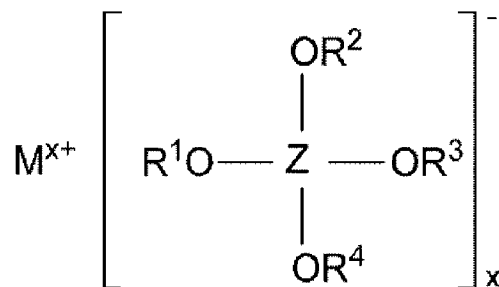




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(54) Titre : PILE RECHARGEABLE
(54) Title: RECHARGEABLE BATTERY CELL



Formula (I)

(57) **Abrégé/Abstract:**

The invention relates to a rechargeable battery cell (2, 20, 40) comprising an active metal, at least one positive electrode (4, 23, 44), at least one negative electrode (5, 22, 45), a housing (1, 28) and an electrolyte, the positive electrode (4, 23, 44) comprising at least one polyanionic compound as an active material and the electrolyte being based on SO₂ and comprising at least one first conducting salt which has the formula (I),

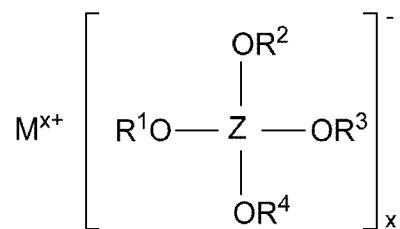
(see formula I)

M being a metal selected from the group formed by alkali metals, alkaline earth metals, metals of group 12 of the periodic table of the elements, and aluminum; x being an integer from 1 to 3; the substituents R¹, R², R³ and R⁴ being selected independently of one another from the group formed by C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, C₂-C₁₀ alkynyl, C₃-C₁₀ cycloalkyl, C₆-C₁₄ aryl and C₅-C₁₄ heteroaryl; and Z being aluminum or boron.



Abstract

The invention relates to a rechargeable battery cell (2, 20, 40) comprising an active metal,
 5 at least one positive electrode (4, 23, 44), at least one negative electrode (5, 22, 45), a
 housing (1, 28) and an electrolyte, the positive electrode (4, 23, 44) comprising at least
 one polyanionic compound as an active material and the electrolyte being based on SO₂
 and comprising at least one first conducting salt which has the formula (I),



10

Formula (I)

M being a metal selected from the group formed by alkali metals, alkaline earth metals,
 metals of group 12 of the periodic table of the elements, and aluminum; x being an integer
 from 1 to 3; the substituents R¹, R², R³ and R⁴ being selected independently of one an-
 15 other from the group formed by C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, C₂-C₁₀ alkynyl, C₃-C₁₀ cycloal-
 kyl, C₆-C₁₄ aryl and C₅-C₁₄ heteroaryl; and Z being aluminum or boron.

Rechargeable battery cell

Description

5

The invention relates to a rechargeable battery cell having an SO₂-based electrolyte.

Rechargeable battery cells are of great importance in many technical fields. They are often used for applications which require only small rechargeable battery cells having relatively low current intensities, for example, for the operation of cell phones. In addition, 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 propulsion 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 has proven to be particularly advantageous as an active metal 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 when the cell is being charged or discharged and participate in electrochemical processes there. These electrochemical processes 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 comprising lithium as an active metal are also referred to as lithium-ion cells. The energy density of these lithium-ion cells can either be increased by increasing the specific capacity 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 the present invention refers to electrodes which have a crystal structure into which ions of the active material can be stored and removed 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. 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.

35

The electrolyte is also an important functional element of every rechargeable battery cell. It usually comprises a solvent or a solvent blend and at least one conducting salt. Solid electrolytes or ionic liquids, for example, do not comprise a solvent, but only the conducting salt. 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 sufficiently mobile in the electrolyte such 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 oxidatively electrochemically decomposed from 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 chosen such that the cell voltage is below or above the decomposition voltage of the electrolyte. The electrolyte thus determines the voltage window, in the range of which a rechargeable battery cell can be operated reversibly, that is, repeatedly charged and discharged.

The lithium-ion cells known from the prior art comprise 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 comprise, for example, ethylene carbonate. The electrolyte LP57, which has the composition 1 M LiPF_6 in EC:EMC 3:7, is an example of such an electrolyte. Due to the organic solvent or solvent blend, these kinds of lithium ion cells are also referred to as organic lithium-ion cells.

The negative electrode of these organic lithium-ion cells consists of a carbon coating which is applied to a discharge element made of copper. The discharge element provides the electronically conductive connection required between the carbon coating and the external circuit. The positive electrode consists of lithium cobalt oxide (LiCoO_2), which is applied to a discharge element made of aluminum. Both electrodes typically have a thickness of less than 100 μm and are therefore very thin.

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 this decomposition and the resulting gaseous products are responsible for the subsequent so-called "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 the cell voltage as an indicator of the end of charging. Accidents caused by the thermal runaway are particularly likely to occur when using multi-cell battery packs in which a plurality of organic lithium-ion cells having dissimilar capacities are connected in series.

5 Organic lithium-ion cells are therefore problematic in terms of their stability and long-term operational reliability. Safety risks are also caused in particular by the flammability of the organic solvent or solvent blend. When an organic lithium-ion cell catches fire or even explodes, the organic solvent in the electrolyte forms a combustible material. Additional measures must be taken to avoid such safety risks. These measures include, in particular,
10 a very precise regulation of the charging and discharging processes of the organic lithium-ion cell and an optimized battery design. Furthermore, the organic lithium-ion cell comprises components which melt in the event of an unintentional increase in temperature and can thereby flood the organic lithium-ion cell with molten plastic. A further uncontrolled increase in temperature is thus prevented. However, these measures lead to in-
15 creased production costs in the manufacture of the organic lithium-ion cell and to an increased volume and weight. Furthermore, these measures reduce the energy density of the organic lithium-ion cell.

A further disadvantage of organic lithium-ion cells is that any hydrolysis products produced in the presence of 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 often used in organic cells, produces very reactive, aggressive hydrogen fluoride (HF) through reaction with traces of water. Because of this, when manufacturing such rechargeable battery cells having an organic electrolyte, attention must be paid to minimizing the residual water content comprised in the electrolyte and the cell components. Production therefore often takes place in costly drying rooms under extremely low humidity. 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,
20 25 30 by a very high degree of operational reliability and a very long service life, including a particularly high number of usable charge and discharge cycles.

In order to increase the stability of organic lithium-ion cells, other active materials besides LiCoO_2 were used for the positive electrode in the prior art. For example, polyanionic compounds such as lithium metal phosphates have been used as the active material for the
35 positive electrode in organic lithium-ion cells. The term "polyanionic compounds" refers to

a class of materials in which polyanionic structural units and metal oxide (MO_x) polyhedra are bonded to one another by strong covalent bonds. Early experimental studies are reported in

- 5 Padhi et al. "Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries", J. Electrochem. Soc., 1997, 1188-1194
(hereinafter referred to as [V1])

- 10 In [V1], active materials for the positive electrode in organic lithium-ion cells that comprise the polyanion $(\text{PO}_4)^{3-}$ were investigated. The investigation relates to compounds having this polyanion $(\text{PO}_4)^{3-}$ and the metals Mn, Fe, Co and Ni, which exist in two different chemical structures, namely the olivine structure and the NASICON structure. The influence of these structures on the storage of the active metal lithium is described and experiments
15 with organic lithium-ion cells with which a small number of charge cycles (maximum 25 cycles) were performed are reported.

- Attention is also drawn to problems associated with the use of lithium iron phosphate (LEP) electrodes in organic lithium-ion cells. Even for a very small area-specific current load of 0.05 mA/cm^2 , a cell voltage of only 3.5 V is specified. In comparison, the cell voltage using a LiCoO_2 electrode is 4 V, that is, about 14% higher. In addition, the electronic
20 conductivity of the LEP is very poor. This leads to a sharp decrease in the cell voltage even with relatively low current loads. The capacity of the organic lithium-ion cells is also heavily dependent on the current load and drops to values that make these organic lithium-ion cells largely unusable, even at an area-specific current load of less than 0.2
25 mA/cm^2 .

- A further development known from prior art therefore provides for the use of an electrolyte based on sulfur dioxide (SO_2) instead of an organic electrolyte for rechargeable battery cells. Rechargeable battery cells, which comprise an SO_2 -based electrolyte, exhibit,
30 among other things, high ionic conductivity. The term " SO_2 -based electrolyte" in the sense of the present invention refers to an electrolyte which comprises SO_2 not merely as an additive at low concentrations, but in which the mobility of the ions in the conducting salt, which is comprised in the electrolyte and which causes the charge transport, is at least in part, largely or even completely ensured by SO_2 . The SO_2 thus serves as a solvent for the
35 conducting salt. The conducting salt can form a liquid solvate complex with the gaseous SO_2 , whereby the SO_2 is bound and the vapor pressure is noticeably reduced compared

to the pure SO₂. Electrolytes having low vapor pressure are produced. Compared to the organic electrolytes described above, these SO₂-based electrolytes have the advantage of being non-combustible. Safety risks, which might occur due to the electrolyte's flammability, can thus be excluded.

5 For example, EP 1 201 004 B1 (hereinafter referred to as [V2]) discloses an SO₂-based electrolyte having the composition LiAlCl₄ * SO₂ in combination with a positive electrode made of LiCoO₂. [V2] suggests the use of an additional salt to avoid disruptive decomposition reactions, such as the undesired formation of chlorine (Cl₂) from lithium tetrachloro-
aluminum (LiAlCl₄), when the rechargeable battery cell is overcharged from an upper po-
10 tential of 4.1 to 4.2 volts.

EP 2534719 B1 (hereinafter referred to as [V3]) also discloses an SO₂-based electrolyte having, among other things, LiAlCl₄ as the conducting salt. For example, said LiAlCl₄ forms complexes of the formula LiAlCl₄ * 1.5 mol SO₂ or LiAlCl₄ * 6 mol SO₂ with the SO₂. Lithium iron phosphate (LiFePO₄) is used as the positive electrode in [V3]. LiFePO₄ has a
15 lower end-of-charge voltage (3.7 V) compared to LiCoO₂ (4.2 V). The problem of undesired overcharging reactions does not arise in this rechargeable battery cell, since upper potentials of 4.1 volts, which are harmful to the electrolyte, are not reached. A disadvantage that also occurs, among other things, with these SO₂-based electrolytes is that any hydrolysis products formed in the presence of residual amounts of water react with
20 the cell components of the rechargeable battery cell and thus lead to the formation of undesired by-products. Because of this, in the manufacture of such rechargeable battery cells having an SO₂-based electrolyte, attention should be paid to minimizing the residual water content contained in the electrolyte and the cell components.

A further problem with the SO₂-based electrolytes is that many conducting salts, in particular also known for organic lithium-ion cells, are not soluble in SO₂. Measurements
25 showed that SO₂ is a poor solvent for many conducting salts, such as lithium fluoride (LiF), lithium bromide (LiBr), lithium sulfate (Li₂SO₄), lithium bis(oxalato)borate (LiBOB), lithium hexafluoroarsenate (LiAsF₆), lithium tetrafluoroborate (LiBF₄), triliithium hexafluoroaluminum (Li₃AlF₆), lithium hexafluoroantimonate (LiSbF₆), lithium difluoro(oxalato)borate
30 (LiBF₂C₂O₄), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium metaborate (LiBO₂), lithium aluminate (LiAlO₂), lithium triflate (LiCF₃SO₃) and lithium chlorosulfonate (LiSO₃Cl). The solubility of these conducting salts in SO₂ is approx. 10⁻² - 10⁻⁴ mol/L (see Table 1). With these low salt concentrations, it can be assumed that there are at most only low conductivities, which are not sufficient for the useful operation of a rechargeable bat-
35 tery cell.

Table 1: Solubility of various conducting salts in SO₂

Conducting salt	Solubility / mol/L in SO ₂	Conducting 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 ₂ SO ₄	$2.7 \cdot 10^{-4}$	LiBF ₂ (C ₂ O ₄)	$1.4 \cdot 10^{-4}$
LiB(C ₂ O ₄) ₂	$3.2 \cdot 10^{-4}$	CF ₃ SO ₂ NLiSO ₂ CF ₃	$1.5 \cdot 10^{-2}$
Li ₃ PO ₄	-	LiBO ₂	$2.6 \cdot 10^{-4}$
Li ₃ AlF ₆	$2.3 \cdot 10^{-3}$	LiAlO ₂	$4.3 \cdot 10^{-4}$
LiBF ₄	$1.7 \cdot 10^{-3}$	LiCF ₃ SO ₃	$6.3 \cdot 10^{-4}$
LiAsF ₆	$1.4 \cdot 10^{-3}$		

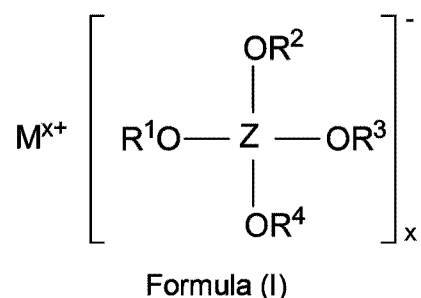
In order to further improve the possible uses and properties of rechargeable battery cells that comprise an SO₂-based electrolyte, the object of the present invention is to specify a rechargeable battery cell having an SO₂-based electrolyte, which, compared to the re-

- has a wide electrochemical window, so that no oxidative electrolyte decomposition occurs at the positive electrode;
- has a stable coating layer on the negative electrode, whereby the coating layer capacity should be low and no further reductive electrolyte decomposition should occur on the negative electrode during further operation;
- comprises an SO₂-based electrolyte which exhibits good solubility for conducting salts and is therefore a good ion conductor and electronic insulator, so that ion transport can be facilitated and self-discharge can be reduced to a minimum;
- comprises an SO₂-based electrolyte that is also inert to other components of the rechargeable battery cell, such as separators, electrode materials and cell packaging materials;
- is resistant against various misuses such as electrical, mechanical or thermal;
- comprises an SO₂-based electrolyte, which exhibits an increased stability against residual amounts of water in the cell components of rechargeable battery cells;
- exhibits improved electrical performance data, in particular high energy density;
- exhibits improved overcharging and deep discharging capabilities and less self-discharge and

- shows an increased service life, in particular a high number of usable charge and discharge cycles.

Such rechargeable battery cells should, in particular, also have very good electrical energy and performance data, high operational reliability and service life, in particular a large number of usable charge and discharge cycles, without the electrolyte decomposing during operation of the rechargeable battery cell.

A rechargeable battery cell according to the invention comprises an active metal, at least one positive electrode, at least one negative electrode, a housing and an electrolyte. The positive electrode comprises at least one polyanionic compound as an active material. The electrolyte is based on SO₂ and comprises at least one first conducting salt. Said first conducting salt has the formula (I).



In formula (I), M is a metal selected from the group formed by 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 R¹, R², R³ and R⁴ are selected independently of one another from the group formed by C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, C₂-C₁₀ alkynyl, C₃-C₁₀ cycloalkyl, C₆-C₁₄ aryl and C₅-C₁₄ heteroaryl. The central atom Z is either aluminum or boron.

The active material in the form of at least one polyanionic compound can store ions of the active metal and release and take up the ions of the active metal during operation of the battery cell. As already mentioned above, the term "polyanionic compound" in the sense

of the present invention refers to a class of materials in which polyanionic structural units and metal oxide (MO_x) polyhedra are bonded to one another by strong covalent bonds. The polyanionic compound acts as a host matrix, which has vacancies that are interconnected. The ions of the active metal can diffuse into these vacancies during the discharge process of the rechargeable battery cell and can be stored there. During the deposition of the ions of the active metal, only minor or no structural changes occur in the host matrix. The ions of the active metal diffuse out of the host matrix again during the charging process.

The SO_2 -based electrolyte used in the rechargeable battery cell according to the invention comprises SO_2 not only as an additive in low concentration, but in concentrations at which the mobility of the ions of the first conducting salt, which is comprised in the electrolyte and causes the charge transport, is at least partially, largely or even completely ensured by the SO_2 . The first conducting salt is dissolved in the electrolyte and shows very good solubility therein. 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 is noticeably reduced compared to the pure SO_2 , producing electrolytes that have a 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 in vapor pressure can occur in the production of the electrolyte according to the invention. In the last-mentioned case, it is preferred for the production of the electrolyte according to the invention to be carried out at low temperature or under pressure. The electrolyte may also comprise a plurality of conducting salts of the formula (I), which differ from one another in their chemical structure.

