components. The oxidative decomposition of the organic solvent and/or the conducting salt takes place on the surface of the positive electrode. The reaction heat generated during the decomposition and the resulting gaseous products lead to the subsequent "thermal runaway" and the resulting destruction of the organic lithium ion cell. The vast majority of charging protocols for these organic lithium-ion cells use cell voltage as an indicator of the end of charging. Accidents caused by a thermal runaway are particularly likely to occur when using multi-cell battery packs consisting of multiple organic lithium-ion cells with dissimilar capacities that are connected in series.

Therefore, organic lithium ion cells are problematic in terms of their stability and long-term operational reliability. Safety risks are also caused by the flammability of the organic solvent or solvent blend. When an organic lithium ion cell catches fire or even explodes, the organic solvent of the electrolyte becomes a combustible material. Additional measures must be taken in order to avoid these safety risks. These measures include a very precise regulation of the charging and discharging processes of the organic lithium ion cell as well as an optimized battery design. Furthermore, the organic lithium-ion cell contains components that may melt due to an unintentional increase in temperature so that the organic lithium ion cell is flooded with molten plastic. A further uncontrolled increase in temperature is thus prevented. However, these measures lead to higher manufacturing costs when producing organic lithium ion cells as well as to increased volume and weight. They also reduce the energy density of the organic lithium ion cell.

A further disadvantage of organic lithium ion cells is that any hydrolysis products produced due to residual amounts of water are very aggressive towards the cell components of the rechargeable battery cell. For example, the conducting salt $LiPF_6$, which is frequently used in organic cells, reacts with traces of water and produces highly reactive, aggressive hydrogen fluoride (HF). For the production of these types of rechargeable battery cells with an organic electrolyte, it is therefore important to ensure that the amount of residual water contained in the electrolyte and the cell components is minimized. This is why these battery cells are produced in costly drying rooms under extremely low humidity conditions. The issues described above regarding stability and long-term operational reliability are of particular importance for the development of organic lithium-ion cells, which on the one hand are characterized by a high energy and power density level, and on the other hand by a very high degree of operational reliability and a very long service life, including a particularly high number of usable charging and discharging cycles.

A further development known from prior art therefore provides for the use of an electrolyte based on sulphur dioxide (SO_2) instead of an organic electrolyte for rechargeable battery cells. Rechargeable battery cells, which contain an electrolyte based on SO_2, exhibit a high level of ionic conductivity. The term "SO_2-based electrolyte" refers to an electrolyte which contains SO_2 not merely as an additive at low concentrations, but whose mobility of the ions in the conducting salt, which is contained in the electrolyte and which causes the charge transport, is at least in part, largely or even completely guaranteed by SO_2. The SO_2 therefore serves as a solvent for the conducting salt. The conducting salt and the gaseous SO_2 can form a liquid solvate complex, whereby the SO_2 is bound and the vapor pressure is noticeably reduced compared to the pure SO_2, producing electrolytes that have a low vapor pressure. Compared to the organic electrolytes described above, these SO_2-based electrolytes offer the advantage that they are non-combustible. Safety risks, which might occur due to the electrolyte's flammability, can thus be excluded.

For example, EP 1 201 004 B1 refers to an SO_2-based electrolyte composed of $LiAlCl_4 * SO_2$ in combination with a positive electrode made of $LiCoO_2$. EP 1 201 004 B1 proposes the use of an additional salt to avoid interfering decomposition reactions when overcharging the rechargeable battery cell from a potential of 4.1 to 4.2 volts, such as the undesired formation of chlorine (Cl_2) from lithium tetrachloroaluminate ($LiAlCl_4$).

EP 2534719 B1 also reveals an SO_2-based electrolyte using $LiAlCl_4$, among others, as conducting salt. The $LiAlCl_4$ and the SO_2 form complexes of the formula $LiAlCl_4$ * 1.5 mol SO_2 or $LiAlCl_4$ * 6 mol SO_2. Lithium iron phosphate ($LiFePO_4$) is used as positive electrode. $LiFePO_4$ has a lower charge potential (3.7 V) compared to $LiCoO_2$ (4.2 V). Undesired overcharging reactions do not occur in this rechargeable battery cell, as the potential of 4.1 volts, that is harmful to the electrolyte, is not reached. A further disadvantage that also occurs with these SO_2-based electrolytes is that any hydrolysis products produced due to residual amounts of water react to the cell components of the rechargeable battery. This in turn results in the formation of undesired by-products. When producing these types of rechargeable battery cells with an SO_2-based electrolyte, it is important to ensure that the amount of residual water contained in the electrolyte and the cell components is minimized.

Another problem caused by electrolytes based on SO_2 is that many conducting salts, especially those known for organic lithium ion cells, are not soluble in SO_2. Measurements have shown that SO_2 is a poor solvent for many salts, such as Lithium fluoride (LiF), lithium bromide (LiBr), lithium sulfate (Li_2SO_4), lithium bis(oxalato)borate (LiBOB), lithium hexafluoroarsenate ($LiAsF_6$), lithium tetrafluoroborate ($LiBF_4$), trilithium hexafluoroaluminate (Li_3AlF_6), lithium hexafluoroantimonate ($LiSbF_6$), lithium difluoro(oxalato)borate ($LiBF_2C_2O_4$), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium metaborate ($LiBO_2$), lithium aluminate ($LiAlO_2$), lithium triflate ($LiCF_3SO_3$) and lithium chlorosulfonate ($LiSO_3Cl$).

The solubilities of these salts in SO_2 are approx. $10^{-2} – 10^{-4}$ mol/L (Table 1). At these low concentrations, it can be assumed that only low conductivities are present, which are not sufficient for an efficient operation of the rechargeable battery cell.

Table 1: Solubility of different salts in SO_2

Salt	Solubility / mol/L in SO_2	Salt	Solubility / mol/L in SO_2
LiF	$2.1 \cdot 10^{-3}$	$LiPF_6$	$1.5 \cdot 10^{-2}$
LiBr	$4.9 \cdot 10^{-3}$	$LiSbF_6$	$2.8 \cdot 10^{-4}$
Li_2SO_4	$2.7 \cdot 10^{-4}$	$LiBF_2(C_2O_4)$	$1.4 \cdot 10^{-4}$
$LiB(C_2O_4)_2$	$3.2 \cdot 10^{-4}$	$CF_3SO_2NLiSO_2CF_3$	$1.5 \cdot 10^{-2}$
Li_3PO_4	-	$LiBO_2$	$2.6 \cdot 10^{-4}$
Li_3AlF_6	$2.3 \cdot 10^{-3}$	$LiAlO_2$	$4.3 \cdot 10^{-4}$
$LiBF_4$	$1.7 \cdot 10^{-3}$	$LiCF_3SO_3$	$6.3 \cdot 10^{-4}$
$LiAsF_6$	$1.4 \cdot 10^{-3}$		

In order to further improve the range of applications and properties of SO_2-based electrolytes and rechargeable battery cells containing this electrolyte, the object of the present invention is to specify an SO_2-based electrolyte, which, compared to state-of-the art electrolytes,

- has a wide electrochemical window, so that no oxidative electrolyte decomposition occurs at the positive electrode;
- forms a stable top layer on the negative electrode, whereby the top layer capacity should be low and no further reductive electrolyte decomposition should occur on the negative electrode during further operation;
- allows for operating rechargeable battery cells with high-voltage cathodes due to a wide electrochemical window;

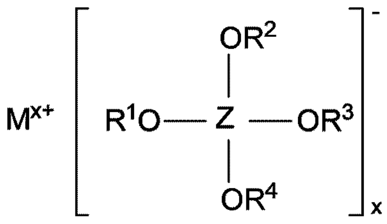
- exhibits good solubility for conducting salts and is therefore a good ionic conductor and electronic insulator, which facilitates ion transport and reduces self-discharge to a minimum;
- is also inert to other components of the rechargeable battery cell, such as separators, electrode materials and cell packaging materials,
- is resistant to various misuses (e.g. electrical, mechanical or thermal misuse) and
- exhibits increased stability against amounts of residual water in cell components of rechargeable battery cells.

These types of electrolytes should be designed for use in rechargeable battery cells, especially those which exhibit a very high energy and power density level, a high degree of operational reliability and a long service life, including a particularly high number of usable charging and discharging cycles, without causing electrolyte decomposition during operation of the rechargeable battery cell.

Another object of the invention is to provide a rechargeable battery cell, which contains an electrolyte based on SO_2 and, in contrast to state-of-the-art rechargeable battery cells, offers

- increased electrical performance, in particular a high energy density level,
- improved overcharge and excessive discharge capability,
- less self-discharge,
- an increased service life, especially a high number of usable charging and discharging cycles,
- a reduced total weight,
- increased operational safety, even under more difficult environmental conditions inside a vehicle, and
- reduced production costs.

An SO_2-based electrolyte for a rechargeable battery cell according to the invention comprises at least one first conducting salt with the formula (I)



$$M^{x+}\left[\begin{array}{ccc} & OR^2 & \\ & | & \\ R^1O - & Z & - OR^3 \\ & | & \\ & OR^4 & \end{array}\right]^{-}_{x}$$

formula (I)

In formula (I), M is a metal chosen from the group consisting of alkali metals, alkaline earth metals, metals of group 12 of the periodic table of the elements, and aluminum. x is an integer from 1 to 3. The substituents R^1, R^2, R^3 and R^4 are independently chosen from the group consisting of C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10}alkynyl, C_3-C_{10} cycloalkyl, C_6-C_{14} aryl and C_5-C_{14} heteroaryl. The central atom Z is either aluminum or boron.

The SO_2-based electrolyte according to the invention contains SO_2 as an additive at low concentrations as well as at concentrations, which ensure mobility of the ions of the first conducting salt (which is contained in the electrolyte and causes the charge transport), at least in part, largely or even completely by means of SO_2. The first conducting salt is dissolved in the electrolyte and exhibits a very good solubility. It can form a liquid solvate complex with the gaseous SO_2 in which the SO_2 is bound. In this case, the vapor pressure of the liquid solvate complex decreases significantly compared to the pure SO_2, leading to the production of electrolytes with low vapor pressure.

However, it is also within the scope of the invention that, depending on the chemical structure of the first conducting salt according to formula (I), no reduction of the vapor pressure might occur during the production of the electrolyte according to the invention. In the latter case, it is preferable to work at low temperature or under pressure when producing the electrolyte according to the invention. The electrolyte may also contain several conducting salts of formula (I), which differ in their chemical structure.

The term "C_1-C_{10} alkyl", as used in the present invention, covers linear or branched saturated hydrocarbon groups with one to ten carbon atoms. These include in particular methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, 2.2-dimethylpropyl, n-hexyl, iso-hexyl, 2-ethylhexyl, n-heptyl, iso-heptyl, n-octyl, iso-octyl, n-nonyl, n-decyl and the like.

The term “C_2-C_{10} alkenyl“, as used in the present invention, covers unsaturated linear or branched hydrocarbon groups with two to ten carbon atoms, whereby the hydrocarbon groups have at least one C-C-double bond. These include in particular ethenyl, 1-propenyl, 2- propenyl, 1-n-butenyl, 2-n-butenyl, iso-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl, 1-nonenyl, 1- decenyl and the like.

The term “C_2-C_{10} alkynyl“, as used in the present invention, covers unsaturated linear or branched hydrocarbon groups with two to ten carbon atoms, whereby the hydrocarbon groups have at least one C-C-triple bond. These include in particular ethinyl, 1-propynyl, 2-propynyl, 1-n-butinyl, 2-n-butinyl, iso-butinyl, 1-pentinyl, 1-hexinyl,1-heptinyl, 1-octinyl, 1-noninyl, 1- decinyl and the like.

The term "C_3-C_{10} cycloalkyl", as used in the present invention, covers cyclical, saturated hydrocarbon groups with three to ten carbon atoms. These include in particular cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclohexyl, cyclononbooknyl and cyclodecanyl.

The term "C_6-C_{14} aryl", as used in the present invention, covers aromatic hydrocarbon groups with six to fourteen rings of carbon atoms. These include in particular phenyl (C_6H_5 group), naphthyl ($C_{10}H_7$ group) and anthracyl ($C_{14}H_9$ group).

