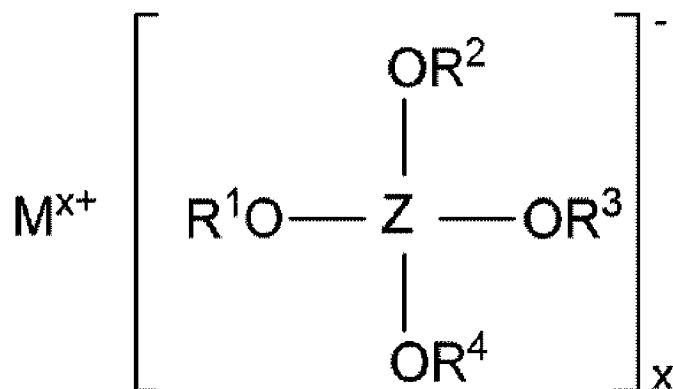




(86) **Date de dépôt PCT/PCT Filing Date:** 2020/07/30
(87) **Date publication PCT/PCT Publication Date:** 2021/02/04
(45) **Date de délivrance/Issue Date:** 2023/08/29
(85) **Entrée phase nationale/National Entry:** 2021/11/09
(86) **N° demande PCT/PCT Application No.:** EP 2020/071579
(87) **N° publication PCT/PCT Publication No.:** 2021/019047
(30) **Priorité/Priority:** 2019/07/31 (EP19189435.1)

(51) **Cl.Int./Int.Cl.** *H01M 10/056* (2010.01),
H01M 10/0525 (2010.01), *H01M 4/131* (2010.01),
H01M 4/136 (2010.01)
(72) **Inventeurs/Inventors:**
ZINCK, LAURENT, FR;
WOLLFARTH, CLAUDIA, DE;
BIOLLAZ, HEIDE, DE
(73) **Propriétaire/Owner:**
INNOLITH TECHNOLOGY AG, CH
(74) **Agent:** NORTON ROSE FULBRIGHT CANADA
LLP/S.E.N.C.R.L., S.R.L.

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



Formula (I)

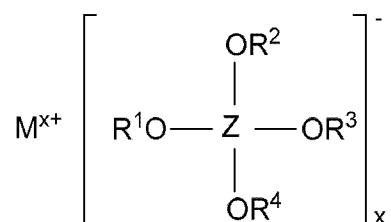
(57) Abrégé/Abstract:

The invention relates to a rechargeable battery cell (2, 20, 40) comprising an active metal, at least one positive electrode (4, 23, 44) having a discharge element (26), at least one negative electrode (5, 22, 45) having a discharge element (27), a housing (1, 28) and an electrolyte, the negative electrode comprising metallic lithium at least in the charged state of the rechargeable battery cell 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, at least one positive electrode (4, 23, 44) having a discharge element (26), at least one negative electrode (5, 22, 45) having a discharge element (27), a housing (1, 28) and an electrolyte, the negative electrode comprising metallic lithium at least in the charged state of the rechargeable battery cell 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.

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,
 10 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
 15 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. Lithium is the metal having the lowest atomic number and therefore having the largest theoretical specific capacity of 3.884 mAh/g. It is the most electronegative metal (-3.10 V vs. standard hydrogen electrode, abbr.: SHE),
 20 thereby generating the highest possible cell voltage with respect to a given positive electrode. It is also the lightest metal (0.54 g/cm³), which contributes to the highest possible gravimetric energy density (Wh/Kg) or specific energy density (Wh/L).

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 the active metal of the negative electrode are also referred to as lithium
 25 cells.

The positive electrodes of lithium 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 cell. This means that the electrode processes can take place not only on the surface of the electrode, but also within the crystalline structure. The positive
 35 electrode, for example, consists of lithium cobalt oxide (LiCoO₂). When charging the lith-

ium cell, the ions of the active metal are removed from the positive electrode and deposited in the negative electrode as metallic lithium. The reverse process takes place when the lithium cell is discharged.

The electrolyte is also an important functional element of every rechargeable battery cell.

5 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 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 (ethylene carbonate) : EMC (ethyl methyl carbonate) 3:7, is an example of such an electrolyte. Due to the organic solvent or solvent blend, these kinds of lithium cells are also referred to as organic lithium cells.