In the sense of the present invention, the term "C₁-C₁₀ alkyl" includes linear or branched saturated hydrocarbon groups having one to ten carbon atoms. These include, in particular, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, isopentyl, 2,2-dimethylpropyl, n-hexyl, iso-hexyl, 2-ethylhexyl, n-heptyl, iso-heptyl, n-octyl, iso-octyl, n-nonyl, n-decyl and the like.

In the sense of the present invention, the term "C₂-C₁₀ alkenyl" includes unsaturated linear or branched hydrocarbon groups having two to ten carbon atoms, wherein 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, isobutenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl, 1-nonenyl, 1-decenyl and the like.

In the sense of the present invention, the term "C₂-C₁₀ alkynyl" includes unsaturated linear or branched hydrocarbon groups having two to ten carbon atoms, wherein the hydrocarbon groups have at least one C-C triple bond. This includes, in particular, ethynyl, 1-propynyl, 2-propynyl, 1-n-butynyl, 2-n-butynyl, isobutynyl, 1-pentynyl, 1-hexynyl, 1-heptyn-
 5 tyl, 1-octynyl, 1-nonyl, 1-decynyl, and the like.

In the sense of the present invention, the term "C₃-C₁₀ cycloalkyl" includes cyclic, saturated hydrocarbon groups having three to ten carbon atoms. These include, in particular, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclohexyl, cyclononyl and cyclodecanyl.

10 In the sense of the present invention, the term "C₆-C₁₄ aryl" includes aromatic hydrocarbon groups having six to fourteen ring carbon atoms. This includes, in particular, phenyl (C₆H₅ group), naphthyl (C₁₀H₇ group) and anthracyl (C₁₄H₉ group).

In the sense of the present invention, the term "C₅-C₁₄ heteroaryl" includes aromatic hydrocarbon groups having five to fourteen ring hydrocarbon atoms in which at least one hydrocarbon atom is replaced by a nitrogen, oxygen or sulfur atom. These include, in particular, pyrrolyl, furanyl, thiophenyl, pyridinyl, pyranal, thiopyranal and the like. All of the hydrocarbon groups mentioned above are each bonded to the central atom according to formula (I) via the oxygen atom.

20 A rechargeable battery cell having such an electrolyte has the advantage over rechargeable battery cells having electrolytes known from the prior art in that the first conducting salt comprised therein has higher oxidation stability and consequently shows essentially no decomposition at higher cell voltages. Said electrolyte is resistant to oxidation, preferably at least up to an upper potential of 4.0 volts, more preferably at least up to an upper potential of 4.2 volts, more preferably at least up to an upper potential of 4.4 volts, more preferably at least up to an upper potential of 4.6 volts, more preferably at least up to an upper potential of 4.8 volts and most preferably at least up to an upper potential of 5.0 volts.

Thus, when using such an electrolyte in a rechargeable battery cell, there is little or no electrolyte decomposition within the working potentials, that is, in the range between the end-of-charge voltage and the end-of-discharge voltage of both electrodes of the rechargeable battery cell. As a result, rechargeable battery cells according to the invention can have an end-of-charge voltage of at least 4.0 volts, more preferably of at least 4.4 volts, more preferably of at least 4.8 volts, more preferably of at least 5.2 volts, more preferably of at least 5.6 volts and most preferably of at least 6.0 volts. The service life of the rechargeable battery cell comprising this electrolyte is significantly longer than that of rechargeable battery cells comprising electrolytes known from the prior art.

Furthermore, a rechargeable battery cell having such an electrolyte is also resistant to low temperatures. At a temperature of -40°C , for example, 61% of the charged capacity can still be discharged. The conductivity of the electrolyte at low temperatures is sufficient to operate a battery cell.

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Furthermore, a rechargeable battery cell having such an electrolyte exhibits increased stability with respect to residual amounts of water. If there are still small residual amounts of water in the electrolyte (in the range of ppm), the electrolyte or the first conducting salt forms hydrolysis products with the water, which products, compared to the SO_2 -based electrolytes known from the prior art, are significantly less aggressive towards the cell components. Because of this, the absence of water in the electrolyte plays a less important role in SO_2 -based electrolytes in comparison to those known from the prior art. These advantages of the electrolyte according to the invention outweigh the disadvantage that arises from the fact that the first conducting salt according to formula (I) has a significantly larger anion size than the conducting salts known from the prior art. This higher anion size leads to a lower conductivity of the first conducting salt according to formula (I) compared to the conductivity of LiAlCl_4 .

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Positive electrode

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Advantageous developments of the rechargeable battery cell according to the invention with regard to the positive electrode are described below:

As mentioned above, the positive electrode comprises at least one polyanionic compound as the active material. In a first advantageous development of the rechargeable battery cell according to the invention, the compound has the composition $\text{A}_x\text{M}_y(\text{X}_{r1}\text{O}_{s1})_a\text{F}_b$. In this composition $\text{A}_x\text{M}_y(\text{X}_{r1}\text{O}_{s1})_a\text{F}_b$,

25

- A is at least one metal selected from the group formed by the alkali metals, the alkaline earth metals, the metals of group 12 of the periodic table or aluminum,
- M is at least one metal selected from the group formed by the elements of groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 and 16 of the periodic table of the elements, and
- $(\text{X}_{r1}\text{O}_{s1})^{n-}$ is at least one first polyanion structural unit in which X is at least one element selected from the group formed by the elements phosphorus (P), silicon (Si),

30

sulfur (S), boron (B), carbon (C), arsenic (As), molybdenum (Mo), tungsten (W) and vanadium (V), and O is the element oxygen (O),

- F is the element fluorine (F),
- n is a number greater than 0,
- 5 – x and y independently of one another are numbers greater than 0,
- r1 and s1 independently of one another are numbers greater than 0,
- a is a number greater than 0 and
- b is a number greater than or equal to 0.

- 10 A is preferably the metal lithium, that is, the compound can have the composition $\text{Li}_x\text{M}_y(\text{X}_{r1}\text{O}_{s1})_a\text{F}_b$.

The polyanionic compound preferably has the composition $\text{A}_x\text{M}_y(\text{X}_{r1}\text{O}_{s1})_a\text{F}_b$, wherein x, y, a, r1, s1 and n are, independently of one another, numbers greater than 0 and b is a number greater than or equal to 0.

15 The index y refers to the entirety of the metals represented by M. If, for example, M' comprises two metals $\text{M}^{1'}$ and $\text{M}^{2'}$, the following applies to the index y: $y=y_1+y_2$, wherein y_1 and y_2 represent the indices of the metals $\text{M}^{1'}$ and $\text{M}^{2'}$. The indices x and y, r1 and s1, a and b must be chosen so that there is charge neutrality within the composition.

- 20 Examples of compounds in which M comprises two metals are lithium manganese iron phosphates of the composition $\text{Li}_x\text{Mn}_{y1}\text{Fe}_{y2}\text{PO}_4$ with $\text{M}^1=\text{Mn}$ and $\text{M}^2=\text{Fe}$.

In a further advantageous development of the battery cell according to the invention, the metal M is selected from the group formed by the elements titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc.

25 Furthermore, the metal A can also be selected from the group formed by lithium, sodium, calcium or zinc. The metal A is preferably lithium or sodium.

- 30 The first polyanion structural unit can be, for example, structures of the compositions $(\text{XO}_4)^{n-}$, $(\text{X}_m\text{O}_{3m+1})^{n-}$ or $(\text{XO}_3)^{n-}$, in which m and n, independently of one another, are numbers greater than 0. Examples of such anions are $(\text{SO}_4)^{2-}$, $(\text{PO}_4)^{3-}$, $(\text{SiO}_4)^{2-}$, $(\text{AsO}_4)^{3-}$, $(\text{MoO}_4)^{2-}$, $(\text{WO}_4)^{2-}$, $(\text{P}_2\text{O}_7)^{4-}$, $(\text{CO}_3)^{2-}$ and $(\text{BO}_3)^{3-}$.

Polyanionic compounds having the $(\text{PO}_4)^{3-}$ polyanion structural unit preferably have the composition $\text{A}_x\text{M}_y(\text{PO}_4)_a\text{F}_b$. The compositions LiFePO_4 , NaFePO_4 , LiMnPO_4 , LiCoPO_4 , LiNiPO_4 , LiVPO_4F , $\text{Li}(\text{Mn}_{0.7}\text{Fe}_{0.3})\text{PO}_4$ and $\text{Li}(\text{Mn}_{0.6}\text{Fe}_{0.4})\text{PO}_4$ are further preferred.

5 Polyanionic compounds having the $(\text{SiO}_4)^{4-}$ polyanion structural unit preferably have the composition $\text{A}_x\text{M}_y(\text{SiO}_4)_a\text{F}_b$. The compositions $\text{Li}_2\text{FeSiO}_4$, $\text{Li}_2\text{MnSiO}_4$, $\text{Li}_2\text{CoSiO}_4$, $\text{Li}_2\text{Mn}_{0.2}\text{Fe}_{0.8}\text{SiO}_4$ and $\text{Li}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{SiO}_4$ are further preferred.

Polyanionic compounds having the $(\text{SO}_4)^{4-}$ polyanion structural unit preferably have the composition $\text{A}_x\text{M}_y(\text{SO}_4)_a\text{F}_b$. The compositions LiFeSO_4F , LiCoSO_4F , LiNiSO_4F and LiMnSO_4F are further preferred.

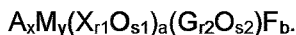
10 Polyanionic compounds having the $(\text{BO}_3)^{3-}$ polyanion structural unit preferably have the composition $\text{A}_x\text{M}_y(\text{BO}_3)_a\text{F}_b$. The compositions LiFeBO_3 , LiCoBO_3 and LiMnBO_3 are further preferred.

The polyanionic compounds can also have at least two different polyanion structural units
15 $(\text{X}_{r1}\text{O}_{s1})^{n-}$ and $(\text{G}_{r2}\text{O}_{s2})^{k-}$, wherein n, k, r1, r2, s1 and s2 are, independently of one another, numbers greater than 0. In this case, the polyanionic compound preferably has the composition $\text{A}_x\text{M}_y(\text{X}_{r1}\text{O}_{s1})^{n-}_a(\text{G}_{r2}\text{O}_{s2})^{k-}_b\text{F}_b$, wherein

- $(\text{X}_{r1}\text{O}_{s1})^{n-}$ is at least one first polyanion structural unit in which X is at least one element selected from the group formed by the elements phosphorus (P), silicon (Si), sulfur (S), boron (B), carbon (C), arsenic (As), molybdenum (Mo), tungsten (W) and vanadium (V), and O is the element oxygen (O),
- 20 – $(\text{G}_{r2}\text{O}_{s2})^{k-}$ is at least one first polyanion structural unit in which X is at least one element selected from the group formed by the elements phosphorus (P), silicon (Si), sulfur (S), boron (B), carbon (C), arsenic (As), molybdenum (Mo), tungsten (W) and vanadium (V), and O is the element oxygen (O),
- 25 – A is at least one metal selected from the group formed by the alkali metals, the alkaline earth metals, the metals of group 12 of the periodic table or aluminum,
- M is at least one metal selected from the group formed by the elements of groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 and 16 of the periodic table of the elements,
- 30 – F is the element fluorine (F),
- x and y independently of one another are numbers greater than 0;
- a is a number greater than 0 and
- b is a number greater than or equal to 0.

35

The indices x and y, r₁, s₁, r₂, s₂, a and b must be chosen such that there is charge neutrality within the composition



The second polyanion structural unit can also be structures of the compositions (XO₄)^{k-}, (X_mO_{3m+1})^{k-} or (XO₃)^{k-}, wherein m and k are, independently of one another, numbers greater than 0. Examples of such polyanion structural units are (SO₄)²⁻, (PO₄)³⁻, (SiO₄)²⁻, (AsO₄)³⁻, (MoO₄)²⁻, (WO₄)²⁻, (P₂O₇)⁴⁻, (CO₃)²⁻ and (BO₃)³⁻.

The polyanionic compound having at least two different polyanion structural units can in particular have the composition A_xM_y(XO₃)(XO₄). In particular, the XO₃ structural unit is (CO₃)²⁻ or (BO₃)³⁻ and the XO₄ structural unit is (SO₄)²⁻, (PO₄)³⁻ or (SiO₄)²⁻. Examples of polyanionic compounds having two different polyanion structural units are Li₃Fe_{0.2}Mn_{0.8}CO₃PO₄ and Na₃Fe_{0.2}Mn_{0.8}CO₃PO₄.

It is within the scope of the invention for the positive electrode to comprise at least one of the polyanionic compounds described above or a combination of the polyanionic compounds as the active material. A combination of the polyanionic compounds refers to a positive electrode which comprises at least two of the polyanionic compounds described as the active material.

It is also within the scope of the invention for the positive electrode to also comprise, as an active material, a combination of at least one of the polyanionic compounds described above and at least one further compound which is not a polyanionic compound. The combination can also comprise a plurality of the polyanionic compounds described above and/or a plurality of further compounds that are not polyanionic compounds. Said further compound can, for example, be a layered oxide, such as lithium nickel manganese cobalt oxide.

A further advantageous development of the battery cell according to the invention provides that the positive electrode has a discharge element. This means that the positive electrode also comprises a discharge element in addition to the active material. Said discharge element serves to enable the required electronically conductive connection of the active material of the positive electrode. For this purpose, the discharge element is in contact with the active material involved in the electrode reaction of the positive electrode.

Said discharge element can be designed in a planar manner 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 planar discharge element can also consist of a plastic film coated with metal.

Said metal coatings have a thickness in the range from 0.1 μm to 20 μm . The active material of the positive electrode is preferably applied to the surface of the thin metal sheet, the thin metal foil or the metal-coated plastic foil. The active material can be applied to the front and/or the rear side of the planar discharge element. Such planar discharge elements have a thickness in the range from 5 μm to 50 μm . A thickness of the planar discharge element in the range from 10 μm to 30 μm is preferred. When using planar discharge elements, the positive electrode can have a total thickness of at least 20 μm , preferably at least 40 μm and particularly preferably at least 60 μm . The maximum thickness is at most 200 μm , preferably at most 150 μm and particularly preferably at most 100 μm .

The area-specific capacity of the positive electrode based on the coating on one side is preferably at least 0.5 mAh/cm^2 when using a planar discharge element, wherein 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 , 15 mAh/cm^2 , 20 mAh/cm^2 .

Furthermore, there is also the possibility for the discharge element of the positive electrode to be designed three-dimensionally in the form of a porous metal structure, in particular in the form of a metal foam. The three-dimensional porous metal structure is sufficiently porous such 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 on the positive electrode. When the discharge element is designed three-dimensionally in the form of a porous metal structure, in particular in the form of a metal foam, then the positive electrode preferably has a thickness of at least 0.2 mm, more preferably at least 0.3 mm, more preferably at least 0.4 mm, more preferably at least 0.5 mm and most preferably at least 0.6 mm. A further advantageous embodiment provides that the area-specific capacity of the positive electrode when using a three-dimensional discharge element, in particular in the form of a metal foam, is preferably at least 2.5 mAh/cm^2 , wherein the following values are further preferred in this order: 5 mAh/cm^2 , 15 mAh/cm^2 , 25 mAh/cm^2 , 35 mAh/cm^2 , 45 mAh/cm^2 , 55 mAh/cm^2 , 65 mAh/cm^2 , 75 mAh/cm^2 . When the discharge element is designed three-dimensionally in the form of a porous metal structure, in particular in the form of a metal foam, the amount of active material of the positive electrode, that is, the loading of the electrode, based on its area, 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 process and the discharging process of the rechargeable battery cell.

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

Electrolyte

Advantageous developments of the rechargeable battery cell with regard to the SO₂-based electrolyte are described below.

In a further advantageous embodiment of the rechargeable battery cells, the substituents R¹, R², R³ and R⁴ of the first conducting salt are selected independently of one another from the group formed by

- C₁-C₆ alkyl; preferably from C₂-C₄ alkyl; particularly preferably from the alkyl groups 2-propyl, methyl and ethyl;
- C₂-C₆ alkenyl; preferably from C₂-C₄ alkenyl; particularly preferably from the alkenyl groups ethenyl and propenyl;
- C₂-C₆ alkynyl; preferably from C₂-C₄ alkynyl;
- C₃-C₆ cycloalkyl;
- phenyl; and
- C₅-C₇ heteroaryl.