The term "C_5-C_{14} heteroaryl", as used in the present invention, covers aromatic hydrocarbon groups with five to fourteen rings of carbon atoms, with at least one -atom replaced by one nitrogen, oxygen or sulphur-atom. These include in particular pyrrolyl, furanyl, thiophenyl, pyrridinyl, pyranyl, thiopyranyl and the like. All of the hydrocarbon groups mentioned above are bonded to the central atom via the oxygen atom according to formula (I).

The advantage of such an electrolyte over the state-of-the-art electrolytes lies in the fact that the first conducting salt contained in it has a higher oxidation stability level and consequently shows essentially no decomposition at higher cell voltages. This electrolyte is resistant to oxidation, preferably at least up to 4.0 volts, more preferably at least up to a potential of 4.2 volts, more preferably at least up to a potential of 4.4 volts, more preferably at least up to a potential of 4.6 volts, more preferably at least up to a potential of 4.8 volts and most preferably at least up to a potential of 5.0 volts. As a result, there is little or no electrolyte decomposition within the working potential of both electrodes of the rechargeable battery cell, when using such an electrolyte in a rechargeable battery cell. This significantly prolongs the service life of the electrolyte compared to state-of-the-art electrolytes. Such an electrolyte is also resistant to low temperatures. If there are small residual amounts of water (in the ppm-range) in the electrolyte, the electrolyte or the first conducting salt reacts with the water and forms hydrolisis products that are significantly less aggressive towards the cell components when using SO_2-based electrolytes (compared to state-of-the-art electrolytes). As a result, the absence of water in the electrolyte is less important for SO_2-based electrolytes than for state-of-the-art electrolytes.

The advantages of the electrolyte according to the invention outweigh the disadvantage, which lies in the fact that the first conducting salt based on the formula (I) has a significantly larger anion size compared to state-of-the-art conducting salts. This larger anion size leads to a lower conductivity of the first conducting salt according to formula (I) in comparison to the conductivity of $LiAlCl_4$.

According to another aspect of the invention, there is provided a rechargeable battery cell. This rechargeable battery cell contains the previously described electrolyte according to the invention or an electrolyte on the basis of the advantageous embodiments of the electrolyte according to the invention described below. Furthermore, the rechargeable battery cell according to the invention comprises an active metal, at least one positive electrode, at least one negative electrode and a housing.

A first preferred embodiment of the electrolyte according to the invention provides substituents R^1, R^2, R^3 and R^4 that are independently chosen from the group made of

- C_1-C_6 alkyl; preferably of C_2-C_4 alkyl; particularly preferred of alkyl groups 2-propyl, methyl and ethyl;
- C_2-C_6 alkenyl; preferably of C_2-C_4 alkenyl; particularly preferred of alkenyl groups ethenyl and propenyl;
- C_2-C_6 alkynyl; preferably of C_2-C_4 alkynyl;
- C_3-C_6 cycloalkyl;
- phenyl; and
- C_5-C_7 heteroaryl.

The term "C_1-C_6 alkyl", as used in this advantageous embodiment of the electrolyte according to the invention, covers linear or branched saturated hydrocarbon groups with one to six hydrocarbon groups, in particular methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, 2.2-dimethylpropyl, n-hexyl und iso-hexyl. C_2-C_4 alkyls are preferred here. The C_2-C_4 alkyls 2-propyl, methyl and ethyl are particularly preferred.

The term "C_2-C_6 alkenyl", as used in this advantageous embodiment of the electrolyte according to the invention, covers unsaturated linear or branched hydrocarbon groups with two to six carbon atoms, whereby the hydrocarbon groups have at least one C-C double bond. These include in particular ethenyl, 1-propenyl, 2- propenyl, 1-n-butenyl, 2-n-butenyl, iso-butenyl, 1-pentenyl and 1-hexenyl, whereby C_2-C_4 alkenyls are preferred. Ethenyl and 1-propenyl are particularly preferred.

The term "C_2-C_6 alkynyl", as used in this advantageous embodiment of the electrolyte according to the invention, covers unsaturated linear or branched hydrocarbon groups with two to six carbon atoms, whereby the hydrocarbon groups have at least one C-C triple bond. These include in particular ethinyl, 1-propynyl, 2-propynyl, 1-n-butinyl, 2-n-butinyl, iso-butinyl, 1-pentinyl and 1-hexinyl. Here, C_2-C_4-alkynyls are preferred.

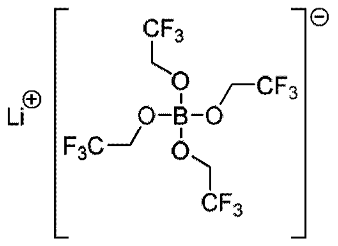
The term "C_3-C_6 cycloalkyl", as used in this advantageous embodiment of the electrolyte according to the invention, covers cyclical, saturated hydrocarbon groups with three to six carbon atoms. These include in particular cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

The term "C_5-C_7 heteroaryl", as used in this advantageous embodiment of the electrolyte according to the invention, covers phenyl und naphtyl.

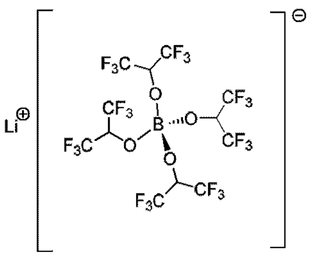
In order to improve solubility of the first conducting salt in the SO_2-based electrolyte, R^1, R^2, R^3 and R^4 are substituted by at least one fluorine atom and/or by at least one chemical group, said chemical group being selected from the group consisting of C_1-C_4 alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynyl, phenyl and benzyl. The chemical groups C_1-C_4 alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynyl, phenyl and benzyl have the same properties or chemical structures as the hydrocarbon groups described above. Substituted in this context means that individual atoms or atom groups of the substituents R^1, R^2, R^3 and R^4 are replaced by the fluorine atom and/or by the chemical group.

A particularly high solubility of the first conducting salt in the SO_2-based electrolyte can be achieved by ensuring that at least one of the substituents R^1, R^2, R^3 and R^4 form a CF_3-group or an OSO_2CF_3-group.

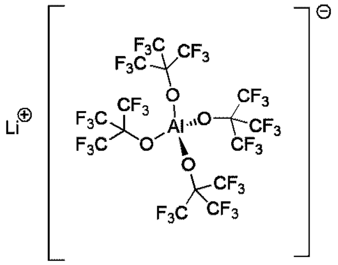
In another advantageous embodiment of the electrolyte according to the invention, the first conducting salt is chosen from a group consisting of



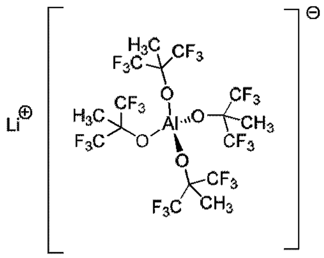
$Li[B\ (OCH_2CF_3)_4]$



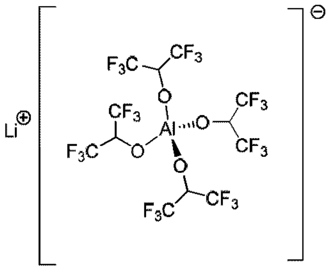
$Li[B(OCH(CF_3)_2)_4]$



$Li[Al(OC(CF_3)_3)_4]$



$Li[Al(OC(CH_3)(CF_3)_2)_4]$



$Li[Al(OCH(CF_3)_2)_4]$.

In order to adjust the conductivity and/or further properties of the electrolyte to a desired value, another advantageous embodiment of the electrolyte provides at least a second conducting salt, which differs from the first conducting salt according to formula (I). This means that in addition to the first conducting salt, the electrolyte may also contain one or several second conducting salts which differ from the first in their chemical composition and structure.

In another advantageous embodiment of the electrolyte according to the invention, the second conducting salt is an alkali metal compound, in particular a lithium compound.

The alkali metal compound or lithium compound are chosen from the group consisting of an aluminate, a halide, an oxalate, a borate, a phosphate, an arsenate and a gallate. Preferably the second conducting salt is a lithium tetrahalogenoaluminate, especially $LiAlCl_4$.

In another advantageous embodiment, the electrolyte contains at least one additive. This additive is preferably selected from the group formed by vinylene carbonate and its derivatives, vinyl ethylene carbonate and its derivatives, methyl ethylene carbonate and its derivatives, lithium (bisoxalato)borate, lithium difluoro(oxalato)borate, Lithium tetrafluoro(oxalato)phosphate, lithium oxalate, 2-vinylpyridine, 4-vinylpyridine, cyclic exomethylenecarbonates, sultones, cyclic and acyclic sulfonates, acyclic sulfites, cyclic and acyclic sulfinates, organic esters of inorganic acids, acyclic and cyclic alkanes, of which acyclic and cyclic alkanes have a boiling point of at least 36°C at 1 bar, aromatic compounds, halogenated cyclic and acyclic sulfonylimides, halogenated cyclic and acyclic phosphate esters, halogenated cyclic and acyclic phosphines, halogenated cyclic and acyclic phosphites, halogenated cyclic and acyclic phosphazenes, halogenated cyclic and acyclic silylamines, halogenated cyclic and acyclic halogenated esters, halogenated cyclic and acyclic amides, halogenated cyclic and acyclic anhydrides and halogenated organic heterocycles.

In another preferred embodiment based on the total weight of the electrolyte, the electrolyte is composed of

(i) 5 to 99.4% by weight of sulphur dioxide,
(ii) 0.6 to 95% by weight of the first conducting salt,
(iii) 0 to 25% by weight of the second conducting salt; and
(Iv) 0 to 10% by weight of the additive.

As mentioned before, the electrolyte may contain not only a first conducting salt according to formula (I) and a second conducting salt, but also several first conducting salts according to formula (I) and several second conducting salts.

In the latter case, the above percentages also include several first conducting salts and several second conducting salts. The molar concentration of the first conducting salt lies within the range of 0.05 mol/l to 10 mol/l, preferably 0.1 mol/l to 6 mol/l and most preferably 0.2 mol/l to 3.5 mol/l relative to the total volume of the electrolyte.

Another advantageous embodiment of the rechargeable battery cell of the invention specifies that the electrolyteshall contain at least 0.1 mol SO_2, preferably at least 1 mol SO_2, more preferably at least 5 mol SO_2, more preferably at least 10 mol SO_2 and most preferably at least 20 mol SO_2 per mol of conducting salt. The electrolyte may also contain very high molar proportions of SO_2, the preferred upper limit being 2600 moles of SO_2 per mole of conducting salt and upper limits of 1500, 1000, 500 and 100 moles of SO_2 per mole of conducting salt being further preferred in this order. The term "per mole of conducting salt" refers to all conducting salts contained in the electrolyte. SO_2-based electrolytes with such a concentration ratio between SO_2 and the conducting salt offer the advantage that they can dissolve a larger amount of conducting salt than state-of-the-art electrolytes, which are based on an organic solvent blend, for example. Within the scope of the invention, it was found that, surprisingly, an electrolyte with a relatively low concentration of conducting salt is advantageous despite the associated higher vapor pressure, particularly in terms of stability over many charging and discharging cycles of the rechargeable battery cell. The concentration of SO_2 in the electrolyte affects its conductivity. By selecting the SO_2-concentration, the conductivity of the electrolyte can thus be adapted to the intended use of a rechargeable battery cell operated by means of this electrolyte.

The total amount of SO_2 and the first conducting salt may be greater than 50 percent by weight (wt%) of the weight of the electrolyte, more preferably greater than 60 wt%, more preferably greater than 70 wt%, more preferably greater than 80 wt%, more preferably greater than 85 wt%, more preferably greater than 90 wt%, more preferably greater than 95 wt%, or more preferably greater than 99 wt%.

The electrolyte may contain at least 5 wt% of SO_2 based on the total amount of the electrolyte contained in the rechargeable battery cell, with values of 20 wt% of SO_2 , 40% by weight of SO_2 and 60% by weight of SO_2 further preferred. The electrolyte may also contain up to 95 wt% of of SO_2, with maximum values of 80 wt% of SO_2 and 90 wt% of SO_2 being preferred in this order.

It is within the scope of the invention that the electrolyte preferably has only a small or even no percentage of at least one organic solvent. Preferably, the proportion of organic solvents contained in the electrolyte, for example in the form of one solvent or a blend of solvents, shall not exceed 50 wt% off the weight of the electrolyte. Particular preference is given to lower proportions of no more than 40 wt%, no more than 30 wt%, no more than 20 wt%, no more than 15 wt%, no more than 10 wt%, no more than 5 wt% or no more than 1 wt% of the electrolyte. In a further preferred embodiment, the electrolyte is free of organic solvents. Due to the low proportion of organic solvents or even their complete absence, the electrolyte is either hardly combustible or not combustible at all. This increases the operational safety of rechargeable battery cells which use this kind of SO_2-based electrolyte. The SO_2-based electrolyte, that is essentially free of organic materials, is particularly preferred.