In the case of this advantageous embodiment of the SO₂-based electrolyte, the term "C₁-C₆ alkyl" includes linear or branched saturated hydrocarbon groups having 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 and iso-hexyl. C₂-C₄ alkyls are preferred among these. The C₂-C₄ alkyls 2-propyl, methyl and ethyl are particularly preferred.

In the case of this advantageous embodiment of the SO₂-based electrolyte, the term “C₂-C₆ alkenyl” includes unsaturated linear or branched hydrocarbon groups having two to six carbon atoms, wherein 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, isobutenyl, 1-pentenyl and 1-hexenyl, wherein C₂-C₄ alkenyls are preferred. Ethenyl and 1-propenyl are particularly preferred.

In the case of this advantageous embodiment of the SO₂-based electrolyte, the term “C₂-C₆ alkynyl” includes unsaturated linear or branched hydrocarbon groups having two to six carbon atoms, wherein the hydrocarbon groups have at least one C-C triple bond. These include in particular ethynyl, 1-propynyl, 2-propynyl, 1-n-butynyl, 2-n-butynyl, iso-butynyl, 1-pentynyl and 1-hexynyl. Preferred among these are C₂-C₄ alkynyls.

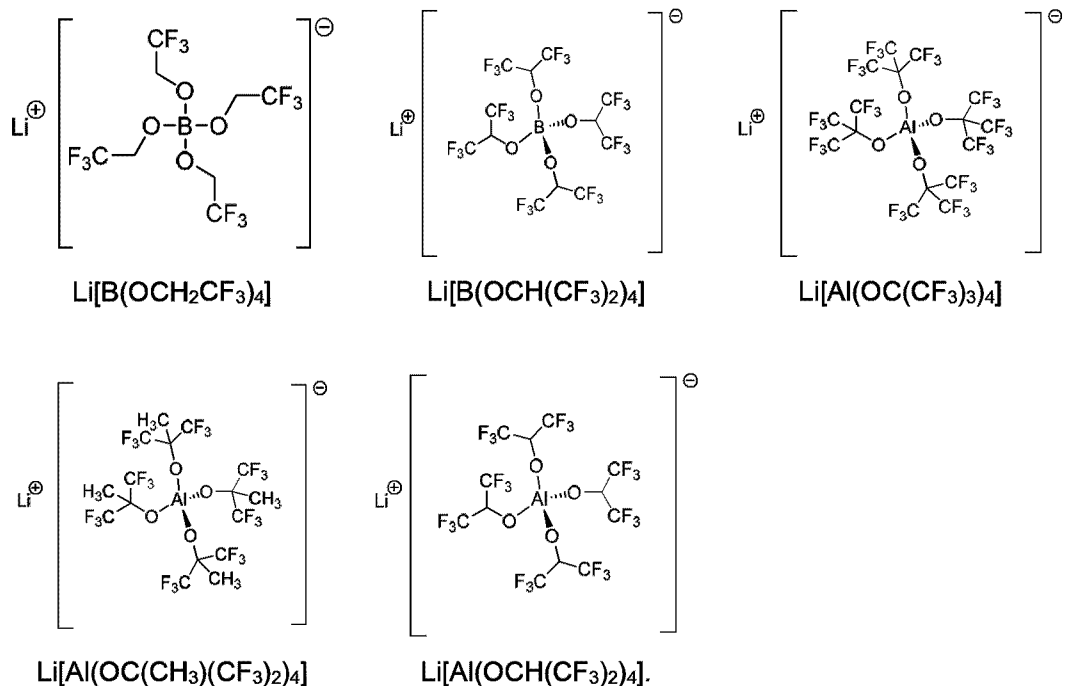
In the case of this advantageous embodiment of the SO₂-based electrolyte, the term “C₃-C₆ cycloalkyl” includes cyclic saturated hydrocarbon groups having three to six carbon atoms. These include in particular cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

In the case of this advantageous embodiment of the SO₂-based electrolyte, the term “C₅-C₇ heteroaryl” includes phenyl and naphthyl.

To improve the solubility of the first conducting salt in the SO₂-based electrolytes, the substituents R¹, R², R³ and R⁴ are substituted, in a further advantageous embodiment of the rechargeable battery cell, by at least one fluorine atom and/or by at least one chemical group, wherein the chemical group is selected from the group formed by C₁-C₄ alkyl, C₂-C₄ alkenyl, C₂-C₄ alkynyl, phenyl and benzyl. The chemical groups C₁-C₄ alkyl, C₂-C₄ alkenyl, C₂-C₄ 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 groups of atoms of the substituents R¹, R², R³ and R⁴ have been replaced by the fluorine atom and/or by the chemical group.

A particularly high solubility of the first conducting salt in the SO₂-based electrolytes can be achieved by at least one of the substituents R¹, R², R³ and R⁴ being a CF₃ group or an OSO₂CF₃ group.

In a further advantageous development of the rechargeable battery cell, the first conducting salt is selected from the group formed by



In order to adjust the conductivity and/or other properties of the electrolyte to a desired value, the electrolyte in a further advantageous embodiment of the rechargeable battery cell according to the invention has at least one second conducting salt different from the first conducting salt according to formula (I). This means that, in addition to the first conducting salt, the electrolyte can comprise a or even further second conducting salts which differ from the first conducting salt in their chemical composition and their chemical structure.

In a further advantageous embodiment of the rechargeable battery cell according to the invention, the second conducting salt is an alkali metal compound, in particular a lithium compound. The alkali metal compound or the lithium compound are selected from the group formed by an aluminate, a halide, an oxalate, a borate, a phosphate, an arsenate and a gallate. The second conducting salt is preferably a lithium tetrahaloaluminate, in particular LiAlCl_4 .

Furthermore, in a further advantageous embodiment of the rechargeable battery cell according to the invention, the electrolyte comprises at least one additive. This additive is preferably selected from the group formed by vinylene carbonate and its derivatives, vinylenethylene carbonate and its derivatives, methyleneethylene carbonate and its derivatives,

lithium (bisoxalato)borate, lithium difluoro(oxalato)borate, lithium tetrafluoro(oxalato)phosphate, lithium oxalate, 2-vinylpyridine, 4-vinylpyridine, cyclic exomethylene carbonates, sultones, cyclic and acyclic sulfonates, acyclic sulfites, cyclic and acyclic sulfinates, organic esters of inorganic acids, acyclic and cyclic alkanes, 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 relation to the total weight of the electrolyte composition, the electrolyte has the following composition in a further advantageous development of the rechargeable battery cell:

- (i) 5 to 99.4% by weight sulfur 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 already mentioned above, the electrolyte can comprise not only a first conducting salt according to formula (I) and a second conducting salt, but also a plurality of first conducting salts according to formula (I) and a plurality of second conducting salts. In the last-mentioned case, the aforementioned percentages also include a plurality of first conducting salts and a plurality of second conducting salts. The molar concentration of the first conducting salt lies in the range from 0.01 mol/L to 10 mol/L, preferably from 0.05 mol/L to 10 mol/L, more preferably from 0.1 mol/L to 6 mol/L and most preferably from 0.2 mol/L to 3.5 mol/L, based on the total volume of the electrolyte.

A further advantageous development of the rechargeable battery cell according to the invention provides that the electrolyte comprises at least 0.1 mol SO₂, preferably at least 1 mol SO₂, more preferably at least 5 mol SO₂, more preferably at least 10 mol SO₂ and most preferably at least 20 mol SO₂ per mole of conducting salt. The electrolyte can also comprise very high molar proportions of SO₂, wherein the preferred upper limit value is 2600 mol SO₂ per mole of conducting salt and upper limits of 1500, 1000, 500 and 100 mol of SO₂ per mole of conducting salt are further preferred in this order. The term "per mole of conducting salt" refers to all conducting salts that are comprised in the electrolyte.

Electrolytes based on SO₂ having such a concentration ratio between SO₂ and the conducting salt have the advantage in that they can dissolve a larger amount of conducting salt compared to the electrolytes known from the prior art, which are based, for example, on an organic solvent blend. In the context of the invention, it was found that, surprisingly,
 5 an electrolyte having a relatively low concentration of conducting salt is advantageous despite the associated higher vapor pressure, in particular with regard to its stability over many charge and discharge cycles of the rechargeable battery cell. The concentration of SO₂ in the electrolyte affects its conductivity. Thus, by choosing the SO₂ concentration, the conductivity of the electrolyte can be adjusted to the planned use of a rechargeable
 10 battery cell operated using this electrolyte.

The total content of SO₂ and the first conducting salt can be greater than 50 percent by weight (% by weight) of the weight of the electrolyte, preferably greater than 60% by weight, more preferably greater than 70% by weight, more preferably greater than 80% by
 15 weight, more preferably greater than 85% by weight, more preferably greater than 90% by weight, more preferably greater than 95% by weight or most preferably greater than 99% by weight.

The electrolyte can comprise at least 5% by weight SO₂ based on the total amount of the electrolyte comprised in the rechargeable battery cell, wherein values of 20% by weight
 20 SO₂, 40% by weight SO₂ and 60% by weight SO₂ are more preferred. The electrolyte can also comprise up to 95% by weight SO₂, wherein maximum values of 80% by weight SO₂ and 90% by weight SO₂ are preferred in this order.

It is within the scope of the invention for the electrolyte to preferably have only a small percentage or even no percentage of at least one organic solvent. The proportion of organic solvents in the electrolyte, which is present, for example, in the form of one solvent or a blend of a plurality of solvents, can preferably be at most 50% by weight of the weight of the electrolyte. Lower proportions of at most 40% by weight, at most 30% by weight, at
 25 most 20% by weight, at most 15% by weight, at most 10% by weight, at most 5% by weight or at most 1% by weight of the electrolyte weight are particularly preferred. More preferably, 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 at all combustible. This increases the operational safety of a rechargeable battery cell operated using such an SO₂-based electrolyte. The SO₂-based electrolyte is particularly
 30 preferably essentially free of organic solvents.

In relation to the total weight of the electrolyte composition, the electrolyte has the following composition in a further advantageous development of the rechargeable battery cell:

- (i) 5 to 99.4% by weight sulfur dioxide,
- 5 (ii) 0.6 to 95% by weight of the first conducting salt,
- (iii) 0 to 25% by weight of the second conducting salt,
- (iv) 0 to 10% by weight of the additive and
- (v) 0 to 50% by weight of an organic solvent.

10 Active metal

Advantageous developments of the rechargeable battery cell according to the invention with regard to the active metal are described below:

- 15 In a first advantageous development of the rechargeable battery cell, the active metal is
- an alkali metal, in particular lithium or sodium;
 - an alkaline earth metal, in particular calcium;
 - a metal from group 12 of the periodic table, in particular zinc; or
 - aluminum.

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Negative electrode

Advantageous developments of the rechargeable battery cell according to the invention with regard to the negative electrode are described below:

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A further advantageous development of the battery cell according to the invention provides that the negative electrode is an insertion element. Said insertion electrode comprises an insertion material as the active material, in which the ions of the active metal can be stored during the charging of the rechargeable battery cell and from which the ions of

30 the active metal can be removed during the discharging of the rechargeable battery cell. This means that the electrode processes can take place not only on the surface of the electrode, but also in the interior of the negative electrode. If, for example, a conducting salt based on lithium is used, then lithium ions can be stored in the insertion material while the rechargeable battery cell is being charged and can be removed therefrom while the

rechargeable battery cell is being discharged. The negative electrode preferably comprises carbon as an active material or insertion material, in particular carbon as the allotrope graphite. However, it is also within the scope of the invention for the carbon to be present in the form of natural graphite (flake conveyor or rounded), synthetic graphite
 5 (mesophase graphite), graphitized mesocarbon microbeads (MCMB), with carbon-coated graphite or amorphous carbon.

In a further advantageous development of the rechargeable battery cell according to the invention, the negative electrode comprises lithium intercalation anode active materials
 10 that do not comprise carbon, such as lithium titanates (for example, $\text{Li}_4\text{Ti}_5\text{O}_{12}$).

A further advantageous development of the rechargeable battery cell according to the invention provides that the negative electrode comprises anode active materials which form an alloy with lithium. These are, for example, lithium-storing metals and metal alloys (for
 15 example, Si, Ge, Sn, SnCo_xC_y , SnSi_x and the like) and oxides of lithium-storing metals and metal alloys (for example, SnO_x , SiO_x , oxidic glasses of Sn, Si and the like).

In a further advantageous development of the rechargeable battery cell according to the invention, the negative electrode comprises conversion anode active materials. Said conversion anode active materials can be, for example, transition metal oxides in the form of
 20 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.

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

A further advantageous development of the rechargeable battery cell according to the invention provides that the negative electrode is porous, wherein the porosity is preferably
 30 at most 50%, more preferably at most 45%, more preferably at most 40%, more preferably at most 35%, more preferably at most 30%, more preferably at most 20% and most preferably at most 10%. The porosity represents the cavity volume in relation to the total volume of the negative electrode, wherein the cavity volume is formed by so-called pores or
 35 cavities. This porosity leads to an increase in the inner surface area of the negative electrode. Furthermore, the porosity reduces the density of the negative electrode and thus

also its weight. The individual pores of the negative electrode can preferably be completely filled with the electrolyte during operation.

A further advantageous development of the battery cell according to the invention provides that the negative electrode has a discharge element. This means that in addition to the active material or insertion material, the negative electrode also comprises a discharge element. This discharge element serves to enable the required electronically conductive connection of the active material of the negative electrode. For this purpose, the discharge element is in contact with the active material involved in the electrode reaction of the negative electrode. Said discharge element can be designed in a planar manner 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 planar discharge element can also consist of a plastic film coated with metal. Said metal coatings have a thickness in the range from 0.1 μm to 20 μm . The active material of the negative electrode is preferably applied to the surface of the thin metal sheet, the thin metal foil or the metal-coated plastic foil. The active material can be applied to the front and/or the rear side of the planar discharge element. Such planar discharge elements have a thickness in the range from 5 μm to 50 μm . A thickness of the planar discharge element in the range from 10 μm to 30 μm is preferred. When using planar discharge elements, the negative electrode can have a total thickness of at least 20 μm , preferably at least 40 μm and particularly preferably at least 60 μm . The maximum thickness is at most 200 μm , preferably at most 150 μm and particularly preferably at most 100 μm . The area-specific capacity of the negative electrode based on the coating on one side is preferably at least 0.5 mAh/cm² when using a planar discharge element, wherein the following values are further preferred in this order: 1 mAh/cm², 3 mAh/cm², 5 mAh/cm², 10 mAh/cm², 15 mAh/cm², 20 mAh/cm².

Furthermore, there is also the possibility for the discharge element to be designed three-dimensionally in the form of a porous metal structure, in particular in the form of a metal foam. The term "three-dimensional porous metal structure" refers to any structure consisting of metal that not only extends over the length and width of the flat electrode like the thin metal sheet or the metal foil, but also over its thickness dimension. The three-dimensional porous metal structure is sufficiently porous such 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 on the negative electrode. When the discharge element is designed three-dimensionally in the form of a porous metal structure, in particular in the form of a metal foam, then the negative electrode preferably has a

thickness of at least 0.2 mm, more preferably at least 0.3 mm, more preferably at least 0.4 mm, more preferably at least 0.5 mm and most preferably at least 0.6 mm. In this case, the thickness of the electrodes is significantly greater compared to negative electrodes, which is the case with organic lithium-ion cells. A further advantageous embodiment provides that the area-specific capacity of the negative electrode when using a three-dimensional discharge element, in particular in the form of a metal foam, is preferably at least 2.5 mAh/cm², wherein the following values are further preferred in this order: 5 mAh/cm², 15 mAh/cm², 25 mAh/cm², 35 mAh/cm², 45 mAh/cm², 55 mAh/cm², 65 mAh/cm², 75 mAh/cm². When the discharge element is designed three-dimensionally in the form of a porous metal structure, in particular in the form of a metal foam, the amount of active material of the negative electrode, that is, the loading of the electrode, based on its area, is at least 10 mg/cm², preferably at least 20 mg/cm², more preferably at least 40 mg/cm², more preferably at least 60 mg/cm², more preferably at least 80 mg/cm² and most preferably at least 100 mg/cm². This loading of the negative electrode has a positive effect on the charging process and the discharging process of the rechargeable battery cell.

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

In a further advantageous development of the battery cell according to the invention, the negative electrode has at least one conductivity additive. The conductivity additive should preferably exhibit low weight, high chemical resistance and high specific surface area. Examples of conductivity additives are particulate carbon (carbon black, Super P, acetylene black), fibrous carbon (carbon nanotubes CNT, carbon (nano)fibers), finely divided graphites and graphene (nanosheets).