Active metal

In the following, advantageous further embodiments of the rechargeable battery cell according to the invention are described with regard to the active metal:

In a first advantageous further embodiment, the rechargeable battery is an active metal

- an alkali metal, in particular lithium or sodium;
- an alkaline earth metal, in particular calcium;
- a metal of group 12 of the periodic table of the elements, in particular zinc; or
- aluminum

Negative electrode

In the following, advantageous further embodiments of the rechargeable battery cell according to the invention are described with regard to the negative electrode:

Another advantageous further embodiment of the rechargeable battery cell specifies that the negative electrode shall be an insertion electrode. This insertion electrode contains an insertion material as active material that the ions of the active metal are stored in during charging of the rechargeable battery cell and that the ions of the active metal can be removed from during discharging of the rechargeable battery cell. This means that the electrode processes can take place not only on the surface of the electrodes, but also inside the negative electrode. For example, if a conducting salt based on lithium is used, lithium ions can be stored in the insertion material during charging of the rechargeable battery cell and removed from the insertion material during discharging of the rechargeable battery cell. The negative electrode preferably contains carbon as active material or insertion material, in particular in the graphite modification. However, it is also in the scope of the invention that carbon is provided in the form of natural graphite (flake or rounded), synthetic graphite (mesophase graphite), graphitized mesocarbon microbeads (MCMB), with carbon-coated graphite or amorphous carbon.

In another advantageous further embodiment of the rechargeable battery cell, the negative electrode includes lithium-intercalation-anode active material that contains no carbon, such as lithium titanate (e.g. $Li_4Ti_5O_{12}$).

Another advantageous further embodiment of the rechargeable battery cell according to the invention specifies that the negative electrode with lithium comprises alloy-forming anode active materials. These include lithium-storing metals and alloys (e.g. Si, Ge, Sn, $SnCo_xC_y$, $SnSi_x$ and the like) and oxides of the lithium-storing metals and alloys (e.g. SnO_x, SiO_x, oxide glasses of Sn, Si and the like).

In another advantageous further embodiment of the rechargeable battery cell according to the invention, the negative electrode contains conversion-anode active materials. These conversion anode active materials can be, for example, transition metal oxides in the form of manganese oxides (MnO_x), iron oxides (FeO_x), cobalt oxides (CoO_x), nickel oxides (NiO_x, copper oxides (CuO_x) or metal hydrides in the form of magnesium hydride (MgH_2), titanium hydride (TiH_2), aluminum hydride (AlH_3) and boron-, aluminum- and magnesium-based ternary hydrides and the like.

In another advantageous further embodiment of the rechargeable battery cell according to the invention, the negative electrode comprises a metal, in particular metallic lithium.

Another advantageous further embodiment of the rechargeable battery cell according to the invention provides that the negative electrode is porous, whereby the maximum porosity shall preferably be 50%, more preferably 45%, more preferably 40%, more preferably 35%, more preferably 30%, more preferably 20%, and most preferably 10%. The porosity represents the cavity volume in relation to the total volume of the negative electrode, whereby the cavity volume is formed by so-called pores or cavities. This porosity enlarges the inner surface of the negative electrode. It also reduces the density of the negative electrode and thus its weight. The individual pores of the negative electrode can preferably be completely filled with the electrolyte during operation.

Another advantageous further embodiment of the battery cell according to the invention provides that the negative electrode has a conducting element. This means that in addition to the active material or insertion material, the negative electrode includes a conducting element. This conducting element is used to enable the necessary electronically conductive connection of the active material of the negative electrode. For this purpose, the conducting element is in contact with the active material of the electrode reaction of the negative electrode. This conducting element can be planar shaped in the form of a thin metal sheet or a thin metal foil. The thin metal foil preferably has a perforated or mesh-like structure.

The active material of the negative electrode is preferably applied to the surface of the thin metal sheet or foil. Such planar conducting elements have a thickness in the range of 5 µm to 50 µm. A thickness of the planar conducting element in the range of 10 µm to 30 µm is preferred. When planar conducting elements are used, the negative electrode can have a total thickness of at least 20 µm, preferably of at least 40 µm and most preferably of at least 60 µm. The maximum thickness is 200 µm or less, preferably 150 µm or less and most preferably 100 µm or less. The area-specific capacitance of the negative electrode is preferably at least 0.5 mAh/cm^2 when a planar conducting element is used, whereby the following values are further preferred in this order: 1 mAh/cm^2, 3 mAh/cm^2, 5 mAh/cm^2, 10 mAh/cm^2.

Furthermore, the conducting element may consist of a three-dimensional porous metal structure, in particular of a metal foam. The term “three-dimensional porous metal structure” refers to any structure made of metal that extends not only like a thin metal sheet or metal foil over the length and width of the electrode surface area, but also over its thickness. The three-dimensional porous metal structure is so porous that the active material of the negative electrode can be incorporated into the pores of the metal structure. The amount of active material incorporated or applied is the loading of the negative electrode. If the conducting element consists of a three-dimensional porous metal structure, in particular of a metal foam, then the negative electrode preferably has a thickness of at least 0.2 mm, preferably of at least 0.3 mm, more preferably of at least 0.4 mm, more preferably of at least 0.5 mm and most preferably of at least 0.6 mm. In this case, the electrodes are significantly thicker in comparison to negative electrodes, which are used for organic lithium-ion-cells. Another advantageous embodiment provides that the area-specific capacitance of the negative electrode, when used with a three-dimensional discharge element, in particular if the latter consists of a metal foam, is preferably at least 2.5 mAh/cm^2, the following values being further preferred in this order: 5 mAh/cm^2, 10 mAh/cm^2, 15 mAh/cm^2, 20 mAh/cm^2, 25 mAh/cm^2, 30 mAh/cm^2.

If the conducting element consists of a three-dimensional porous metal structure, in particular of a metal foam, the amount of active material of the negative electrode, i.e. the loading of the electrode relative to its surface, is at least 10 mg/cm^2, preferably at least 20 mg/cm^2, more preferably at least 40 mg/cm^2, more preferably at least 60 mg/cm^2, more preferably at least 80 mg/cm^2 and most preferably at least 100 mg/cm^2. This charging of the negative electrode has a positive effect on the charging and discharging process of the rechargeable battery cell.

In a further advantageous further embodiment of the battery cell according to the invention, the negative electrode comprises at least one binder. This binder is preferably a fluorinated binder, in particular a polyvinylidene fluoride and/or a terpolymer formed from tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride. However, it may also be a binder consisting of a polymer composed of monomeric structural units of a conjugated carboxylic acid or of the alkali metal, alkaline earth metal or ammonium salt of this conjugated carboxylic acid or of a combination thereof. The binder may also consist of a polymer based on monomeric styrene and butadiene structural units. In addition, the binder may also be a binder of the group of carboxymethylcelluloses. The binder is present in the negative electrode preferably in a maximum concentration of 20% by weight, more preferably of 15% by weight, more preferably of 10% by weight, more preferably of 7% by weight, more preferably of 5% and most preferably of 2% by weight relative to the total weight of the negative electrode.

Positive electrode

In the following, advantageous further embodiments of the rechargeable battery cell according to the invention are described with regard to the positive electrode:

In another advantageous further embodiment of the battery cell according to the invention, the positive electrode contains at least one intercalation compound as active material. For the purpose of this invention, the term “intercalation compound” means a subcategory of the insertion materials described above.

This intercalation compound functions as a host matrix, with empty spaces that are interconnected. The ions of the active metal can diffuse into these empty spaces during the discharge process of the rechargeable battery cell and be stored there. During the deposition of the ions of the active metal, only minor or no structural changes occur in the host matrix. Preferably, the intercalation compound has the following composition $Li_xM'_yM''_zO_a$, wherein

- M' is at least one metal chosen from the group consisting of the elements Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn;
- M" is at least one element chosen from the group, consisting of elements of the groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 and 16 of the periodic table of the elements;
- x and y are greater than 0;
- z is greater than or equal to 0; and
- a is greater than 0.

The indices y and z refer to the totality of metals and elements represented by M' and M" respectively. For example, if M' contains two metals M'_1 and M'_2, the following applies to the index y: y=y1+y2, where y1 and y2 represent the indices of the metals M'_1 and M'_2. The indices x, y, z and a must be selected in such a way that charge neutrality prevails within the composition.

Compositions of the formula $Li_xM'_yM''_zO_4$ are preferred. In another advantageous further embodiment of the rechargeable battery cell according to the invention, M' iron and M" phosphorus are comprised in the composition $Li_xM'_yM''_zO_4$. In this case, the intercalation compound is lithium iron phosphate ($LiFePO_4$). Another advantageous further embodiment of the rechargeable battery cell according to the invention provides that M' manganese and M" cobalt are comprised in the composition $Li_xM'_yM''_zO_4$. In this case, the intercalation compound is lithium cobalt manganese oxide ($LiCoMnO_4$). $LiCoMnO_4$ can be used to produce so-called high-voltage electrodes for high-energy cells with a cell voltage of over 5 volts. This $LiCoMnO_4$ is preferably free of Mn^{3+}.

Another advantageous further embodiment of the rechargeable battery cell according to the invention provides that M' consists of the metals nickel and manganese and M" is cobalt. Those are compositions of the formula $Li_xNi_{y1}Mn_{y2}Co_zO_2$ (NMC). Examples of these intercalation compounds of lithium nickel manganese cobalt oxide are $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111), $LiNi_{0.6}Mn_{0.2}Co_2O_2$ (NMC622) and $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811).

High-voltage electrodes can be cycled at least up to an upper potential of 4.0 volts, more preferably at least up to a potential of 4.2 volts, more preferably at least up to a potential of 4.4 volts, more preferably at least up to a potential of 4.6 volts, more preferably at least up to a potential of 4.8 volts and most preferably at least up to a potential of 5.0 volts in the rechargeable battery according to the invention.

Another advantageous further embodiment of the rechargeable battery cell according to the invention provides that the positive electrode comprises at least one metal compound. This metal compound is chosen from the group consisting of a metal oxide, a metal halide and a metal phosphate. Preferably the metal of this metal compound is a transition metal with an atomic number of 22 to 28 of the periodic table of the elements, in particular cobalt, nickel, manganese or iron are preferred.

Another advantageous further embodiment of the battery cell according to the invention provides that the positive electrode has a conducting element. This means that in addition to the active material, the positive electrode includes a conducting element. This conducting element is used to enable the necessary electronically conductive connection of the active material of the positive electrode. For this purpose, the conducting element is in contact with the active material of the electrode reaction of the positive electrode.

This conducting element can be planar shaped in the form of a thin metal sheet or a thin metal foil. The thin metal foil preferably has a perforated or mesh-like structure.

The active material of the positive electrode is preferably applied to the surface of the thin metal sheet or foil. Such planar conducting elements have a thickness in the range of 5 µm to 50 µm. A thickness of the planar conducting element in the range of 10 µm to 30 µm is preferred. When planar conducting elements are used, the positive electrode can have a total thickness of at least 20 µm, preferably of at least 40 µm and most preferably of at least 60 µm. The maximum thickness is 200 µm or less, preferably 150 µm or less and most preferably 100 µm or less. The area-specific capacitance of the positive electrode is preferably at least 0.5 mAh/cm^2 when a planar conducting element is used, whereby the following values are still preferred in this order: 1 mAh/cm^2, 3 mAh/cm^2, 5 mAh/cm^2, 10 mAh/cm^2.

Furthermore, the conducting element of the positive electrode may consist of a three-dimensional porous metal structure, in particular of a metal foam. The three-dimensional porous metal structure is so porous that the active material of the positive electrode can be incorporated into the pores of the metal structure. The amount of active material incorporated or applied is the loading of the positive electrode. If the conducting element consists of a three-dimensional porous metal structure, in particular of a metal foam, then the positive electrode preferably has a thickness of at least 0.2 mm, preferably of at least 0.3 mm, more preferably of at least 0.4 mm, more preferably of at least 0.5 mm and most preferably of at least 0.6 mm. Another advantageous embodiment provides that the area-specific capacitance of the positive electrode, when used with a three-dimensional discharge element, in particular if the latter consists of a metal foam, is preferably at least 2.5 mAh/cm^2, the following values being further preferred in this order: 5 mAh/cm^2, 10 mAh/cm^2, 15 mAh/cm^2, 20 mAh/cm^2, 25 mAh/cm^2, 30 mAh/cm^2. If the conducting element consists of a three-dimensional porous metal structure, in particular of a metal foam, the amount of active material of the positive electrode, i.e. the loading of the electrode relative to its surface, is at least 10 mg/cm^2, preferably at least 20 mg/cm^2, more preferably at least 40 mg/cm^2, more preferably at least 60 mg/cm^2, more preferably at least 80 mg/cm^2 and most preferably at least 100 mg/cm^2.

This loading of the positive electrode has a positive effect on the charging and discharging process of the rechargeable battery cell.

In another advantageous further embodiment of the battery cell according to the invention, the positive electrode comprises at least one binder. This binder is preferably a fluorinated binder, in particular a polyvinylidene fluoride and/or a terpolymer formed from tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride. However, it may also be a binder consisting of a polymer composed of monomeric structural units of a conjugated carboxylic acid or of the alkali metal, alkaline earth metal or ammonium salt of this conjugated carboxylic acid or of a combination thereof. The binder may also consist of a polymer based on monomeric styrene and butadiene structural units. In addition, the binder may also be a binder of the group of carboxymethylcelluloses. The binder is present in the positive electrode preferably in a maximum concentration of 20% by weight, more preferably of 15% by weight, more preferably of 10% by weight, more preferably of 7% by weight, more preferably of 5% and most preferably of 2% by weight relative to the total weight of the electrode.

Design of the rechargeable battery cell

In the following, advantageous further embodiments of the rechargeable battery cell according to the invention are described with regard to their design:

In order to further improve the function of the rechargeable battery cell, another advantageous further embodiment of the rechargeable battery cell according to the invention provides that the rechargeable battery cell comprises several negative electrodes and several positive electrodes that are alternately stacked in its housing. The positive electrodes and the negative electrodes are preferably electrically separated from each other by separators.

This separator may consist of a non-woven material, a membrane, woven or knitted material, organic material, inorganic material or a combination thereof. Organic separators may consist of unsubstituted polyolefins (e.g. polypropylene or polyethylene), partially to completely halogen-substituted polyolefins (e.g. partially to completely fluorine-substituted, in particular PVDF, ETFE, PTFE), polyesters, polyamides or polysulfones. Separators, which combine organic and inorganic materials, include, for example, glass fiber textile materials whose glass fibers are coated with a suitable polymer. The coating preferably contains a fluorine-containing polymer such as polytetrafluoroethylene (PTFE), ethylene-tetrafluoroethylene (ETFE), perfluoroethylene propylene (FEP), THV (terpolymer of tetrafluoroethylene, hexafluoroethylene and vinylidene fluoride) or a perfluoroalkoxy-polymer (PFA), an aminosilane, a polypropylene (PP) or polyethylene (PE). The separator in the housing of the rechargeable battery cell can also be folded, for example "z-folded". With z-folding, a strip-shaped separator is folded z-like through or around the electrodes. The separator can also be designed as a separator paper.

It is also within the scope of the invention that the separator can be designed as a sheath, whereby each positive electrode or each negative electrode is enveloped by the sheath. This sheath may consist of a non-woven material, a membrane, woven or knitted material, organic material, inorganic material or a combination thereof.

A sheath covering the positive electrode leads to a more uniform ion migration and ion distribution in the rechargeable battery cell. The more even the ion distribution is, especially in the negative electrode, the higher the possible charge of the negative electrode with active material and consequently the usable capacity of the rechargeable battery cell. At the same time, risks associated with uneven charging and the resulting separation of the active metal are avoided. These advantages are particularly effective when the positive electrodes of the rechargeable battery cell are enveloped by a sheath.

The surface dimensions of the electrodes and of the sheath can preferably be matched to each other in such a manner that the outer dimensions of the sheath and the outer dimensions of the electrode coincide in at least one dimension.

The surface area of the sheath can preferably be greater than the surface area of the electrode. In this case, the sheath extends beyond a limitation of the electrode. Two layers of the sheath covering the electrode on both sides can therefore be joined together at the edge of the positive electrode by an edge connector.

In another advantageous embodiment of the rechargeable battery cell according to the invention, the negative electrodes have a sheath, while the positive electrodes do not have a sheath.

Other advantageous properties of the invention are described and explained in more detail below using figures, examples and experiments.

Figure 1:	shows a first embodiment example of a rechargeable battery cell according to the invention in a cross-sectional diagram;
Figure 2:	shows a detailed electron microscope image of the three-dimensional porous structure of the metal foam of the first example in Figure 1;
Figure 3:	shows a second embodiment example of a rechargeable battery cell according to the invention in a cross-sectional diagram;
Figure 4:	shows a detail of the second embodiment example in Figure 3:
Figure 5:	shows a third embodiment example of a rechargeable battery cell according to the invention in an exploded view;

Figure 6: shows the discharge capacity as a function of the number of cycles of full cells containing either a mixed electrolyte of compound 1 or compound 3 in a reference electrolyte or the reference electrolyte;

Figure 7: shows charging and discharging potential curves in volts [V] as a function of the percentage charge of full cells filled with either one of the three embodiment examples 1, 2 or 3 of an electrolyte according to the invention or the reference electrolyte;

Figure 8: shows a potential curve in volts [V] as a function of the percentage charge of a full cell filled with the first embodiment example 1 of the electrolyte according to the invention;

Figure 9: shows potential curves in volts [V] as a function of the accumulated charge of full cells filled with a third embodiment example 3 of an electrolyte, depending on the charge/discharge current;

Figure 10: shows mean values for the discharge capacities of a reference full cell filled with the reference electrolyte and a test full cell filled with the first embodiment example 1 of the electrolyte according to the invention as a function of the cycle number;

Figure 11: shows the course of the internal resistance of the two full cells in Figure 10 across the cycle number;

Figure 12: shows the conductivity in [mS/cm] of the first embodiment example 1 of the electrolyte according to the invention depending on the concentration; and

Figure 13: shows the potential in [V] of a reference full cell and two test full cells when charging a negative electrode against lithium as a function of capacitance, which is related to the theoretical capacitance of the negative electrode, during topcoat formation on the negative electrode.

Figure 1 shows a first embodiment example of a rechargeable battery cell 2 according to the invention in a cross-sectional diagram. This rechargeable battery cell 2 is designed as a prismatic cell and, among other things, has a housing 1. This housing 1 encloses an electrode array 3, comprising three positive electrodes 4 and four negative electrodes 5. The positive electrodes 4 and the negative electrodes 5 are alternately stacked in the electrode array 3. Housing 1 can, however, also accommodate more positive electrodes 4 and/or negative electrodes 5. In general, it is preferred that the number of negative electrodes 5 is one greater than the number of positive electrodes 4. As a result, the front surfaces of the electrode stack consist of the electrode surfaces of the negative electrodes 5. The electrodes 4, 5 are connected via electrode connections 6, 7 with corresponding contacts 9, 10 of the rechargeable battery cell 2. The rechargeable battery cell 2 is filled with an electrolyte based on SO_2 in such a manner that the electrolyte penetrates as completely as possible into all pores or cavities, particularly within the electrodes 4, 5. The electrolyte is not visible in Figure 1. In this embodiment example, the positive electrodes 4 contain an intercalation compound as active material. This intercalation compound is $LiCoMnO_4$.

In this embodiment example, electrodes 4, 5 have a flat design, i.e. layers of low thickness in relation to their surface area. They are separated from each other by separators 11. Housing 1 of the depicted rechargeable battery cell 2 is essentially cuboid in shape, the electrodes 4, 5 and the walls of housing 1 shown in sectional diagram extending perpendicularly to the drawing layer and being essentially straight and flat. However, the rechargeable battery cell 2 can also be used as a winding cell in which the electrodes consist of thin layers wound together with a separator material. The separators 11 separate the positive electrode 4 and negative electrode 5 spatially and electrically, but they are also permeable to the ions of the active metal. In this way, large electrochemically effective surfaces are created, which enable a correspondingly high power yield.

Electrodes 4, 5 also have a discharge element, not depicted in Figure 1, which allows for the necessary electronically conductive connection of the active material of the respective electrode. This conducting element is in contact with the active material involved in the electrode reaction of the respective electrode 4, 5 (not depicted in Figure 1). The conducting element consists of porous metal foam. This metal foam extends over the entire thickness of the electrodes 4, 5. The active material of the positive electrodes 4 and the negative electrodes 5 is incorporated into the pores of this metal foam so that it fills its pores uniformly over the entire thickness of the metal structure. To improve their mechanical strength, the positive electrodes 4 also contain a binder. This binder is a fluoropolymer. The negative electrodes 5 contain carbon as an active material in a form suitable for the absorption of lithium ions. The structure of the negative electrode 5 is similar to that of the positive electrode 4.

Figure 2 shows a detailed electron microscope image of the three-dimensional porous structure of the metal foam 18 of the first embodiment example in Figure 1. The scale shows that the pores P have an average diameter of more than 100 µm, i.e. they are relatively large.

Figure 3 shows a second embodiment example of the rechargeable battery cell according to the invention in a cross-sectional diagram. This second embodiment example differs from the first embodiment example shown in Figure 1 in that the electrode arrangement 3 comprises one positive electrode 4 and two negative electrodes 5. The positive electrode 4 has a conducting element 34 in the form of a planar metal foil to which the active material 24 of the positive electrode 4 is applied on both sides. The negative electrodes 5 also include a conducting element 35 in the form of a planar metal foil to which the active material 25 of the negative electrode 4 is applied on both sides. Alternatively, the planar conducting elements of the edge electrodes, i.e. the electrodes that close off the electrode stack, can only be coated with active material on one side. The uncoated side faces the housing wall.

Figure 4 shows the planar metal foil, which serves as a conducting element 34, 35 for the positive electrodes 4 and the negative electrodes 5 in the second embodiment example in Figure 3. This metal foil has a perforated or mesh-like structure with a thickness of 20 µm.

Figure 5 shows an embodiment example of the rechargeable battery cell 2 according to the invention in a cross-sectional diagram. This third embodiment example differs from the two previously described embodiment examples in that the positive electrode 4 is enveloped with a sheath 13. A surface area of the sheath 13 is greater than a surface area of the positive electrode 4, the boundary 14 of which is drawn as a dashed line in Figure 2. Two layers 15, 16 of the sheath 13, covering the positive electrode 4 on both sides, are connected to each other at the circumferential edge of the positive electrode 4 via an edge connector 17.

Example 1: Preparation of a reference electrolyte

A reference electrolyte used for the examples described below was prepared according to the procedure described in patent specification EP 2 954 588 B1. Lithium chloride (LiCl) was first dried under vacuum at 120 °C for three days. Aluminum particles (Al) were dried under vacuum at 450°C for two days. LiCl, aluminum chloride ($AlCl_3$) and Al were mixed at a molar ratio of $AlCl_3$:LiCl:Al of 1:1.06:0.35 in a glass bottle with an opening allowing gas to escape. This mixture was then heat-treated in stages to produce a molten salt. After cooling, the molten salt formed was filtered, then cooled to room temperature. Finally, SO_2 was added until the desired molar ratio of SO_2 to $LiAlCl_4$ was formed. The reference electrolyte thus formed had the composition $LiAlCl_4 * x\ SO_2$, where x depends on the amount of SO_2 added.