Structure of the rechargeable battery cell

Advantageous developments of the rechargeable battery cell according to the invention are described below with regard to their structure:

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In order to further improve the function of the rechargeable battery cell, a further advantageous development of the rechargeable battery cell according to the invention provides that the rechargeable battery cell comprises a plurality of negative electrodes and a plurality of positive electrodes, which are stacked alternately in the housing. Here, the positive
10 electrodes and the negative electrodes are preferably each electrically separated from one another by separators.

The separator can be formed from a non-woven material, a membrane, a woven material, a knitted material, an organic material, an inorganic material or a combination thereof. Organic separators can consist of unsubstituted polyolefins (for example, polypropylene or
15 polyethylene), partially to completely halogen-substituted polyolefins (for example, partially to completely fluorine-substituted, in particular PVDF, ETFE, PTFE), polyesters, polyamides or polysulfones. Separators that comprise a combination of organic and inorganic materials are, for example, glass fiber textile materials in which the glass fibers are provided with a suitable polymer coating. The coating preferably comprises a fluorine-containing polymer such as polytetrafluoroethylene (PTFE), ethylene-tetrafluoroethylene
20 (ETFE), perfluoroethylene propylene (FEP), THV (terpolymer of tetrafluoroethylene, hexafluoroethylene and vinylidene fluoride), a perfluoroalkoxy polymer (PFA), aminosilane, polypropylene or polyethylene (PE). The separator can also be folded in the housing of the rechargeable battery cell, for example, in the form of so-called "Z-folding". In this Z-
25 folding, a strip-shaped separator is folded in a Z-like manner through or around the electrodes. Furthermore, the separator can also be formed as separator paper.

It is also within the scope of the invention for the separator to be able to be designed as a sheath, wherein each positive electrode or each negative electrode is enveloped by the sheath. The sheath can be formed from a non-woven material, a membrane, a woven material, a knitted material, an organic material, an inorganic material or a combination
30 thereof.

A sheath on the positive electrode leads to more uniform ion migration and ion distribution in the rechargeable battery cell. The more even the ion distribution, in particular in the negative electrode, the higher the possible loading of the negative electrode with active
35 material and, as a result, the usable capacity of the rechargeable battery cell. At the same time, risks are avoided that could be associated with uneven loading and the resulting

deposition of the active metal. These advantages are particularly effective when the positive electrodes of the rechargeable battery cell are enveloped in the sheath.

The surface dimensions of the electrodes and the sheath can preferably be matched to one another such that the external dimensions of the sheath of the electrodes and the external dimensions of the unsheathed electrodes match at least in 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 boundary of the electrode. Two layers of the sheath covering the electrode on both sides can therefore be connected to one another at the edge of the positive electrode by an edge connection.

In a further advantageous embodiment of the rechargeable battery cell according to the invention, the negative electrodes have a sheath, while the positive electrodes have no sheath.

Further advantageous properties of the invention are described and explained in more detail below on the basis of figures, examples and experiments.

Figure 1: shows a first embodiment of a rechargeable battery cell according to the invention in a cross-sectional illustration;

Figure 2: shows an electron microscope image of the three-dimensional porous structure of the metal foam of the first embodiment from Figure 1 as a detailed illustration;

Figure 3: shows a second embodiment of a rechargeable battery cell according to the invention in a cross-sectional illustration;

Figure 4: shows a detail of the second embodiment from Figure 3;

Figure 5: shows a third embodiment of the rechargeable battery cell according to the invention in an exploded illustration;

Figure 6: shows a potential profile in volts [V] as a function of the percentage charge of a test full cell having lithium iron phosphate LiFePO_4 (LEP) as the active material of the positive electrode, wherein the end-of-charge voltage is 5 volts;

- Figure 7: shows the discharge capacity as a function of the number of cycles of test full cells which comprise lithium iron phosphate LiFePO_4 (LEP) as the active material of the positive electrode, wherein the upper potential is increased in steps from 4.5 V to 5.0 V;
- 5
- Figure 8: shows the discharge capacity as a function of the number of cycles of a test full cell having lithium iron phosphate LiFePO_4 as the active material of the positive electrode, wherein the end-of-charge voltage is 3.6 volts;
- 10
- Figure 9: shows the discharge capacity as a function of the number of cycles of a test full cell having lithium iron manganese phosphate $\text{Li}(\text{Fe}_{0.3}\text{Mn}_{0.7})\text{PO}_4$ as the active material of the positive electrode, wherein the end-of-charge voltage is 4.5 volts;
- 15
- Figure 10: shows a potential profile in volts [V] as a function of the percentage charge of a test full cell having lithium iron cobalt phosphate LiFeCoPO_4 as the active material of the positive electrode, wherein the end-of-charge voltage is 5 volts;
- 20
- Figure 11: shows the potential in [V] of a reference test full cell and two test full cells when charging a negative electrode as a function of the capacity, which is related to the theoretical capacity of the negative electrode, during formation of a coating layer on the negative electrode.
- 25
- Figure 12: shows the potential profile during discharge in volts [V] as a function of the percentage charge of three test full cells that have lithium iron phosphate LiFePO_4 (LEP) as the active material of the positive electrode and were filled with three electrolytes 1, 3 and 4;
- 30
- Figure 13: shows the conductivity in [mS/cm] of a first electrolyte 1 as a function of the concentration of compound 1;
- Figure 14: shows the conductivity in [mS/cm] of the third electrolyte 3 as a function of the concentration of compound 3;
- 35

Figure 15: shows the conductivity in [mS/cm] of the fourth electrolyte 4 as a function of the concentration of compound 4.

Figure 1 shows a first embodiment of a rechargeable battery cell 2 according to the invention in a cross-sectional illustration. Said rechargeable battery cell 2 is designed as a prismatic cell and has a housing 1, among other things. Said housing 1 encloses an electrode array 3 which comprises three positive electrodes 4 and four negative electrodes 5. The positive electrodes 4 and the negative electrodes 5 are stacked alternately in the electrode array 3. The housing 1 can, however, also accommodate more positive electrodes 4 and/or negative electrodes 5. In general, it is preferred when the number of negative electrodes 5 is one greater than the number of positive electrodes 4. This has the consequence of the outer end faces of the electrode stack being formed by the electrode surfaces of the negative electrodes 5. The electrodes 4, 5 are connected to corresponding contacts 9, 10 of the rechargeable battery cell 2 via electrode connections 6, 7. The rechargeable battery cell 2 is filled with an SO₂-based electrolyte such that the electrolyte penetrates as completely as possible into all pores or cavities, in particular within the electrodes 4, 5. The electrolyte is not visible in Figure 1. In the present embodiment, the positive electrodes 4 comprise an intercalation compound as an active material. This intercalation compound is LiFePO₄.

The electrodes 4, 5 are designed flat in the present embodiment, that is, as layers having a thickness that is smaller in relation to their surface area. They are each separated from one another by separators 11. The housing 1 of the rechargeable battery cell 2 is essentially designed as a rectangular parallelepiped, wherein the electrodes 4, 5 and the walls of the housing 1 shown in a sectional illustration extend perpendicular to the plane of the drawing and are essentially straight and flat. The rechargeable battery cell 2 can, however, also be designed as a winding cell in which the electrodes consist of thin layers that are wound up together with a separator material. The separators 11, on the one hand, separate the positive electrode 4 and the negative electrode 5 spatially and electrically and, on the other hand, are permeable to the ions of the active metal, among other things. In this way, large electrochemically effective surfaces are created, which enable a correspondingly high current yield.

The electrodes 4, 5 also have a discharge element which serves to enable the required electronically conductive connection of the active material of the respective electrode. Said discharge 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 discharge element is designed in the form of a porous metal foam 18. The metal foam 18 extends over the

thickness dimension of the electrodes 4, 5. The active material of the positive electrodes 4 and the negative electrodes 5 is incorporated into the pores of said metal foam 18, such that it fills the pores of the metal foam evenly over the entire thickness of the metal structure. The positive electrodes 4 comprise a binder to improve the mechanical strength. This binder is a fluoropolymer. The negative electrodes 5 comprise carbon as an active material in a form suitable as an insertion material 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 an electron microscope image of the three-dimensional porous structure of the metal foam 18 of the first embodiment from Figure 1. On the basis of the specified scale, it can be seen that the pores P have an average diameter of more than 100 μm , that is, are relatively large. This metal foam is a metal foam made of nickel.

Figure 3 shows a second embodiment of a rechargeable battery cell 20 according to the invention in a cross-sectional illustration. Said second embodiment differs from the first embodiment shown in Figure 1 in that the electrode array comprises a positive electrode 23 and two negative electrodes 22. They are each separated from one another by separators 21 and surrounded by a housing 28. The positive electrode 23 has a discharge element 26 in the form of a planar metal foil, to which the active material 24 of the positive electrode 23 is applied on both sides. The negative electrodes 22 also comprise a discharge element 27 in the form of a planar metal foil, to which the active material 25 of the negative electrode 22 is applied on both sides. Alternatively, the planar discharge elements of the edge electrodes, that is, of the electrodes that close off the electrode stack, can only be coated with active material on one side. The non-coated side faces the wall of the housing 28. The electrodes 22, 23 are connected to corresponding contacts 31, 32 of the rechargeable battery cell 20 via electrode connections 29, 30.

Figure 4 shows the planar metal foil which serves as a discharge element 26, 27 for the positive electrodes 23 and the negative electrodes 22 in the second embodiment from Figure 3. This metal foil has a perforated or mesh-like structure having a thickness of 20 μm .

Figure 5 shows a third embodiment of a rechargeable battery cell 40 according to the invention in an exploded illustration. This third embodiment differs from the two embodiments explained above in that the positive electrode 44 is enveloped by a sheath 13. In this case, a surface area of the sheath 13 is greater than a surface area of the positive electrode 44, the boundary 14 of which is shown in Figure 5 as a dashed line. Two layers

15, 16 of the sheath 13 that cover the positive electrode 44 on both sides are connected to one another at the circumferential edge of the positive electrode 44 by an edge connection 17. The two negative electrodes 45 are not enveloped. The electrodes 44 and 45 can be contacted via the electrode connections 46 and 47.

5

Example 1: Preparation of a reference electrolyte

A reference electrolyte used for the examples described below was produced according to the method described in patent specification EP 2 954 588 B1 (hereinafter referred to as [V4]). First, lithium chloride (LiCl) was dried under vacuum at 120°C for three days. Aluminum particles (Al) were dried under vacuum for two days at 450°C. LiCl, aluminum chloride (AlCl₃) and Al were mixed together in an AlCl₃:LiCl:Al molar ratio of 1:1.06:0.35 in a glass bottle having an opening to allow gas to escape. This blend was thereafter heat-treated in stages to produce a molten salt. After cooling, the salt melt formed was filtered, then cooled to room temperature and finally SO₂ was added until the desired molar ratio of SO₂ to LiAlCl₄ was formed. The reference electrolyte thus formed had the composition LiAlCl₄ * x SO₂, wherein x is dependent on the amount of SO₂ supplied.

Example 2: Preparation of four embodiments 1, 2, 3 and 4 of an SO₂-based electrolyte for a battery cell

Four embodiments 1, 2, 3 and 4 of the SO₂-based electrolyte were prepared for the experiments described below (hereinafter referred to as electrolytes 1, 2, 3 and 4). For this purpose, four different first conducting salts according to formula (I) were initially prepared using a manufacturing process described in the following documents [V5], [V6] and [V7]:

[V5] „I. Krossing, *Chem. Eur. J.* **2001**, 7, 490;

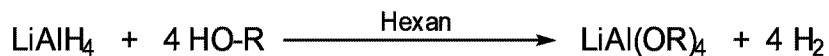
[V6] S. M. Ivanova et al., *Chem. Eur. J.* **2001**, 7, 503;

[V7] Tsujioka et al., *J. Electrochem. Soc.*, **2004**, 151, A1418“

30

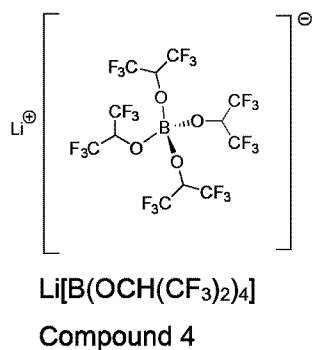
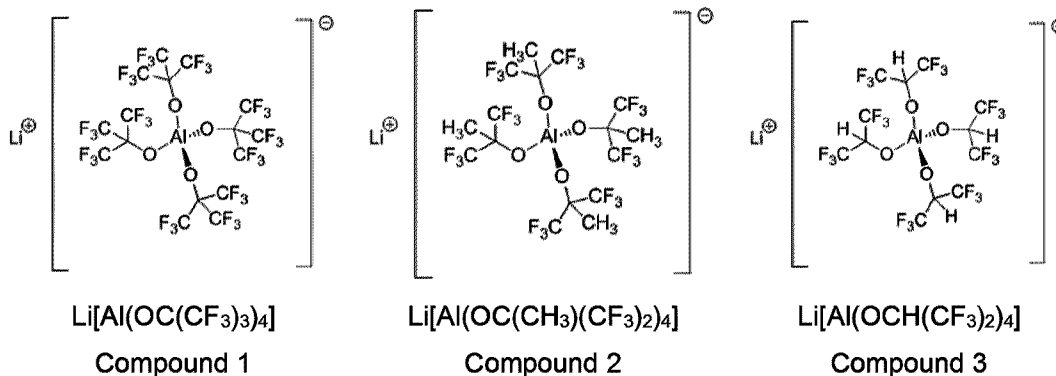
These four different, first conducting salts according to formula (I) are referred to below as compounds 1, 2, 3 and 4. They come from the family of polyfluoroalkoxyaluminates and were prepared in hexane according to the following reaction equation, starting from LiAlH₄ and the corresponding alcohol R-OH with R¹=R²=R³=R⁴.

35



As a result, compounds 1, 2, 3 and 4 shown below were formed using the sum and structural formulas:

5



10

Compounds 1, 2, 3 and 4 were first recrystallized for purification. As a result, residues of the educt LiAlH_4 were removed from the first conducting salt, since said educt could possibly lead to the formation of sparks with possibly existing traces of water in SO_2 .

15 Compounds 1, 2, 3 and 4 were then dissolved in SO_2 . It was found that compounds 1, 2, 3 and 4 dissolve well in SO_2 .

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

20

- 1) receiving of the respective compound 1, 2, 3 and 4 in a pressure piston each with a riser pipe,

- 2) evacuation of the pressure pistons,
- 3) inflow of liquid SO₂ and
- 4) repetition of steps 2 + 3 until the target amount of SO₂ was added.

5 The respective concentration of compounds 1, 2, 3 and 4 in electrolytes 1, 2, 3 and 4 was 0.6 mol/L (molar concentration based on 1 liter of the electrolyte), unless otherwise described in the description of the experiment. The experiments described below were performed using electrolytes 1, 2, 3 and 4 and the reference electrolyte.

10 Example 3: Production of test full cells

The test full cells used in the experiments described below are rechargeable battery cells having two negative electrodes and one positive electrode, each separated by a separator. The positive electrodes included an active material, a conductivity mediator and a
 15 binder. The negative electrodes comprised graphite as the active material and also a binder. As mentioned in the experiment, the negative electrodes can also comprise a conductivity additive. The active material of the positive electrode is named in the respective experiment. The discharge element of the positive and negative electrodes was made of
 20 nickel. Among other things, the aim of the investigations is to confirm the use of various active materials for the positive electrode in a battery cell according to the invention in combination with the electrolyte according to the invention. Table 2 shows which polyanionic compounds were investigated as active materials of the positive electrode and which upper potentials were used.

25 Table 2: Polyanionic compounds investigated

Experi- ment	Active material	Upper po- tential
1	Lithium iron phosphate LiFePO ₄ (LEP)	4.5-5.0 V
2	Lithium iron phosphate LiFePO ₄ (LEP)	3.6 V
3	Lithium iron manganese phosphate Li(Fe _{0.3} Mn _{0.7})PO ₄	4.5 V
4	Lithium iron cobalt phosphate LiFeCoPO ₄	5.0 V

The test full cells were each filled with the electrolyte required for the experiments, that is, either with the reference electrolyte or electrolytes 1, 2, 3 or 4.

Several, that is, two to four, identical test whole cells were produced for each experiment. The results presented in the experiments are each mean values from the measured values obtained for the identical test full cells.