Example 2: Preparation of three embodiment examples 1, 2 and 3 of the electrolyte according to the invention

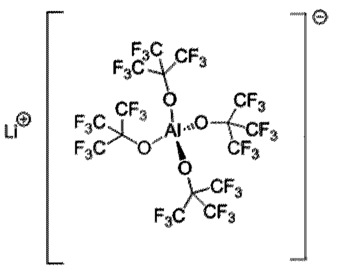
For the experiments described below, three embodiment examples 1, 2 and 3 of the electrolyte according to the invention were prepared (hereinafter referred to as electrolytes 1, 2 and 3). For this purpose, first three different conducting salts were prepared according to formula (I) of a manufacturing process described in the following documents:

I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490;
S. M.Ivanova et al., *Chem. Eur. J.* **2001**, *7*, 503;
Tsujioka et al., *J. Electrochem. Soc.,* **2004**, *151*, A1418"

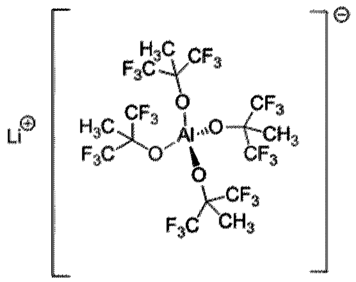
These three different, initial conducting salts according to formula (I) are hereinafter referred to as compounds 1, 2 and 3. They stem from the family of polyfluoroalkoxyaluminates and were prepared in hexane according to the following reaction equation starting with $LiAlH_4$ and the corresponding alcohol R-OH with $R^1=R^2=R^3=R^4$.

$$LiAlH_4 + 4\ HO\text{-}R \xrightarrow{\boxed{\text{hexane}}} LiAl(OR)_4 + 4\ H_2$$

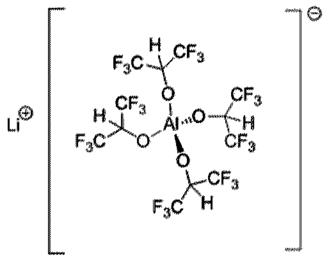
Compounds 1, 2 and 3 with the following sum and structural formulas were formed:



$Li\,[Al(OC(CF_3)_3)_4]$
Compound 1



$Li\,[Al(OC(CH_3)(CF_3)_2)_4]$
Compound 2



$Li\,[Al(OCH(CF_3)_2)_4]$
Compound 3

For purification, compounds 1, 2 and 3 were first recrystallized. This removed residues of the educt $LiAlH_4$ from the first conducting salt, since this educt could possibly lead to spark formation with any traces of water in SO_2.

Subsequently, compounds 1, 2 and 3 were dissolved in SO_2. It was found that compounds 1, 2 and 3 dissolve well in SO_2.

The preparation of electrolytes 1, 2 and 3 was carried out at low temperature or under pressure according to process steps 1 to 4 listed below:

1) Presentation of the respective compound 1, 2 and 3 in a pressure piston with riser pipe,
2) Evacuation of the pressure pistons,
3) Inflow of liquid SO_2 and
4) Repetition of steps 2 + 3 until the target amount of SO_2 was added.

The respective concentration of compounds 1, 2 and 3 in electrolytes 1, 2 and 3 was 1 mol/l (substance concentration related to 1 liter of the electrolyte), unless stated otherwise in the experiment description. The experiments described below were carried out with electrolytes 1, 2 and 3 and the reference electrolyte.

Example 3: Production of full cells

The full cells used in the experiments described below are rechargeable battery cells with two negative electrodes and one positive electrode, each separated by a separator. The positive electrodes contained $LiFePO_4$ as an active material, a conductivity mediator and a binder. The negative electrodes contained graphite as active material and a binder. The full cells were each filled with the electrolyte required for the experiments, i.e. either with the reference electrolyte or electrolytes 1, 2 or 3.

Several, i.e. two to four identical full cells were produced for each experiment. The results presented in the experiments are mean values of the measurement values obtained for the identical full cells.

Experiment 1: Investigation of possible negative effects of electrolytes 1 and 3 on the cycling behavior of full cells

In order to test whether the electrolyte according to the invention had no negative effects on the cycling behavior of full cells, mixed electrolytes were first prepared which contained a small proportion of either compound 1 or compound 3 in the reference electrolyte.

Mixed electrolytes consisting of 95 weight percent (wt%) reference electrolyte and 5 wt% compound 1 or 5 wt% compound 3 were prepared for this purpose. The two mixed electrolytes were compared with a pure reference electrolyte (100 wt%). For this purpose, experiments were carried out in full cells according to example 3. Full cells were filled with different electrolytes. The full cells were charged with 50 mA up to a potential of 3.6 V. The potential of 3.6 volts was maintained until the current dropped to 40 mA. The discharge was performed with a current of 50 mA up to a potential of 2.5 V. 500 charge/discharge cycles were performed. Figure 6 shows three discharge curves, i.e. the discharge capacities as a function of the number of cycles. All electrolytes show nearly the same discharge capacity.

It can be concluded from this that electrolytes 1 and 3, as well as the first conducting salt according to formula (I), have no serious negative effects on cycling behavior.

Experiment 2: Function of the electrolytes in a battery cell according to the invention

With the reference electrolyte prepared in example 1 and the electrolytes 1, 2 or 3 prepared in example 2, experiments were carried out in full cells according to example 3. The reference electrolyte and the electrolytes 1, 2 and 3 each had a concentration of 0.6 mol/l of conducting salt. Four full cells were filled with the electrolytes. The full cells were charged with 50 mA up to a potential of 3.6 V. The potential of 3.6 volts was maintained until the current dropped to 40 mA.

The discharge was performed with a current of 50 mA up to a potential of 2.5 V. In the upper part, Figure 7 shows the charging curves with reference to the scale of the left y-axis. In the lower part, it shows the discharging curves with reference to the scale of the right y-axis. With electrolytes 1, 2 and 3 the full cells could be charged and discharged again.

<u>Experiment 3:</u> Verification of high voltage capability of electrolytes 1, 2 and 3

To demonstrate the high voltage capability of electrolytes 1, 2 and 3, an experiment was carried out in full cells according to example 3. The full cell was filled with electrolyte 1 as described in example 2, which contained compound 1 as the first conducting salt in a concentration of 1 mol/l, based on 1 liter of the electrolyte.

Figure 8 shows the potential curve of the previously described full cell in volts [V] above the percentage charge in relation to the maximum charge of the full cell. The full cell was charged with an amperage of 50 mA up to a potential of 5 V. The potential was maintained until the charging current dropped to 40 mA. Afterwards the discharge took place with an amperage of 50 mA up to a discharge potential of 2.5 V. Figure 6 shows the charge/discharge curve of the full cell obtained in this experiment 3. Cycling efficiency was greater than 99.5%. This means that no capacity was used for secondary or overcharging reactions of the electrolyte. Electrolyte 1 is stable in this potential range. From this it can be concluded that the electrolyte which contains the first conducting salt can also be used for high-energy cells in which high cell voltages occur, without the first conducting salt decomposing.

<u>Experiment 4:</u> Cycling efficiency

The charge/discharge experiment 3 was repeated, with the difference that the upper potential limit for charging was increased from 3.6 volts to 5.0 volts in 0.2-volt steps. This means that eight cycles were performed. Table 2 shows the cycling efficiencies achieved in each case.

Table 2: Cycling efficiency as a function of charge potential

Charging potential	Cycling efficiency
3.60	99.7%
3.80	99.6%
4.00	99.7%
4.20	99.7%
4.40	99.7%
4.60	99.7%
4.80	99.7%
5.00	99.7%

The achieved cycling efficiencies are identical for each charging potential and show a stable behavior of electrolyte 1 in the entire potential range up to 5.0 volts.

Experiment 5:

The electrolyte 3 according to the invention was compared with the reference electrolyte in a cycling experiment. Three full cells, as described in example 3, were used for this purpose. One full cell each was filled with the reference electrolyte and two full cells with electrolyte 3. The full cell was charged up to a potential of 3.6 volts and discharged up to 2.5 volts. The full cell with the reference electrolyte was operated with a current of 100 mA, the two full cells with electrolyte 3, adapted to the lower conductivity, were charged or discharged once with 10 mA and once with 5 mA respectively. Figure 9 shows the charge/discharge curves obtained. All full cells show a stable charge and a stable discharge. At lower currents, the attainable capacity for electrolyte 3 increases.

Experiment 6: Comparison of discharge capacities and internal resistance of full cells with reference electrolyte and electrolyte 1

In this experiment, the use of the electrolyte according to the invention as an alternative to the state-of-the-art reference electrolyte was investigated.

The experiment was also carried out with the full cells described in example 3. The full cells were filled either with reference electrolyte (hereinafter referred to as reference full cell) or with the previously described electrolyte 1 according to the invention (hereinafter referred to as test full cell). Thus, the reference full cell and the test full cell differed only in the type of electrolyte used.

Several cycling experiments were performed, starting with a formation cycle. Table 3 shows the charging and discharging currents used and the final charging and discharging voltages during charging and discharging of the two full cells. In addition, the limit of the charge current (I_{cutoff}) at the final charge voltage is 3.6 volts. There was a break of ten minutes between charging and discharging the two full cells.

Table 3: Data of the cycling experiments

- Formation: Charge / Discharge	- 1 cycle: 15 mA to 125 mAh / 15 mA to 2.5V
- Cycling: Charge / Discharge	- 90 cycles: 50 mA to 3.6 V (I_{cutoff} = 40 mA) / 50 mA to 2.5 V
- 24 h Rest	- 1 cycle: 50 mA to 3.6 V (I_{cutoff} = 40 mA) / 24 h Rest / 50 mA to 2.5 V
- Cycling: Charge / Discharge	- 410 cycles: 50 mA to 3.6 V (I_{cutoff} = 40 mA) / 50 mA to 2.5 V

Figure 10 shows mean values for the discharge capacities of the two full cells as a function of the number of cycles. The dashed line with long dashes shows the average values obtained for discharging capacities of the test full cell. For this purpose, mean values obtained from three identical measurements were used. The dashed line with short lines shows the discharging capacities of the reference full cell. For this purpose, mean values obtained from two identical measurements were used.

These average discharge capacity values are expressed as a percentage of the nominal capacity. The nominal capacity is obtained by subtracting from the theoretical capacity of the positive electrode the capacity consumed in the first cycle to form a coating on the negative electrode. This top layer is formed on the negative electrode when the full cell is charged for the first time. Lithium ions are irreversibly consumed for this coating formation, so that the respective full cell has less cycling capacity available for the subsequent cycles.

The starting value of the discharge capacity of both full cells is approx. 90 % of the nominal capacity. Both full cells show a discharge capacity drop across the number of cycles. The capacity drop for the reference full cell was 19% up to the 500th cycle and the remaining capacity was 71%. The test full cell had a discharge capacity drop of 22% and a remaining capacity of 68% after 500 cycles. Capacity progression in both curves is almost parallel from the 300th cycle onwards and suggests further steady progression. The behavior of the full cells is similar and shows that the electrolyte according to the invention can be used as an alternative to the reference electrolyte.

During experiment 6, progression of the internal resistance of the two full cells was also recorded via the cycle number. Figure 11 shows the results for the reference full cell and for the test full cell. The internal resistance is a loss factor inside the full cell due to its design. The internal resistance of the reference full cell is slightly above 0.2 Ohm. The test full cell shows a higher internal resistance of initially approx. 0.95 Ohm, which is stable at a value of 0.8 Ohm from approx. cycle 200 onwards.

These results are in line with the applicant's expectations, as the lithium ionic conductivity in an electrolyte with large anions used according to the present invention is somewhat more difficult.

Experiment 7: Determining conductivities

The conductivity was determined by preparing the electrolyte 1 with different concentrations of compound 1. For each concentration of compound 1, the conductivity of electrolyte 1 was determined using a conductive measurement method. After temperature control, a two-electrode sensor was held in contact with the solution and measurement was carried out in a range of 0 - 50 mS/cm. Table 4 shows the different concentrations, the corresponding SO_2 contents and the conductivity values determined.

Table 4: Conductivity as a function of the concentration of compound 1 in the electrolyte 1

c of compound 1 in mol/L	wt% SO_2	Conductivity in mS/cm
1.00	34%	13.6
0.60	60%	24.7
0.40	75%	20.8
0.20	87%	11.7

Figure 12 shows the conductivity of electrolyte 1 as a function of the concentration of compound 1. A maximum conductivity of of 24.7 mS/cm is depicted at a concentration of compound 1 of 0.6 mol/L. In comparison, state-of-the-art organic electrolytes such as LP30 (1 M LiPF6 / EC-DMC (1:1 weight)) have a conductivity of only approx. 10 mS/cm.

Experiment 8: Determination of a capacitance consumed for the formation of a coating layer on the negative electrode

In this experiment, the capacitance consumed in the first cycle for the formation of a top layer on the negative electrode was investigated. This top layer is formed on the negative electrode when the full cell is charged for the first time. Lithium ions are irreversibly consumed for this coating formation, so that the full cell has less cycling capacity available for the subsequent cycles.

The reference electrolyte, electrolyte 1 and electrolyte 3 were each examined in a full cell for this experiment. The desgin corresponded to the design described in example 3.

The composition of the reference electrolyte used in a first experiment was LiAlCl4 * x SO_2 with x > 1.5. In a second and third experiment, electrolytes 1 and 3 were examined.

Figure 13 shows the potential in volts of the full cells when charging the negative electrode against lithium as a function of capacitance, which is related to the theoretical capacitance of the negative electrode. The dotted line shows the results for the reference electrolyte and the dotted or solid line shows the results for the electrolytes 1 and 3 according to the invention. The three curves show averaged results of several experiments with the full cells described above. First the full cells were charged with a current of 15 mA until a capacitance of 125 mAh (Q_{cha}) was reached. The full cells were then discharged at 15 mA until a potential of 2.5 volts was reached. This is when the discharging capacity (Q_{dis}) was determined.

The capacitance in % of the theory used to form the top layer on the negative electrode is calculated according to the following formula:

Cover layer capacity = (Q_{cha} (125mAh) – Q_{dis} (x mAh)) / Q_{NEL}

Q_{NEL} is the theoretical capacitance of the negative electrode used. In the case of graphite, the theoretical capacitance calculated is 372 mAh/g. The absolute capacity losses are 7.58% and 11.51% respectively for electrolytes 1 and 3 and 6.85% for the reference electrolyte. The capacity for the formation of the top layer is slightly higher for both electrolytes according to the invention than for the reference electrolyte. Values in the range of 7.5% - 11.5% for absolute capacity losses are good results in combination with the possibility of using high-voltage cathodes of up to 5 volts.

Experiment 9: Low-temperature behavior

In order to determine the low-temperature behavior of an electrolyte according to the invention in comparison to the reference electrolyte, two full cells, as described in experiment 1, were filled with reference electrolyte on the one hand and electrolyte 1 on the other hand.

Both full cells were charged at 20°C and discharged again. The discharge capacity achieved was rated 100%. In temperature steps of 10°C, the temperature of the full cells was lowered, and a charge/discharge cycle was carried out again. The discharge capacity obtained was described in % of the discharge capacity at 20°C. Table 5 shows the results.

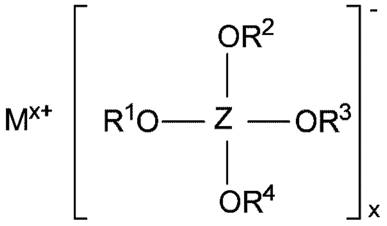
Table 5: Discharge capacities as a function of temperature

Temperature	Discharge capacity of electrolyte 1	Discharge capacity of reference electrolyte
20°C	100%	100%
10°C	87%	99%
0°C	72%	46%
-10°C	61%	21%
-20°C	31%	n/a
-30°C	3%	n/a
-40°C	0%	n/a

The full cell with electrolyte 1 shows an excellent low-temperature behavior. At -10°C, 61% of the capacity is reached. At -20°C the capacity reached is still 31%. Even at -30 °C, a small amount can still be discharged. In contrast, the full cell with the reference electrolyte only shows a discharge capacity at up to -10°C. Then a capacity of 21% is achieved.

Claims

1. SO_2-based electrolyte containing SO_2 for a rechargeable battery cell comprising at least a first conducting salt of the formula (I),



$$M^{x+}\left[\begin{array}{c} \qquad OR^2 \\ \qquad | \\ R^1O - Z - OR^3 \\ \qquad | \\ \qquad OR^4 \end{array}\right]^{-}_{x}$$

formula (I)

wherein

- M is a metal selected from the group consisting of alkali metals, alkaline earth metals, metals of group 12 of the periodic table of the elements and aluminum;
- x is an integer from 1 to 3;
- the substituents R^1, R^2, R^3 and R^4 are independently chosen from the group consisting of C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkyl, C_6-C_{14} aryl, and C_5-C_{14} heteroaryl; and
- wherein Z is aluminum or boron.

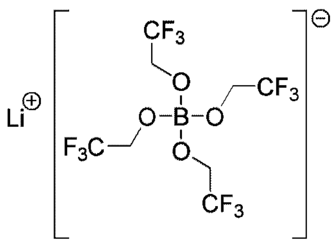
2. Electrolyte according to claim 1,
wherein the substituents R^1, R^2, R^3 and R^4 are independently chosen from the group consisting of
   - C_1-C_6 alkyl;
   - C_2-C_6 alkenyl;
   - C_2-C_6 alkynyl;
   - C_3-C_6 cycloalkyl;
   - phenyl; and
   - C_5-C_7 heteroaryl.

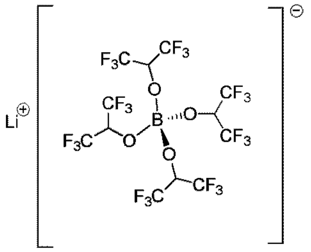
3. Electrolyte according to claim 1 or 2,

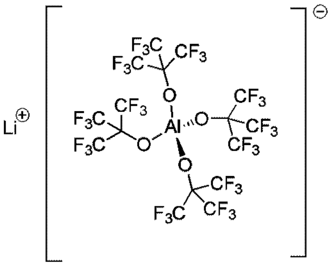
wherein at least one of the substituents R^1, R^2, R^3 and R^4 is substituted by at least one fluorine atom and/or by at least one chemical group, said chemical group being chosen from the group consisting of C_1-C_4 alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynyl, phenyl and benzyl.

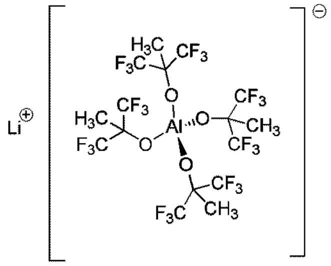
4. Electrolyte according to any one of claims 1 to 3,
wherein at least one of the substituents R^1, R^2, R^3 and R^4 is a CF_3-group or a OSO_2CF_3-group.

5. Electrolyte according to any one of claims 1 to 4,
wherein the first conducting salt is chosen from the group consisting of

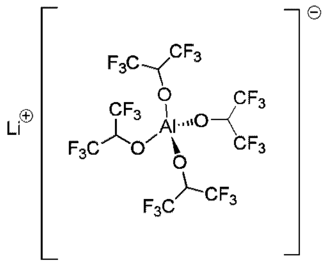

$Li[B(OCH_2CF_3)_4]$


$Li[B(OCH(CF_3)_2)_4]$


$Li[Al(OC(CF_3)_3)_4]$


$Li[Al(OC(CH_3)(CF_3)_2)_4]$

and



Li[Al(OCH(CF_3)$_2$)$_4$].

6. Electrolyte according to any one of claims 1 to 5, which contains at least one second conducting salt which differs from the first conducting salt according to formula (I).

7. Electrolyte according to claim 6, wherein the second conducting salt is an alkali metal compound.

8. Electrolyte according to claim 6 or 7, wherein the second conducting salt is a lithium tetrahalogenoaluminate.

9. Electrolyte according to any one of claims 1 to 8, which further contains at least one additive.

10. Electrolyte according to claim 9, wherein the additive is chosen from the group consisting of vinylene carbonate and its derivatives, vinyl ethylene carbonate and its derivatives, methyl ethylene carbonate and its derivatives, lithium (bisoxalato)borate, lithium difluoro(oxalato)borate, lithium tetrafluoro(oxalato)phosphate, lithium oxalate, 2-vinylpyridine, 4-vinylpyridine, cyclic exomethylenecarbonates, sultones, cyclic and acyclic sulfonates, acyclic sulfites, cyclic and acyclic sulfinates, organic esters, inorganic acids, acyclic and cyclic alkanes, wherein said acyclic and cyclic alkanes have a boiling point at 1 bar of at least 36 °C, aromatic compounds, halogenated cyclic and acyclic sulfonylimides, halogenated cyclic and acyclic phosphate esters, halogenated cyclic and acyclic phosphines, halogenated cyclic and acyclic phosphites, halogenated cyclic and acyclic phosphazenes, halogenated cyclic and acyclic silylamines, halogenated cyclic and acyclic halogenated esters, halogenated

cyclic and acyclic amides, halogenated cyclic and acyclic anhydrides and halogenated organic heterocycles.

11. Electrolyte according to any one of claims 9 to 10, comprising a composition of
    (i) 5 to 99.4% by weight of sulphur dioxide,
    (ii) 0.6 to 95% by weight of the first conducting salt,
    (iii) 0 to 25% by weight of the second conducting salt; and
    (iv) 0 to 10% by weight of the additive,

    based on the total weight of the electrolyte composition.

12. Electrolyte according to any one of claims 1 to 11, wherein the molar concentration of the first conducting salt is in the range of 0.05 mol/l to 10 mol/l based on to the total volume of the electrolyte.

13. Electrolyte according to any one of claims 1 to 12, containing at least 0.1 mol SO_2 per mol of all conducting salts.