5 Example 4: Measurement in test full cells

For measurements in test full cells, for example, the discharge capacity is determined from the number of cycles.

For this purpose, the test full cells are charged with a certain charge current intensity up to
 10 a certain upper potential. The corresponding upper potential is held until the charge current has dropped to a certain value. The discharge then takes place with a certain discharge current intensity up to a certain discharge potential. This charging method is a so-called I/U charging. This process is repeated depending on the desired number of cycles.

15 The upper potentials or the discharge potential and the respective charge or discharge current intensities are given in the experiments. The value to which the charge current must have dropped is also described in the experiments.

The term "upper potential" is used as a synonym for the terms "charge potential", "charge voltage", "end-of-charge voltage" and "upper potential limit". The terms denote the volt-
 20 age/potential up to which a cell or battery is charged with the aid of a battery charger.

The battery is preferably charged at a current rate of C/2 and at a temperature of 22°C. With a charge or discharge rate of 1C, by definition, the nominal capacity of a cell is charged or discharged in one hour. A charge rate of C/2 means a charge time of 2 hours.

25 The term "discharge potential" is used synonymously with the term "lower cell voltage". This describes the voltage/potential up to which a cell or battery is discharged with the aid of a battery charger.

The test full cell is preferably discharged at a current rate of C/2 and at a temperature of 22°C.

30 The discharge capacity is obtained from the discharge current and the time until the criteria for ending the discharge are fulfilled. These mean values of the discharge capacities are expressed as a percentage of the nominal capacity, often standardized to the maximum capacity that was achieved in the respective test. These mean values of the discharge capacities are expressed as a percentage of the nominal capacity. The nominal
 35 capacity is obtained by subtracting from the theoretical capacity of the positive electrode that capacity that is consumed in the first cycle for the formation of a coating layer on the

negative electrode. This coating layer is formed on the negative electrode when the test full cell is charged for the first time. Lithium ions are irreversibly consumed for this formation of a coating layer, so that the respective test full cell has less cyclic capacity available for the subsequent cycles.

- 5 Experiment 1: Test full cells having lithium iron phosphate LiFePO_4 (LEP) as the active electrode material - high upper potential

A test full cell according to Example 3 was produced using lithium iron phosphate LiFePO_4 (LEP) as the active electrode material of the positive electrode. The test full cell was filled
10 with electrolyte 1 described in Example 2.

Figure 6 shows the potential profile in volts [V] as a function of the percentage charge, which is related to the maximum charge of the test full cell. The test full cell was charged at a current of 50 mA up to an upper potential of 5 V. The potential was held until the charge current had dropped to 40 mA. The discharge then took place with a current inten-
15 sity of 50 mA up to a discharge potential of 2.5 volts.

The charge/discharge experiment was repeated again, with the difference that the upper potential limit when charging was increased from 4.5 volts to 5.0 volts in 0.1 volt steps. 5 cycles were performed with each potential. Figure 7 shows the discharge capacity and the associated charge potential (upper potential).

20 The achieved discharge capacities are almost identical for each charge potential and are 99%. This means that the discharge capacities obtained are independent of the charge potential. A higher charge potential does not cause any undesired reactions, such as decomposition of the electrolyte or irreversible destruction of the active material LEP.

- 25 Experiment 2: Test full cells having lithium iron phosphate LiFePO_4 (LEP) as the active electrode material

A test full cell according to Example 3 was produced using lithium iron phosphate LiFePO_4 (LEP) as the active electrode material of the positive electrode. The test full cell was filled
30 with electrolyte 1 described in Example 2. The test full cell was cycled as described in Experiment 1 to determine the discharge capacities (see Example 4). The upper potential of test full cell was 3.6 volts. Figure 8 shows the discharge capacities of the test full cell as a function of the number of cycles. These mean values of the discharge capacities are expressed as a percentage of the nominal capacity. The test full cell shows exceptionally
35 stable behavior of the discharge capacity over more than 1880 cycles. A capacity of 78% is still obtained even after this very high number of cycles. The combination of a positive

electrode with a polyanionic compound, such as lithium iron phosphate, in connection with the electrolyte 1 leads to an extremely long-lasting test full cell having good stability.

Experiment 3: Test full cells having lithium iron manganese phosphate $\text{Li}(\text{Fe}_{0.3}\text{Mn}_{0.7})\text{PO}_4$ as the active electrode material

In order to test further lithium metal phosphates as the active electrode material, a test full cell according to Example 3 was produced in a further experiment. The active material of the positive electrodes (cathodes) consisted of lithium iron manganese phosphate

$\text{Li}(\text{Fe}_{0.3}\text{Mn}_{0.7})\text{PO}_4$.

The test full cell was filled with electrolyte 1 described in Example 2. The test full cell was cycled as described in Experiment 1 to determine the discharge capacities (see Example 4). The upper potential of the cells according to the invention is 4.5 volts.

Figure 9 shows mean values for the discharge capacities of the test full cell as a function of the number of cycles. These mean values of the discharge capacities are expressed as a percentage of the nominal capacity. The cell shows very stable behavior of the discharge capacity. A capacity of 97% is still obtained at cycle 200.

Experiment 4: Test full cells having lithium iron cobalt phosphate LiFeCoPO_4 as the active electrode material

In order to test further lithium metal phosphates as the active electrode material, a test full cell according to Example 3 was produced in a further experiment. The active material of the positive electrodes (cathodes) consisted of lithium iron cobalt phosphate (LiFeCoPO_4).

The test full cell was filled with electrolyte 1 described in Example 2.

Figure 10 shows the potential profile of the first cycle in volts [V] as a function of the percentage charge, which is related to the maximum charge of the test full cell [% of the max. charge]. A coating layer forms on the negative electrode in the first cycle of the full test cell. Lithium ions are irreversibly consumed for said formation of a coating layer, such that the discharge capacity of the test full cell is less than the charge capacity. The test full cell was charged at a charge rate of C/10 up to an upper potential of 5.0 V. The discharge then took place at a discharge rate also of C/10 up to a discharge potential of 4.0 volts.

The test full cell can be charged up to a high upper potential of 5 volts and then discharged again. No electrolyte decomposition can be seen even at high potentials.

Experiment 5: Test full cells having lithium iron phosphate LiFePO_4 (LEP) as the active electrode material in combination with electrolyte 1 and electrolyte 3 and the reference electrolyte

5 Various experiments were performed to investigate electrolytes 1 and 3 in combination with lithium iron phosphate as the active material. On the one hand, the coating layer capacities of electrolytes 1 and 3 were determined. This coating layer is formed on the negative electrode when the test full cell is charged for the first time. Lithium ions are irreversibly consumed for this formation of a coating layer, so that the test full cell has less cyclic
10 capacity available for the subsequent cycles. On the other hand, the discharge capacities in electrolytes 1 and 3 were determined. Both experiments were also performed in the reference electrolyte for comparison.

The reference electrolyte, electrolyte 1 and electrolyte 3 were each investigated in a test full cell for this experiment. The structure corresponded to the structure described in Ex-
15 ample 3. The reference electrolyte used in a first experiment had the composition $\text{LiAlCl}_4 \cdot x \text{SO}_2$ with $x > 1.5$. Electrolytes 1 and 3 were investigated in a second and third experiment.

Figure 11 shows the potential in volts of the test full cells when charging the negative electrode as a function of capacity, which is related to the theoretical capacity of the negative
20 electrode. Here, the dotted line shows the results for the reference electrolyte and the dashed and solid lines show the results for electrolytes 1 and 3 according to the invention. The three curves depicted show averaged results of several experiments with the test whole cells described above. First, the test full cells were charged with a current of 15 mA until a capacity of 125 mAh (Q_{lad}) was reached. The test full cells were then discharged at
25 15 mA until a potential of 2.5 volts was reached. The discharge capacity (Q_{ent}) was determined.

The capacity in % of the theory that was used to form the coating layer on the negative electrode is calculated according to the following formula:

30
$$\text{Coating layer capacity} = (Q_{\text{lad}} (125\text{mAh}) - Q_{\text{ent}} (x \text{ mAh})) / Q_{\text{NEL}}$$

Q_{NEL} is the theoretical capacity of the negative electrode used. The theoretical capacity is calculated, in the case of graphite, to a value of 372 mAh/g. The absolute capacity losses are 7.58% and 11.51% for electrolytes 1 and 3, respectively, and 6.85% for the reference
35 electrolyte. The capacity for the formation of the coating layer is somewhat higher in both electrolytes according to the invention than in the reference electrolyte. Values in the

range of 7.5% - 11.5% for the absolute capacity losses are good results in combination with the possibility of using positive cathodes up to 5 volts.

For the discharge experiments, three test full cells according to Example 3 were filled with electrolytes 1 and 3 described in Example 2 and the reference electrolyte. The test full cells had lithium iron phosphate as the active material of the positive electrode. To determine the discharge capacities (see Example 4), the test full cells were charged with a current intensity of 15 mA up to a capacity of 125 mAh. The discharge then took place with a current intensity of 15 mA up to a discharge potential of 2.5 volts.

Figure 12 shows the potential profile during the discharge over the discharged amount of charge in % [% of the maximum charge]. All test full cells show a flat discharge curve, which is necessary for good operation of a battery cell.

Experiment 6: Determination of the conductivities of electrolytes 1, 3 and 4

To determine the conductivity, electrolytes 1, 3 and 4 were prepared using different concentrations of compounds 1, 3 and 4. The conductivities of the electrolytes were determined using a conductive measurement method for each concentration of the various compounds. After temperature control, a two-electrode sensor was held touching in the solution and measured in a measuring range of 0-50 mS/cm. During the measurements, it was noted that the sensor can react with the SO₂-containing electrolyte solution.

Figure 13 shows the conductivity of electrolyte 1 as a function of the concentration of compound 1. A maximum of the conductivity can be seen at a concentration of compound 1 of 0.6 mol/L - 0.7 mol/L having a value of approx. 37.9 mS/cm. In comparison, the organic electrolytes known from the prior art, such as LP30 (1 M LiPF₆ / EC-DMC (1:1 weight)) have a conductivity of only approx. 10 mS/cm.

Figures 14 (electrolyte 3) and 15 (electrolyte 4) show the conductivity values for electrolytes 3 and 4 determined for the different concentrations.

With electrolyte 4, a maximum of 18 mS/cm is achieved at a conducting salt concentration of 1 mol/L. Electrolyte 3 shows its highest conductivity of 0.5 mS/cm at a conducting salt concentration of 0.6 mol/L. Although electrolyte 3 shows a lower conductivity, as in experiment 4, charging or discharging of a test full cell is quite possible.

Experiment 7: Low temperature behavior

Two test full cells according to example 3 were produced in order to determine the low-temperature behavior of electrolyte 1 in comparison to the reference electrolyte. One test full cell was filled with reference electrolyte of the composition $\text{LiAlCl}_4 \cdot 6\text{SO}_2$ and the other test full cell with electrolyte 1. The test full cell having the reference electrolyte comprised lithium iron phosphate (LEP) as the active material, the test full cell having electrolyte 1 comprised lithium nickel manganese cobalt oxide (NMC) as the active material of the positive electrode. The test full cells were charged to 3.6 volts (LEP) or 4.4 volts (NMC) at 20°C. and discharged again to 2.5 volts at the respective temperature to be investigated. The discharge capacity reached at 20°C was rated as 100%. The temperature for the discharge was lowered in temperature steps of 10°K. The discharge capacity obtained was described in % of the discharge capacity at 20°C. Since the low-temperature discharges are almost independent of the active materials used for the positive and negative electrodes, the results can be transferred to all combinations of active materials. Table 3 shows the results.

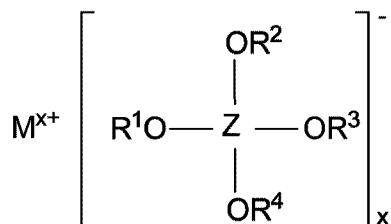
Table 3: Discharge capacities as a function of the temperature

Temperature	Discharge capacity of electrolyte 1	Discharge capacity of the reference electrolyte
20°C	100%	100%
10°C	99%	99%
0°C	95%	46%
-10°C	89%	21%
-20°C	82%	n/a
-30°C	73%	n/a
-35°C	68%	n/a
-40°C	61%	n/a

The test full cell having electrolyte 1 shows very good low-temperature behavior. At – 20°C, 82% of the capacity is reached, at -30°C, 73%. Even at a temperature of -40°C, 61% of the capacity can still be discharged. In contrast, the test full cell having the reference electrolyte only shows a discharge capacity down to -10°C. A capacity of 21% is achieved here. The test full cell having the reference electrolyte can no longer be discharged at lower temperatures.

Amended Claims

1. A rechargeable battery cell (2, 20, 40) comprising an active metal, at least one positive electrode (4, 23, 44), at least one negative electrode (5, 22, 45), a housing (1, 28) and an electrolyte,
the positive electrode (4, 23, 44) having at least one polyanionic compound as an active material and
the electrolyte being based on SO₂ and comprising at least one first conducting salt which has the formula (I)



Formula (I)

- M being a metal selected from the group formed by alkali metals, alkaline earth metals, metals of group 12 of the periodic table of the elements, and aluminum;
 - x being an integer from 1 to 3;
 - the substituents R¹, R², R³ and R⁴ being selected independently of one another from the group formed by C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, C₂-C₁₀ alkynyl, C₃-C₁₀ cycloalkyl, C₆-C₁₄ aryl and C₅-C₁₄ heteroaryl;
and
 - Z being aluminum or boron.
2. The rechargeable battery cell (2, 20, 40) according to claim 1,
in which the polyanionic compound has the composition A_xM_y(X_{r1}O_{s1})_aF_b, wherein
 - A is at least one metal selected from the group formed by the alkali metals, the alkaline earth metals, the metals of group 12 of the periodic table or aluminum,

- M is at least one metal selected from the group formed by the elements of groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 and 16 of the periodic table of the elements,
 - $(X_{r1}O_{s1})^{n-}$ is at least one first polyanion structural unit in which X is at least one element selected from the group formed by the elements phosphorus (P), silicon (Si), sulfur (S), boron (B), carbon (C), arsenic (As), molybdenum (Mo), tungsten (W) and vanadium (V), and O is the element oxygen (O),
 - F is the element fluorine (F),
 - n is a number greater than 0,
 - x and y independently of one another are numbers greater than 0;
 - r1 and s1 independently of one another are numbers greater than 0,
 - a is a number greater than 0 and
 - b is a number greater than or equal to 0.
3. The rechargeable battery cell (2, 20, 40) according to claim 2, in which the metal A is selected from the group formed by the elements lithium, sodium, calcium or zinc.
 4. The rechargeable battery cell (2, 20, 40) according to claim 2, in which the metal M is selected from the group formed by the elements titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc.
 5. The rechargeable battery cell (2, 20, 40) according to any one of claims 2 to 4, in which the first polyanion structural unit has the composition $(XO_4)^{n-}$, $(X_mO_{3m+1})^{n-}$ or $(XO_3)^{n-}$, wherein m and n are, independently of one another, numbers greater than 0.
 6. The rechargeable battery cell (2, 20, 40) according to claim 5, in which the polyanionic compound has the composition $A_xM_y(PO_4)_aF_b$.
 7. The rechargeable battery cell (2, 20, 40) according to claim 5, in which the polyanionic compound has the composition $A_xM_y(SiO_4)_aF_b$.
 8. The rechargeable battery cell (2, 20, 40) according to claim 5,

in which the polyanionic compound has the composition $A_xM_y(SO_4)_aF_b$.

9. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 8, in which the polyanionic compound has at least two different polyanion structural units $(X_{r1}O_{s1})^{n-}$ and $(G_{r2}O_{s2})^{k-}$, wherein n, k, r1, r2, s1 and s2 are, independently of one another, numbers greater than 0,

wherein the polyanionic compound has the composition $A_xM_y(X_{r1}O_{s1})_a(G_{r2}O_{s2})_bF$, wherein

- $(X_{r1}O_{s1})^{n-}$ is at least one first polyanion structural unit in which X is at least one element selected from the group formed by the elements phosphorus (P), silicon (Si), sulfur (S), boron (B), carbon (C), arsenic (As), molybdenum (Mo), tungsten (W) and vanadium (V), and O is the element oxygen (O),
- $(G_{r2}O_{s2})^{k-}$ is at least one second polyanion structural unit in which G is at least one element selected from the group formed by the elements phosphorus (P), silicon (Si), sulfur (S), boron (B), carbon (C), arsenic (As), molybdenum (Mo), tungsten (W) and vanadium (V), and O is the element oxygen (O),
- A is at least one metal selected from the group formed by the alkali metals, the alkaline earth metals, the metals of group 12 of the periodic table or aluminum,
- M is at least one metal selected from the group formed by the elements of groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 and 16 of the periodic table of the elements,
- F is the element fluorine (F),
- x and y independently of one another are numbers greater than 0;
- a is a number greater than 0 and

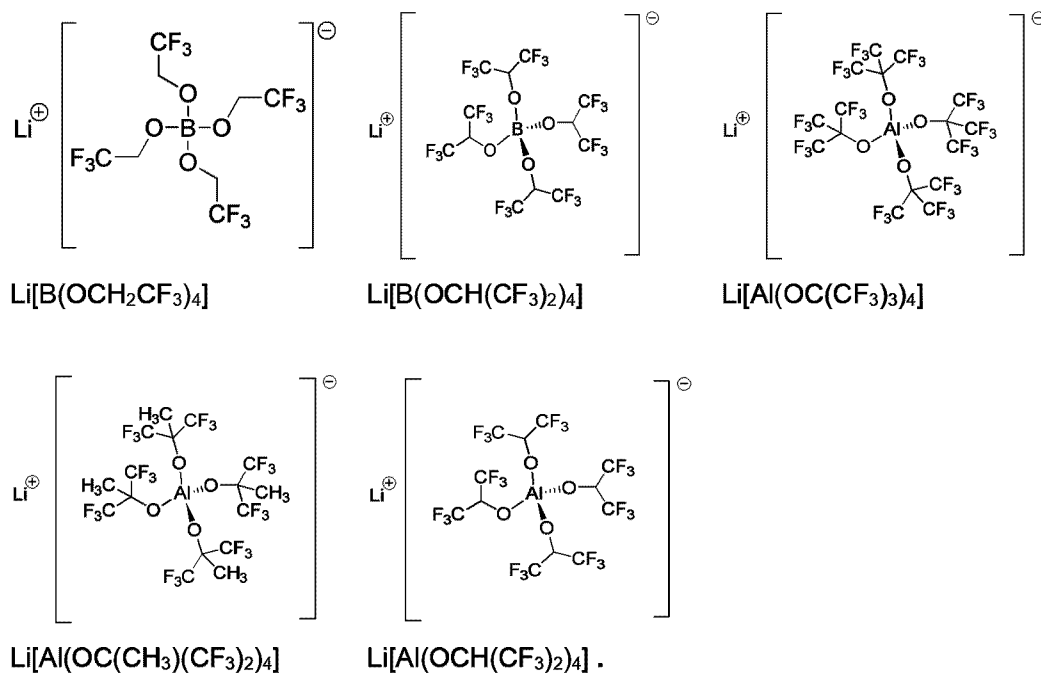
b is a number greater than or equal to 0.

10. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 9, in which the substituents R^1 , R^2 , R^3 and R^4 of the first conducting salt are selected independently of one another from the group formed by

- C_1 - C_6 alkyl;
- C_2 - C_6 alkenyl;
- C_2 - C_6 alkynyl;

- C₃-C₆ cycloalkyl;
- phenyl; and
- C₅-C₇ heteroaryl.

11. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 10 ,
in which at least one of the substituents R¹, R², R³ and R⁴ of the first conducting salt
is substituted by at least one fluorine atom and/or by at least one chemical group,
wherein the chemical group is selected from the group formed by C₁-C₄ alkyl, C₂-C₄
alkenyl, C₂-C₄ alkynyl, phenyl and benzyl.
12. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 11,
in which at least one of the substituents R¹, R², R³ and R⁴ of the first conducting salt
is a CF₃ group or an OSO₂CF₃ group.
13. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 12,
in which the first conducting salt is selected from the group formed by



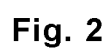
14. The rechargeable battery cell (2) according to any one of claims 1 to 13,
wherein the electrolyte comprises at least one second conducting salt different from
the first conducting salt according to formula (I).

15. The rechargeable battery cell (2, 20, 40) according to claim 14,
in which the second conducting salt of the electrolyte is an alkali metal compound,
which is selected from the group formed by an aluminate, a halide, an oxalate, a bo-
rate, a phosphate, an arsenate and a gallate.
16. The rechargeable battery cell (2, 20, 40) according to claim 14 or 15,
in which the second conducting salt of the electrolyte is a lithium tetrahaloaluminate.
17. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 16,
in which the electrolyte comprises at least one additive.
18. The rechargeable battery cell (2, 20, 40) according to claim 17,
in which the additive of the electrolyte is selected from the group formed by vinylene
carbonate and its derivatives, vinylethylene carbonate and its derivatives, methyleth-
ylene carbonate and its derivatives, lithium (bisoxalato)borate, lithium difluoro(oxa-
lato)borate, lithium tetrafluoro(oxalato)phosphate, lithium oxalate, 2-vinylpyridine, 4-
vinylpyridine, cyclic exomethylene carbonates, sultones, cyclic and acyclic sul-
fonates, acyclic sulfites, cyclic and acyclic sulfinates, organic esters, inorganic acids,
acyclic and cyclic alkanes, which acyclic and cyclic alkanes have a boiling point of at
least 36°C at 1 bar, aromatic compounds, halogenated cyclic and acyclic sul-
fonylimides, halogenated cyclic and acyclic phosphate esters, halogenated cyclic
and acyclic phosphines, halogenated cyclic and acyclic phosphites, halogenated cy-
clic and acyclic phosphazenes, halogenated cyclic and acyclic silylamines, halogen-
ated cyclic and acyclic halogenated esters, halogenated cyclic and acyclic amides,
halogenated cyclic and acyclic anhydrides, and halogenated organic heterocycles.
19. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 18,
in which the electrolyte has the composition
 - (i) 5 to 99.4% by weight sulfur 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.
20. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 19,

in which the molar concentration of the first conducting salt is in the range from 0.01 mol/L to 10 mol/L based on the total volume of the electrolyte.

21. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 20, in which the electrolyte comprises at least 0.1 mol SO₂ per mole of conducting salt.
22. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 21, in which the active metal is
 - an alkali metal;
 - an alkaline earth metal;
 - a metal from group 12 of the periodic table; or
 - aluminum.
23. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 22, in which the negative electrode (5, 22, 45) is an insertion electrode.
24. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 23, in which the positive electrode (4, 23, 44) and/or the negative electrode (5, 22, 45) have a discharge element (34, 35), which is formed
 - either planar in the form of a metal sheet or a metal foil, or
 - three-dimensional in the form of a porous metal structure.
25. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 24, in which the positive electrode (4, 23, 44) and/or the negative electrode (5, 22, 45) comprises at least one binder, a fluorinated binder or
 - a binder consisting of a polymer which is built up from monomeric structural units of a conjugated carboxylic acid or from the alkali, alkaline earth or ammonium salt of said conjugated carboxylic acid or from a combination thereof, or
 - a binder consisting of a polymer based on monomeric styrene and butadiene structural units, or a binder from the group of carboxymethyl celluloses,
 - wherein the binder is present in a concentration of at most 20% by weight based on the total positive electrode weight.
26. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 25,

which comprises a plurality of negative electrodes (5, 22, 45) and a plurality of positive electrodes (4, 23, 44) which are stacked alternately in the housing (1, 28), wherein the positive electrodes and the negative electrodes (5, 22, 45) are each electrically separated from one another by separators (11, 21, 13) .