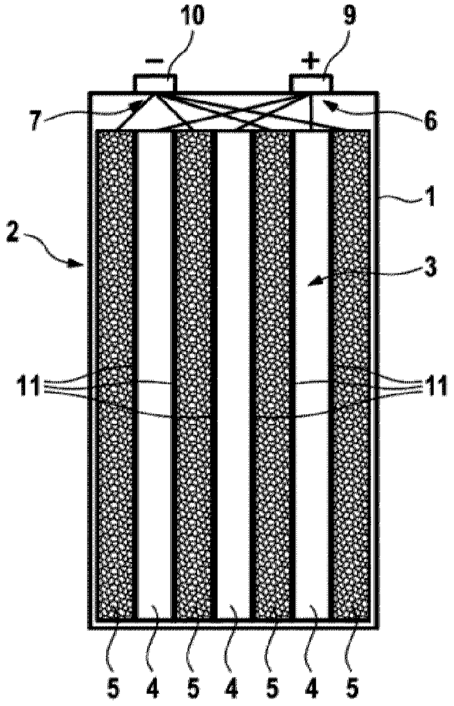


Fig. 1

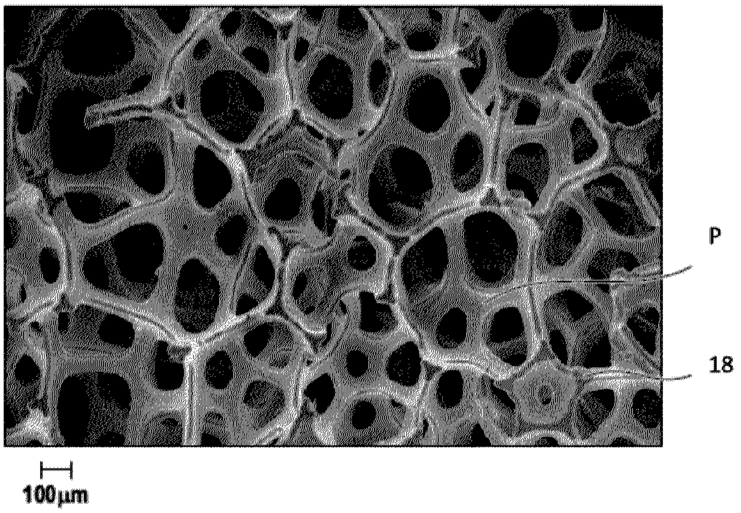


Fig. 2

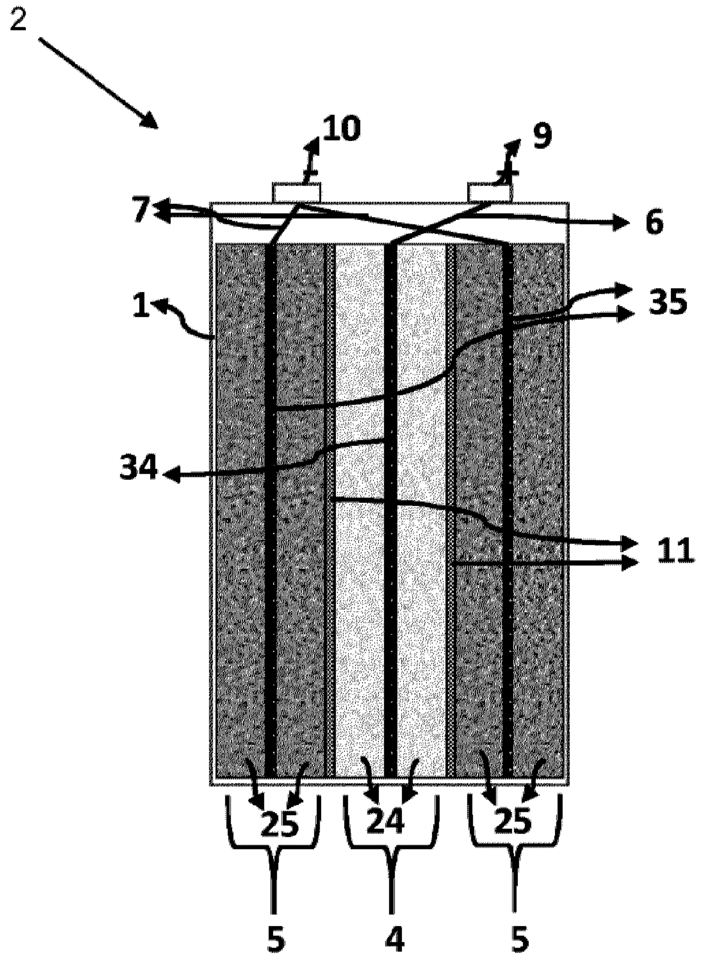


Fig. 3

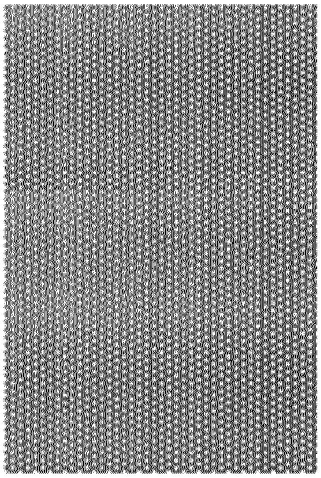


Fig. 4

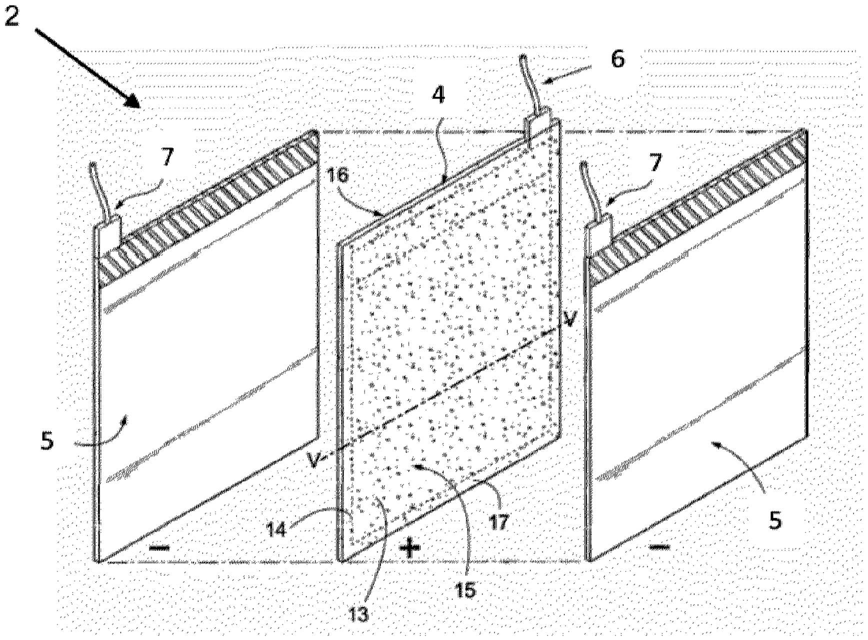


Fig. 5

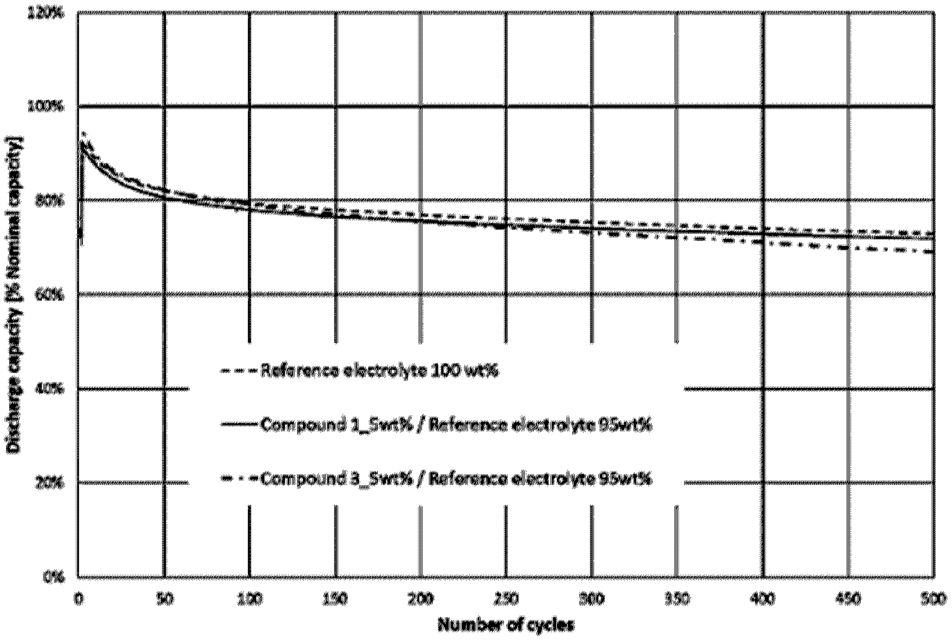

120%
100%
80%
60%
40%
20%
0%
Discharge capacity [% Nominal capacity]
0
50
100
150
200
250
300
350
400
450
500
Number of cycles
Reference electrolyte 100 wt%
Compound 1_5wt% / Reference electrolyte 95wt%
Compound 3_5wt% / Reference electrolyte 95wt%

Fig. 6

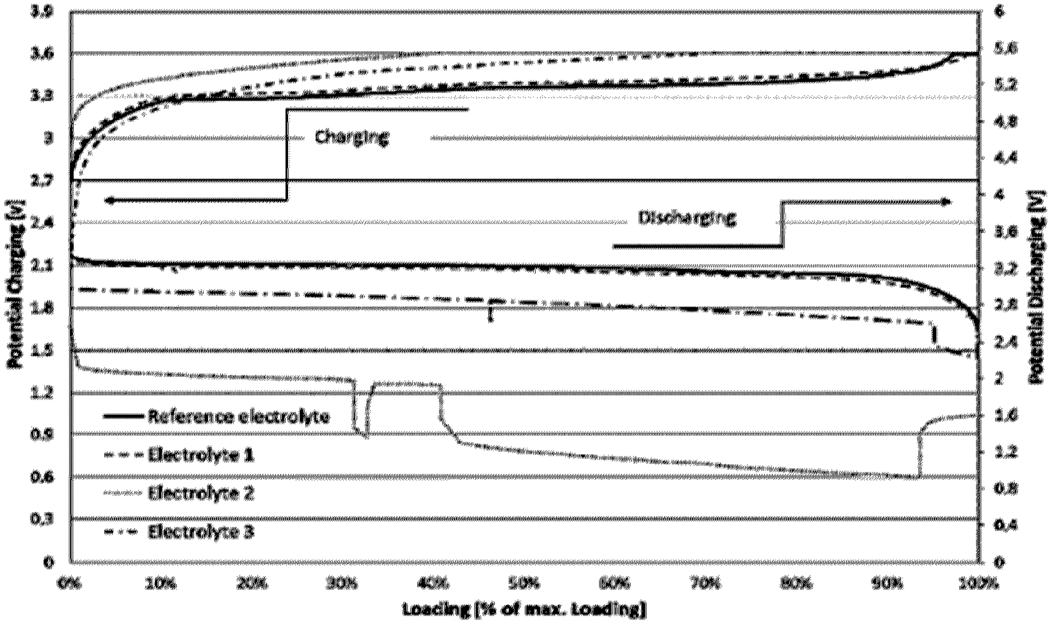

3,9
3,6
3,3
3
2,7
2,4
2,1
1,8
1,5
1,2
0,9
0,6
0,3
0
Potential Charging [V]
6
5,6
5,2
4,8
4,4
4
3,6
3,2
2,8
2,4
2
1,6
1,2
0,8
0,4
0
Potential Discharging [V]
Charging
Discharging
Reference electrolyte
Electrolyte 1
Electrolyte 2
Electrolyte 3
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
Loading [% of max. Loading]

Fig. 7

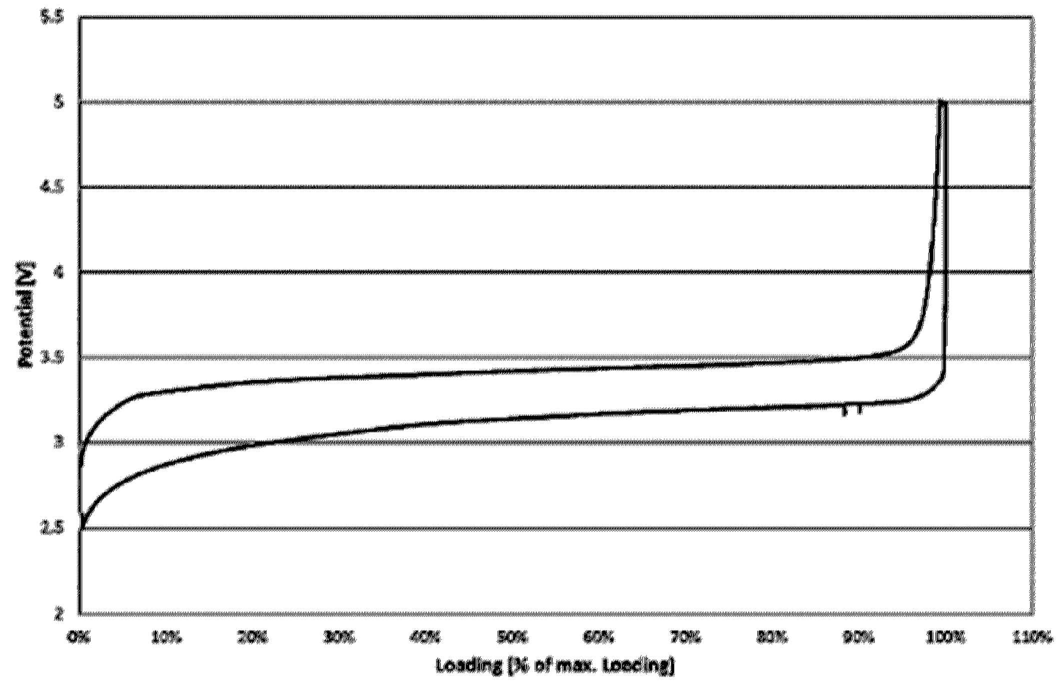

5,5
5
4,5
4
3,5
3
2,5
2
Potential [V]
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
110%
Loading [% of max. Loading]

Fig. 8

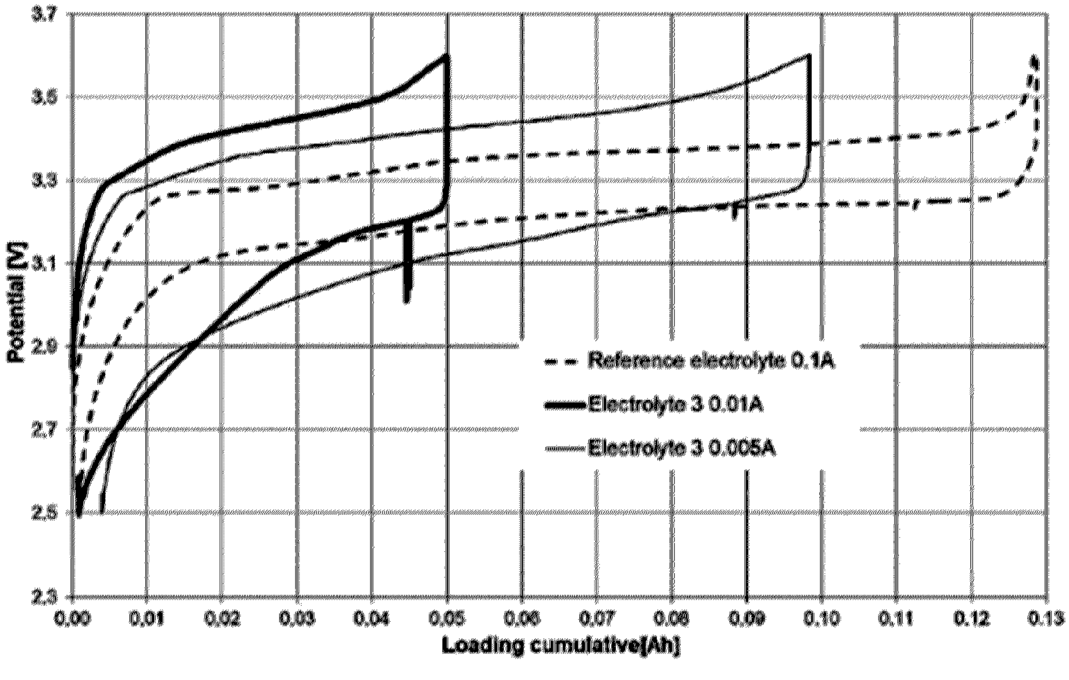

3,7
3,5
3,3
3,1
2,9
2,7
2,5
2,3
Potential [V]
- - Reference electrolyte 0.1A
Electrolyte 3 0.01A
Electrolyte 3 0.005A
0,00
0,01
0,02
0,03
0,04
0,05
0,06
0,07
0,08
0,09
0,10
0,11
0,12
0,13
Loading cumulative[Ah]