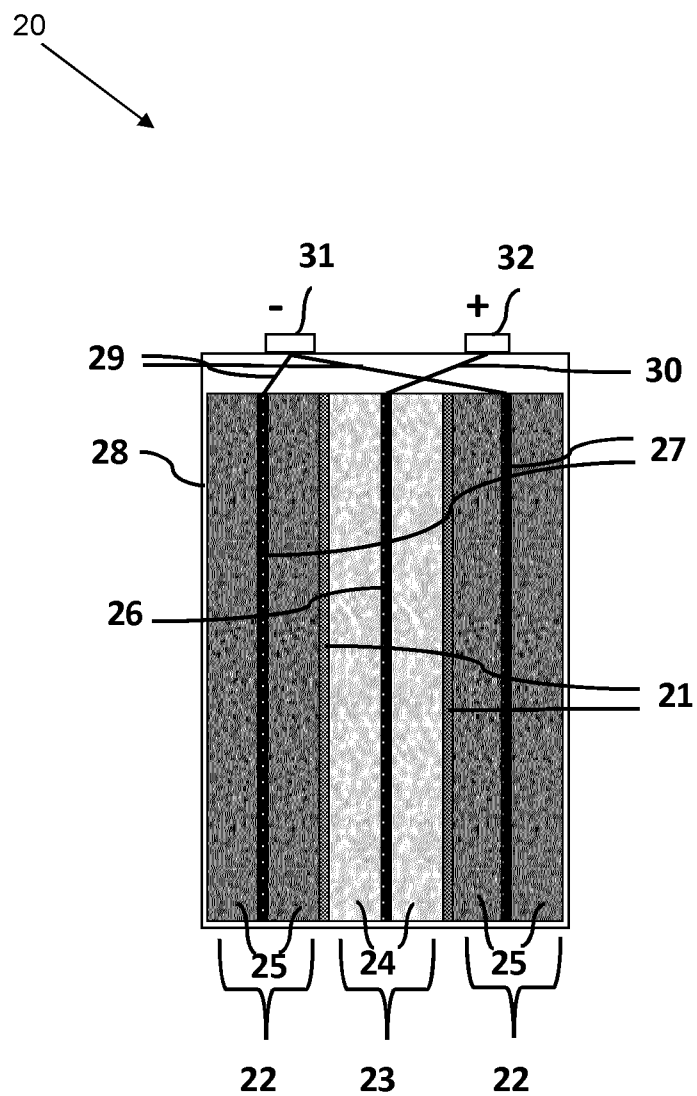


Fig. 3

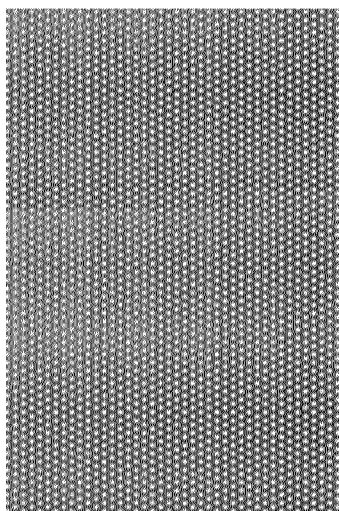


Fig. 4



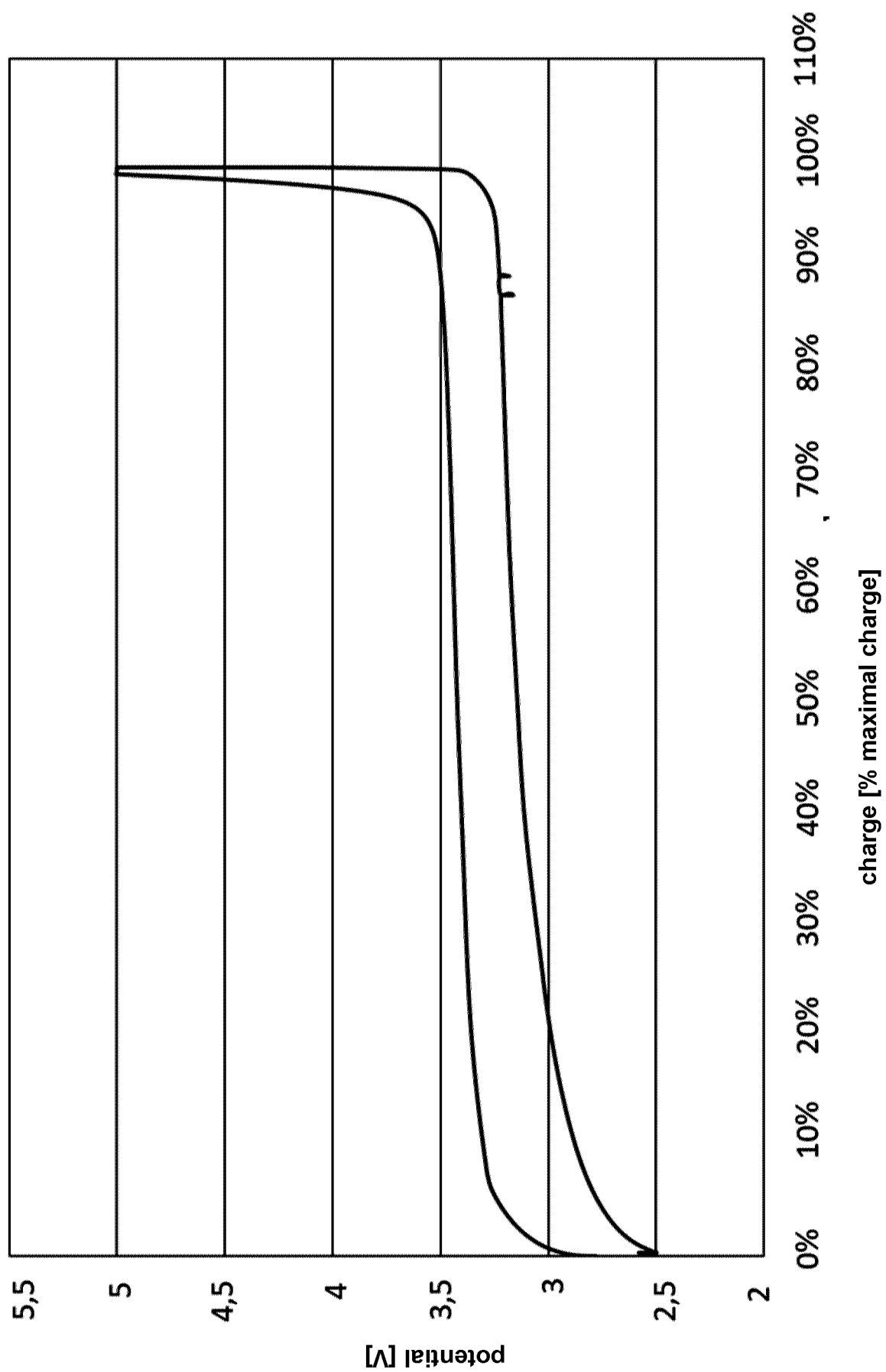


Fig. 6

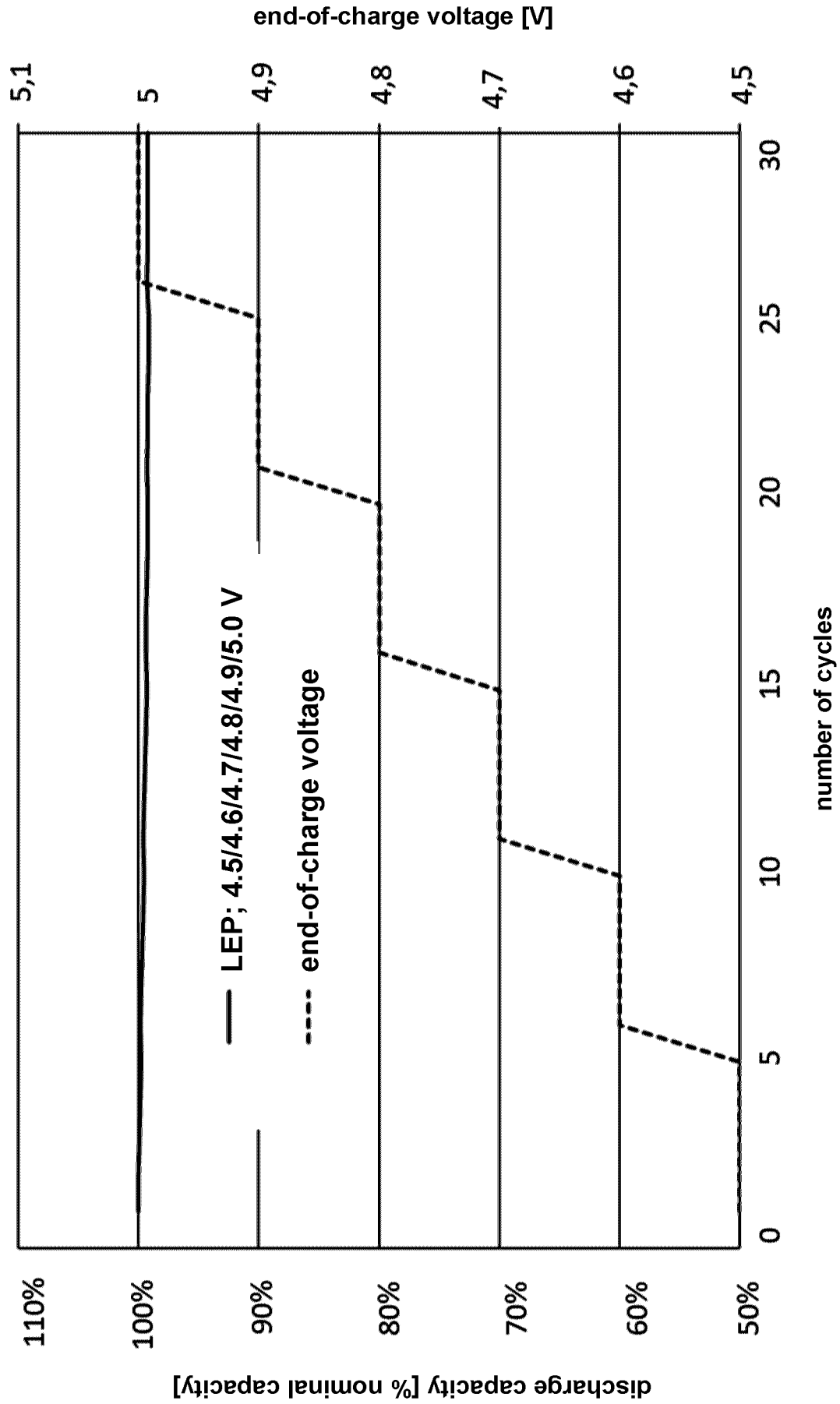


Fig. 7

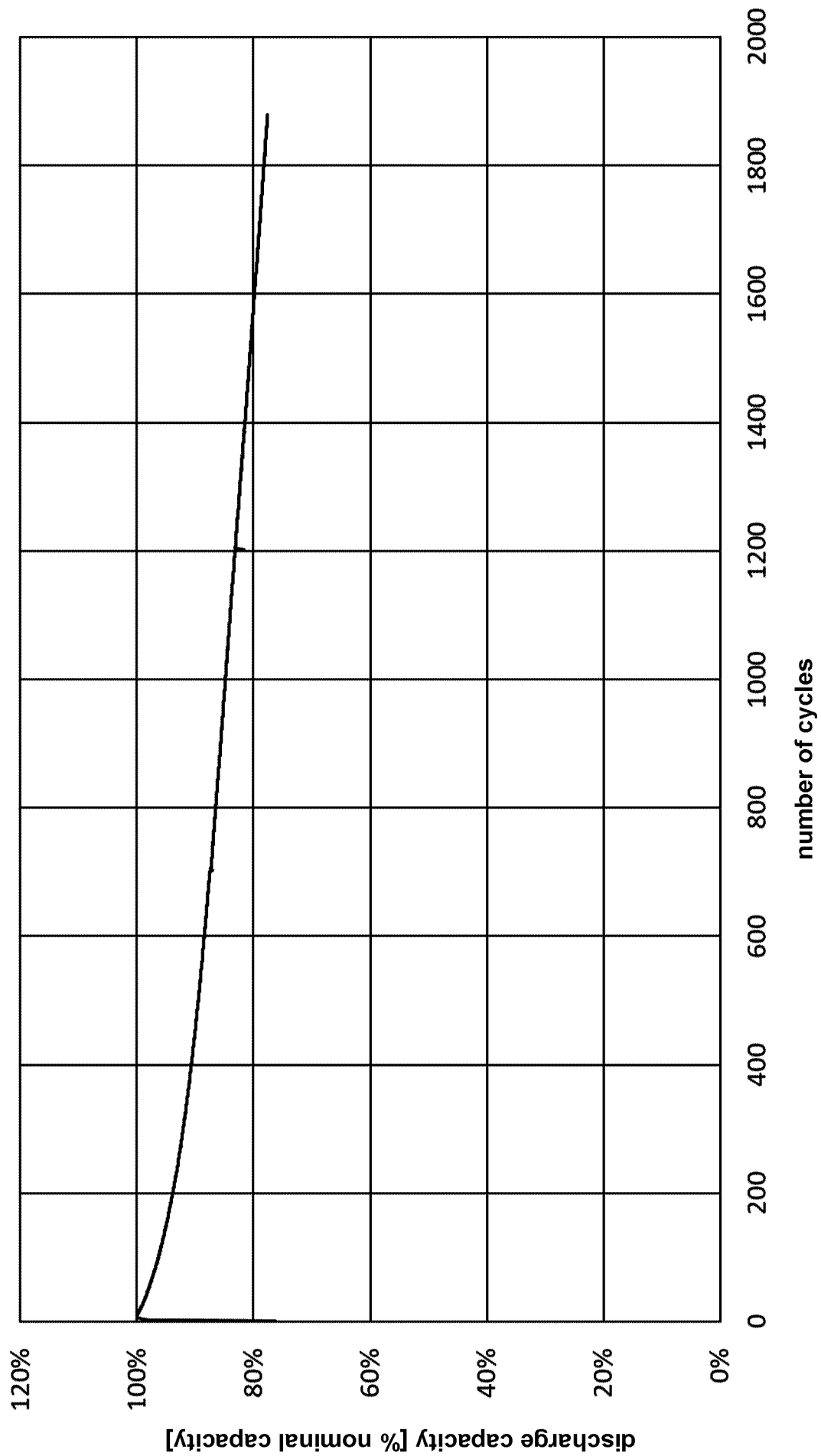


Fig. 8

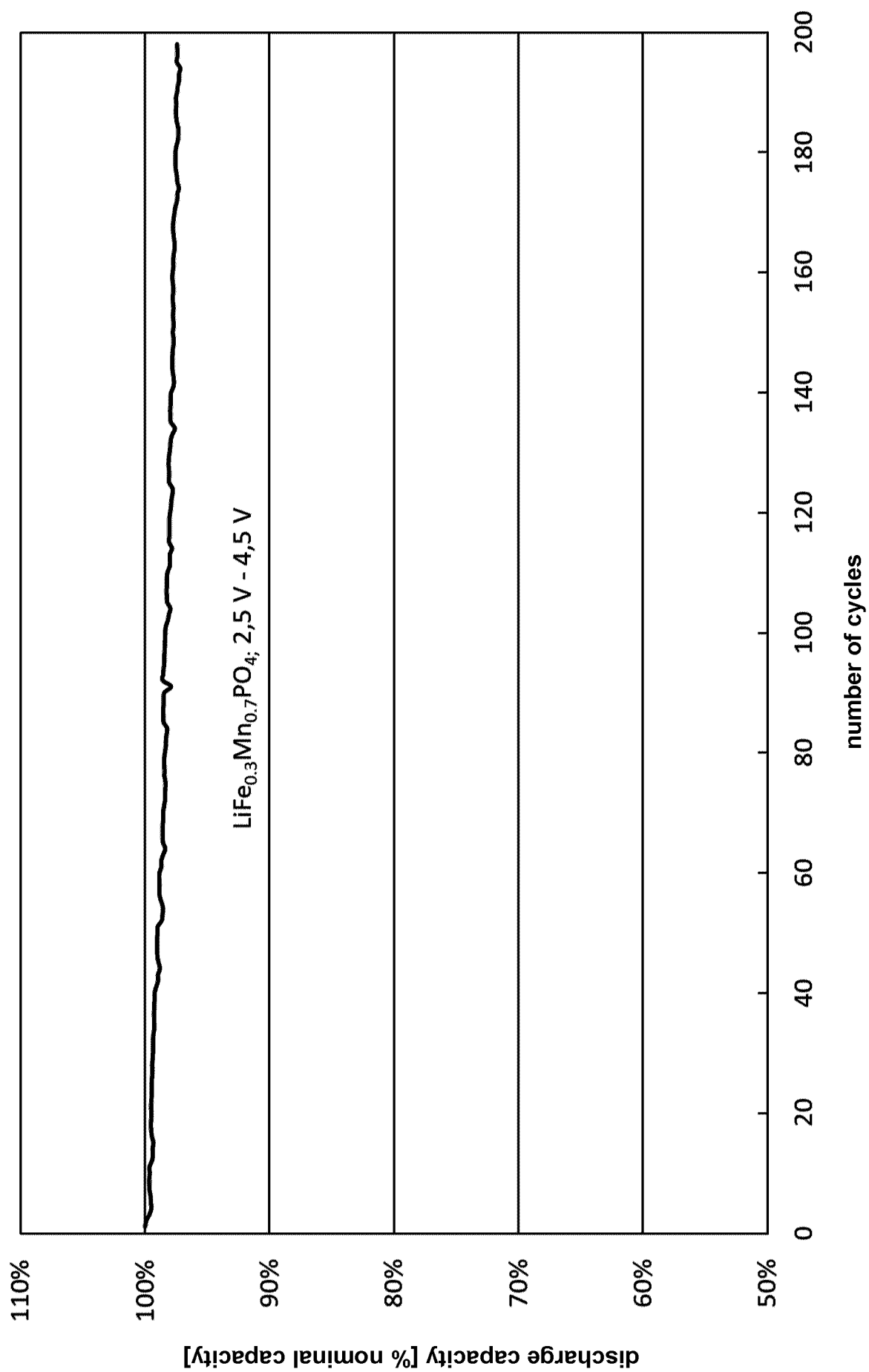


Fig. 9

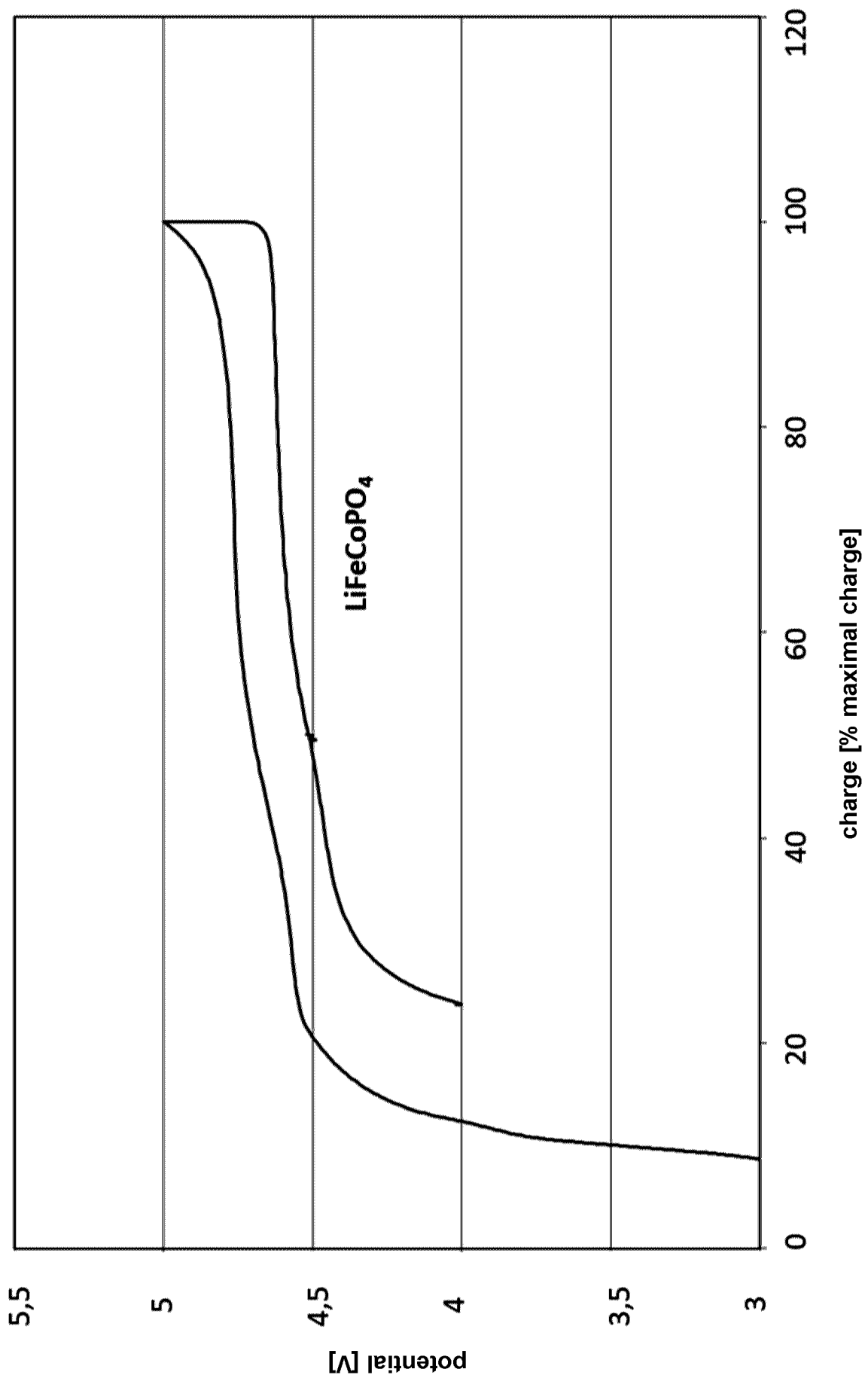