Fig. 9

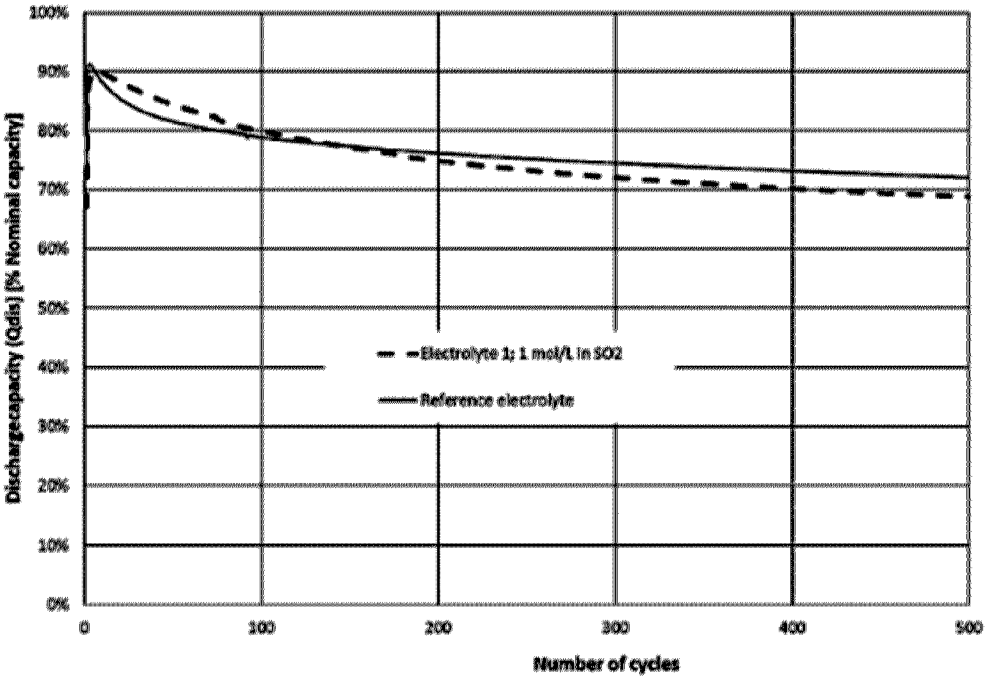

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Dischargecapacity (Qdis) [% Nominal capacity]
0
100
200
300
400
500
Number of cycles
Electrolyte 1; 1 mol/L in SO2
Reference electrolyte

Fig. 10

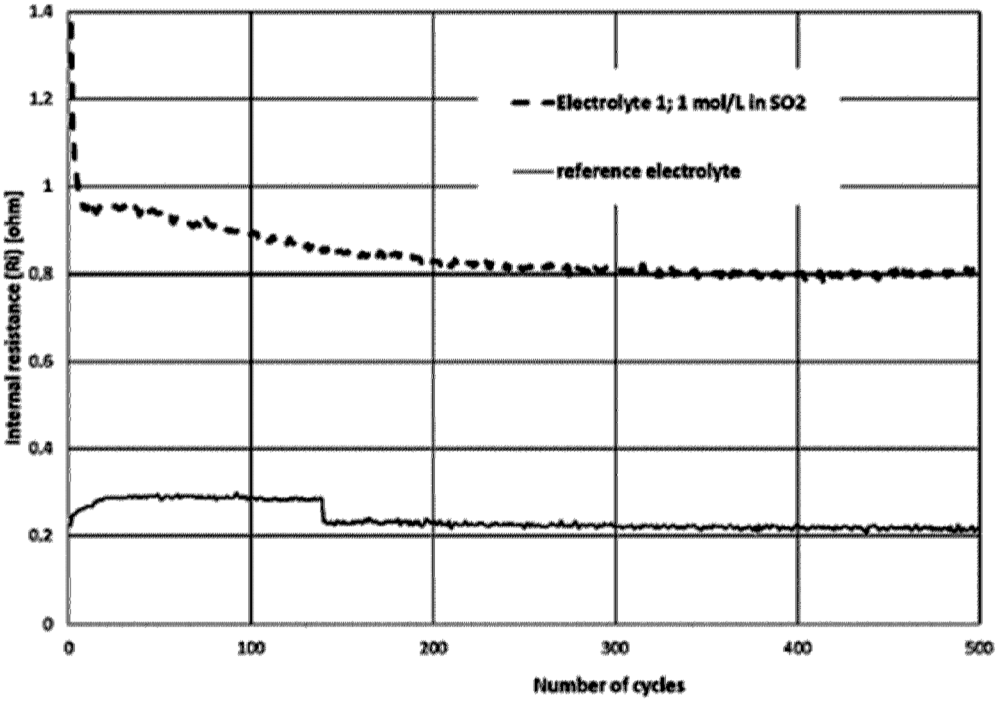

1.4
1.2
1
0,8
0,6
0,4
0,2
0
Internal resistance (Ri) [ohm]
0
100
200
300
400
500
Number of cycles
Electrolyte 1; 1 mol/L in SO2
reference electrolyte

Fig. 11

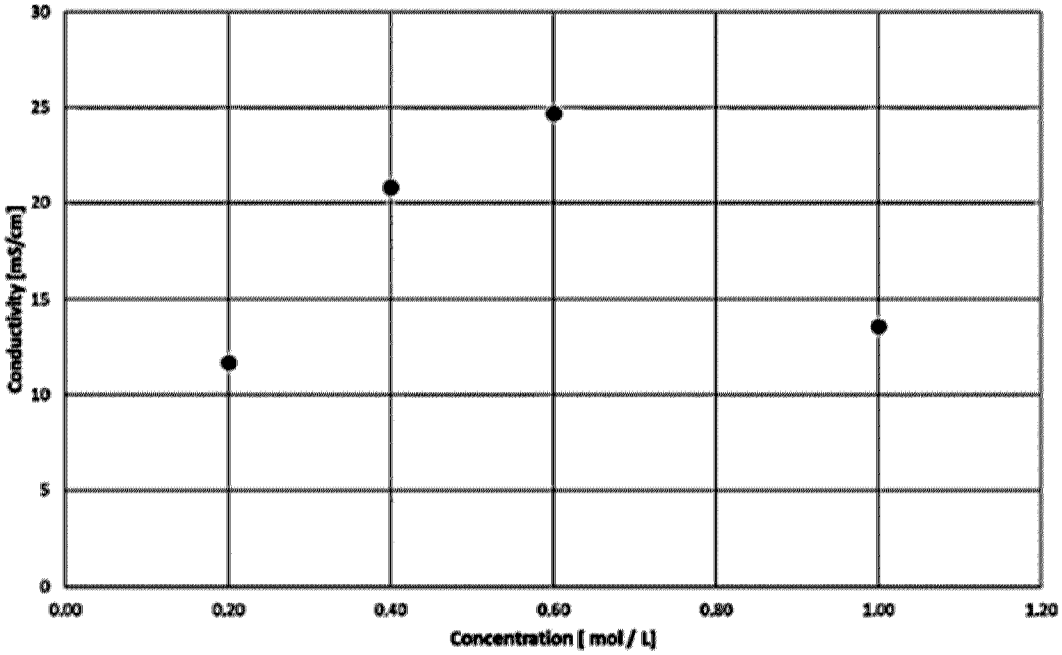

30
25
20
15
10
5
0
Conductivity [mS/cm]
0.00
0.20
0.40
0.60
0.80
1.00
1.20
Concentration [mol / L]

Fig. 12

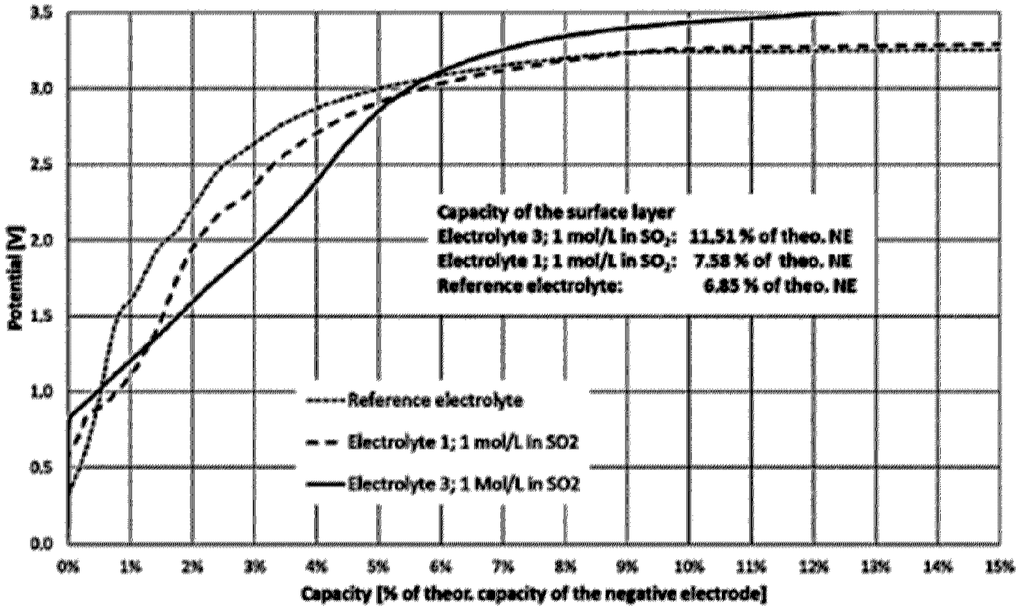
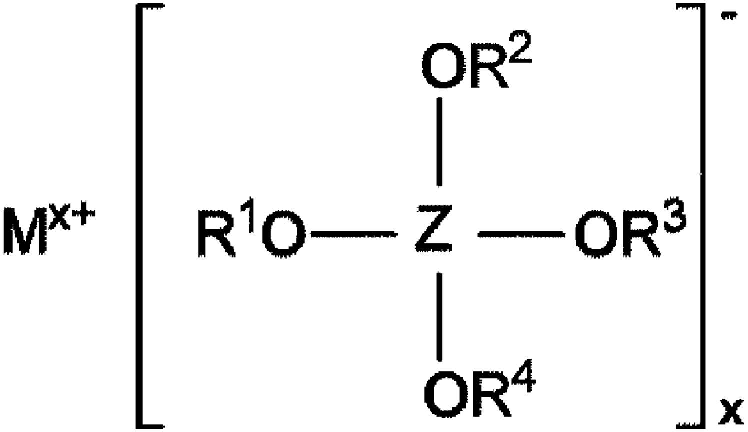

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Potential [V]
0%
1%
2%
3%
4%
5%
6%
7%
8%
9%
10%
11%
12%
13%
14%
15%
Capacity [% of theor. capacity of the negative electrode]
Capacity of the surface layer
Electrolyte 3; 1 mol/L in SO₂: 11.51 % of theo. NE
Electrolyte 1; 1 mol/L in SO₂: 7.58 % of theo. NE
Reference electrolyte: 6.85 % of theo. NE
Reference electrolyte
Electrolyte 1; 1 mol/L in SO2
Electrolyte 3; 1 Mol/L in SO2

Fig. 13



$$M^{x+}\left[\begin{array}{ccc} & \mathrm{OR^2} & \\ & | & \\ \mathrm{R^1O}- & \mathrm{Z} & -\mathrm{OR^3} \\ & | & \\ & \mathrm{OR^4} & \end{array}\right]^{-}_{x}$$

formula (I)