Fig. 10

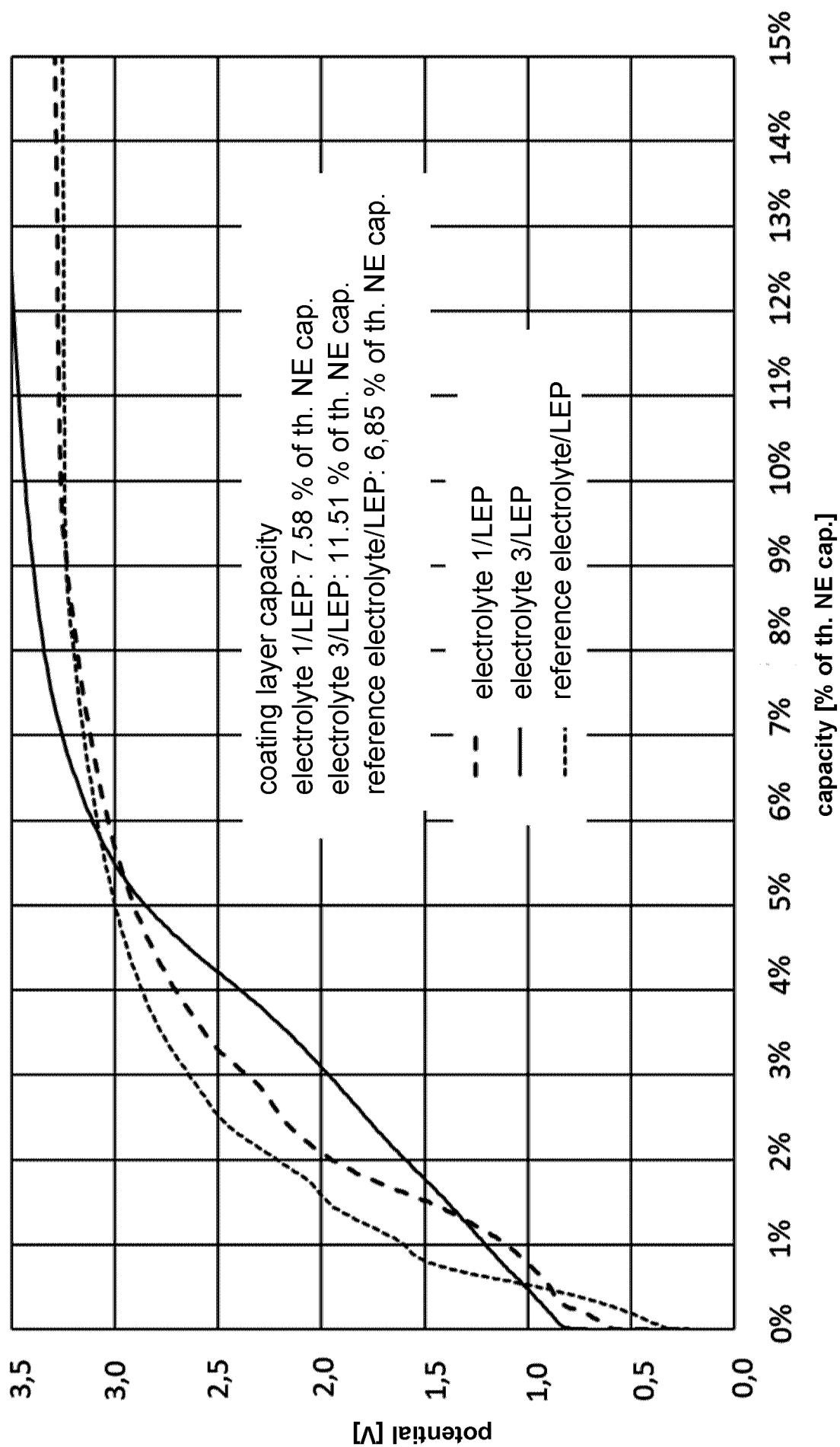


Fig. 11

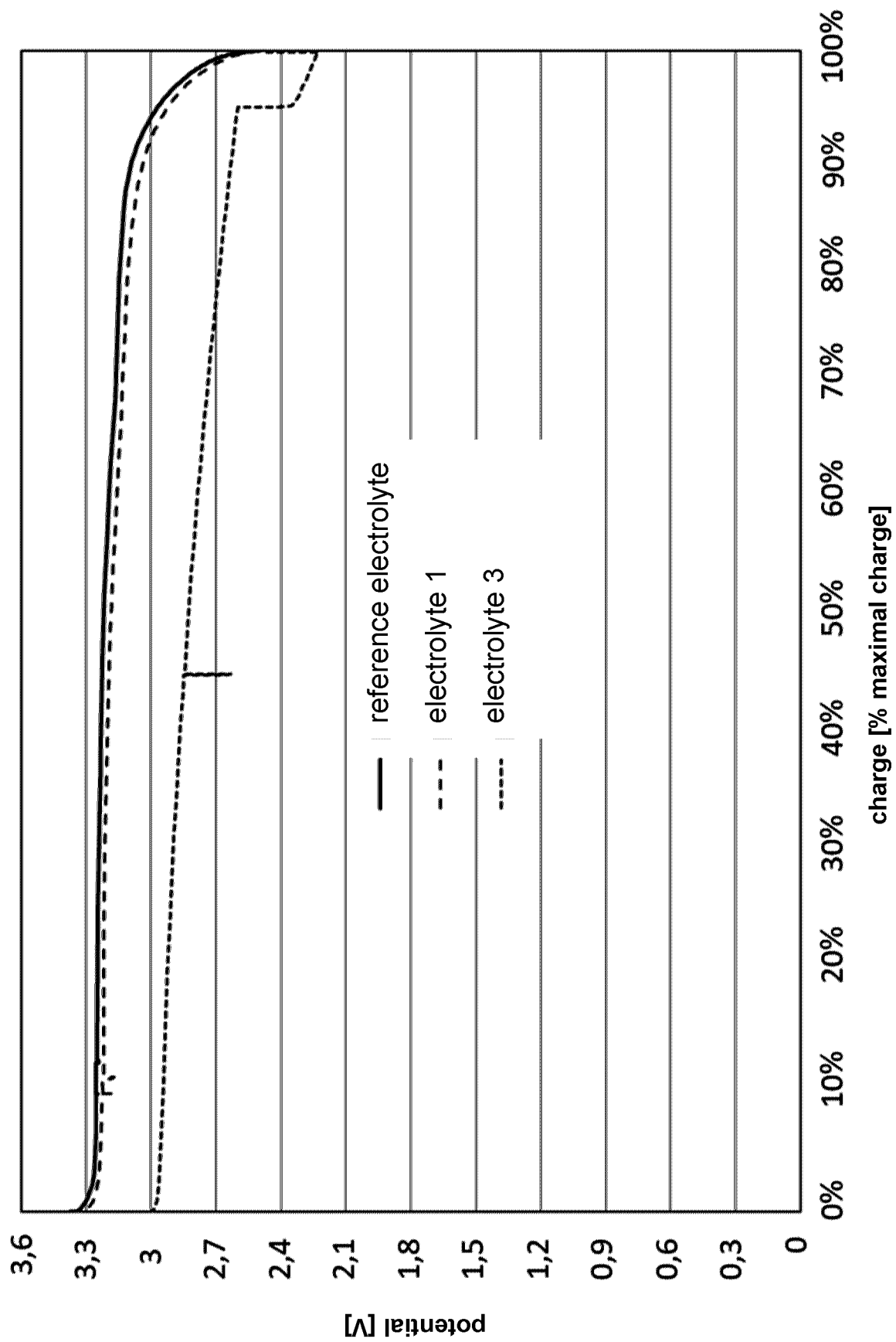


Fig. 12

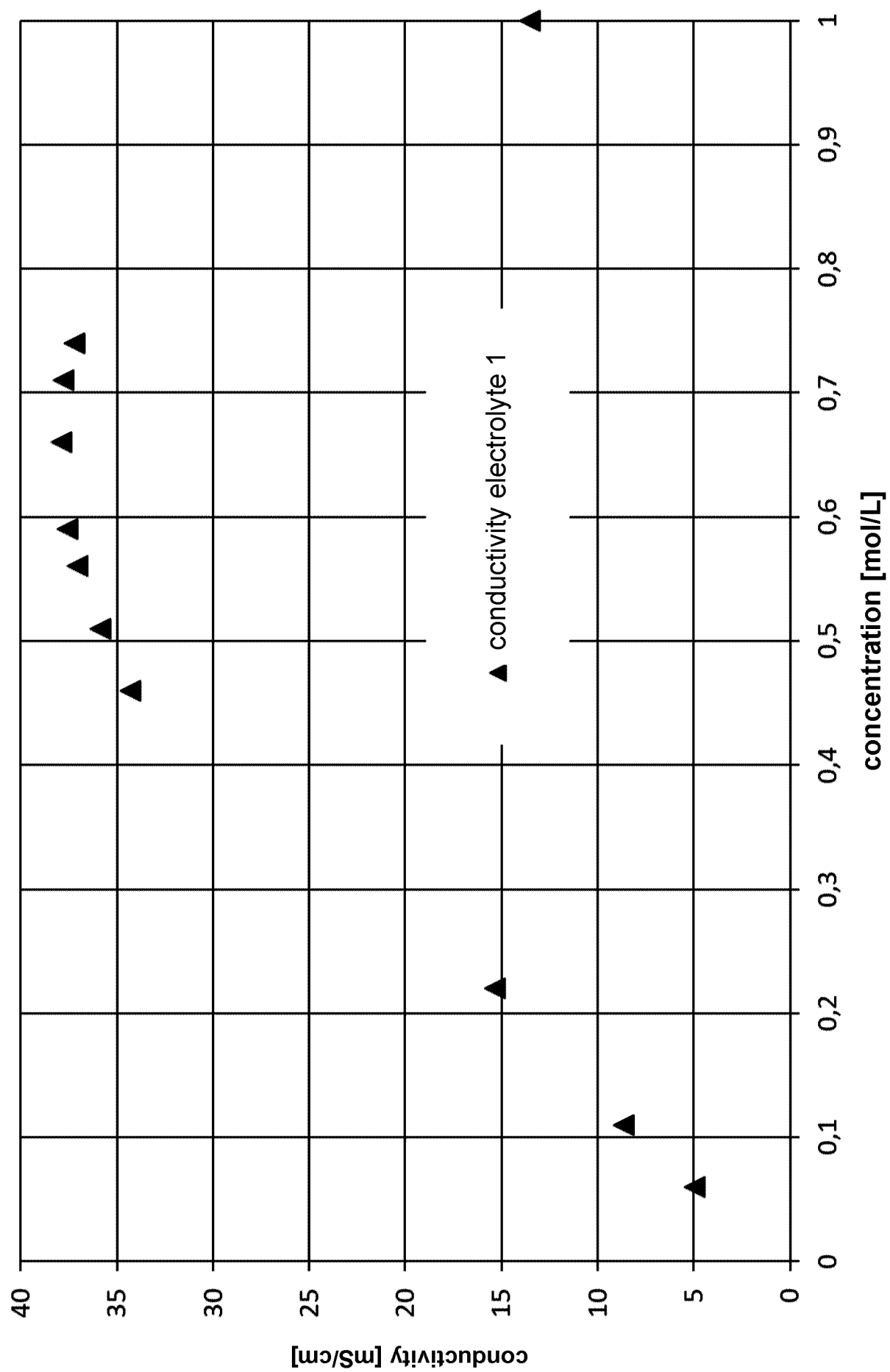


Fig. 13

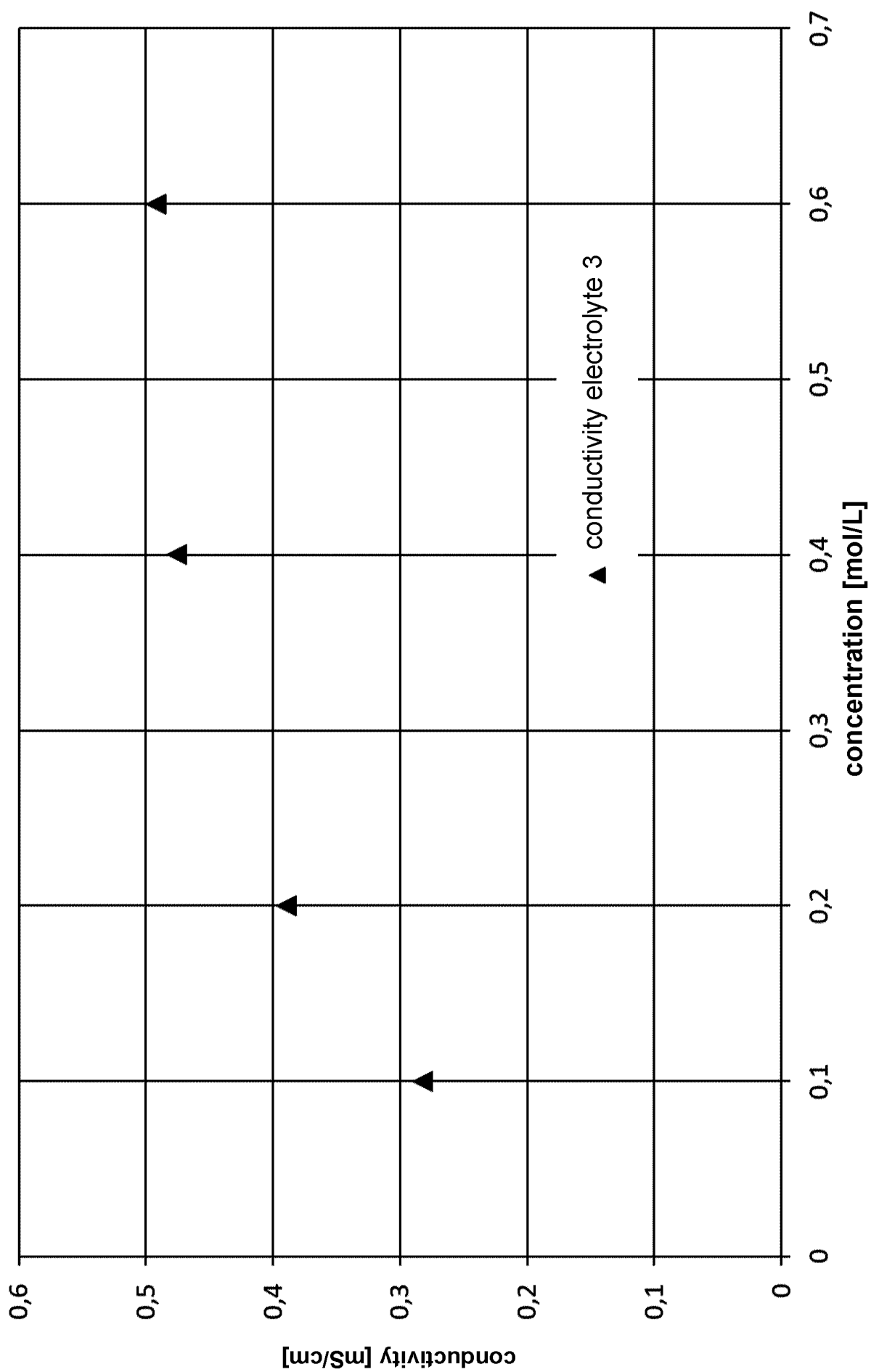


Fig. 14

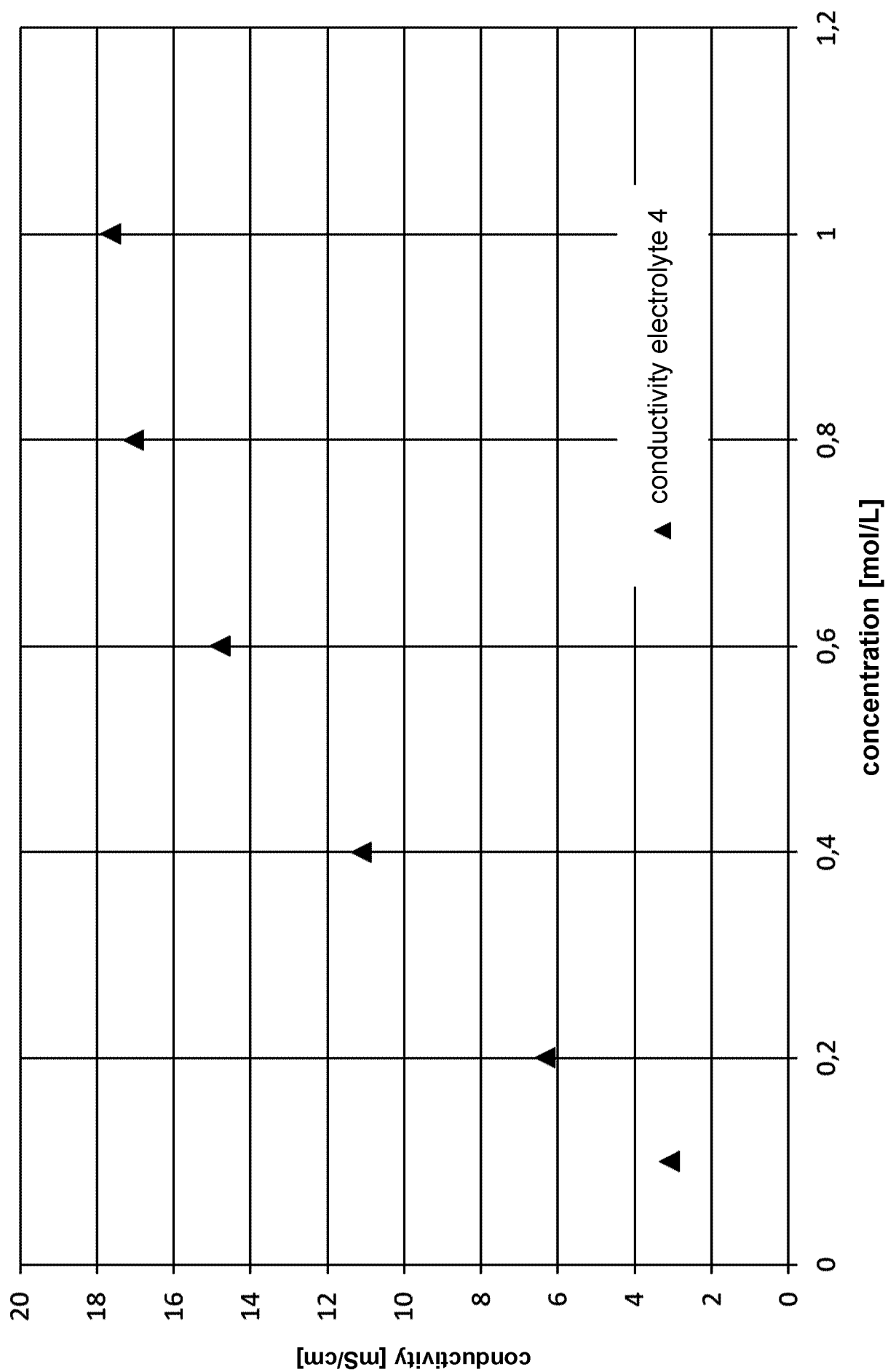
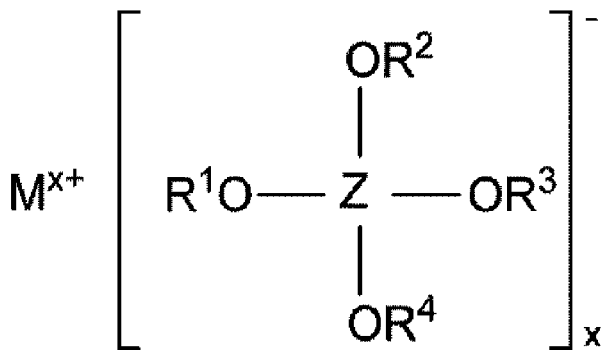


Fig. 15



Formula (I)