Unintentional overcharging of organic lithium cells leads to 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 cell. The vast majority of charging protocols for these organic lithium cells use the cell voltage as an indicator of the end of charging. Accidents caused by a thermal runaway are particularly likely to occur when using multi-cell battery packs in which a plurality of organic lithium cells having dissimilar capacities are connected in series.

Also this reductive decomposition of the organic electrolyte of a lithium cell on the negative electrode is irreversible. No organic solvents are thermodynamically stable with respect to lithium or with respect to lithium which is stored in carbon (Li_xC_6). However, many solvents form a passivation film on the electrode surface of the negative electrode. This film spatially separates the solvent from the electrode, but is ionically conductive and thus enables the passage of lithium ions. The passivation film, the so-called "Solid Electrolyte Interphase" (SEI), gives stability to the system, by which the production of lithium cells is made possible. Lithium is integrated into the passivation film during the formation of the SEI. This process is irreversible and is therefore observed as a loss of capacity.

This irreversible loss of capacity, also referred to as the coating layer capacity, depends on the electrolyte formulation and the electrodes used. In organic lithium cells, the electrolyte decomposition and formation of layers comprising lithium ions often continues during further operation of the lithium cell and is responsible for the loss of capacity and thus for a shorter service life of the cell. Capacity losses can also occur during the storage of charged lithium cells. This so-called self-discharge can be based on both irreversible processes (electrolyte decomposition) and reversible processes in which the lithium stored in the negative electrode is transferred to the electrolyte solution and is available again the next time it is charged.

Organic lithium 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 cell catches fire or even explodes, the metallic lithium forms a highly reactive substance and the organic solvent in the electrolyte forms a combustible material. Additional measures must be taken to avoid such safety risks.

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, among other things, high ionic conductivity. The term " SO_2 -based electrolyte" 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 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 SO_2 . 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. The use of metallic lithium as the negative electrode active material in rechargeable cells poses various problems. Lithium does not deposit uniformly during charging, but rather in the form of dendrites. The uncontrollable lithium dendrite growth leads to an accumulation of a highly reactive metal having a large surface area and can lead to safety-critical states. The thermodynamic instability of metallic lithium causes irreversible and continuous reactions between said lithium and the electrolyte. As a result, unintentionally thick passivation layers (SEI), which consume lithium and electrolyte components, are created on the lithium metal surface. This increases the internal resistance, and the service life of the lithium cell is shortened. Large volumetric and morphological changes can occur in the lithium metal anode with repeated charging and discharging. The SEI films mentioned are too unstable to completely suppress such significant changes.

Solutions to the above-mentioned problems in connection with a metallic lithium anode are being sought both in lithium cells having organic electrolyte solutions and in battery cells having the SO₂-based electrolyte.

The authors of the document [V1]

"Dendrite-Free Lithium Deposition Induced by Uniformly Distributed Lithium Ions for Efficient Lithium Metal Batteries"

Xin-Bing Cheng, Ting-Zheng Hou, Rui Zhang, Hong-Jie Peng, Chen-Zi Zhao,
Jia-Qi Huang and Qiang Zhang
Adv. Mater. 2016, 28, 2888–2895

report on a lithium metal battery having an organic electrolyte. A 3D glass fiber fabric having a large number of polar groups is used for the deposition of lithium to obtain a dendrite-free lithium metal anode.

US 7,901,811 B2 (hereinafter referred to as [V2]) describes a lithium metal cell having an SO₂-based electrolyte having the conducting salt lithium tetrachloroaluminate (LiAlCl₄). In order to avoid the disadvantages of dendritic deposition, a porous structure formed from solid particles is proposed, the structure being designed and arranged such that the lithium deposited during charging of the lithium metal cell penetrates from the surface of the discharger into the pores of the porous structure and is deposited again there.

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 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 comprised in the electrolyte and the cell components.

A further problem with SO₂-based electrolytes is that many conducting salts, in particular also known for organic lithium cells, are not soluble in SO₂. Measurements 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), trilithium hexafluoroaluminate (Li₃AlF₆), lithium hexafluoroantimonate (LiSbF₆), lithium difluoro(oxalato)borate (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 battery cell.

Table 1: Solubility of various salts in SO₂

<u>Conducting salt</u>	<u>Solubility / mol/L in</u> <u>SO₂</u>	<u>Conducting salt</u>	<u>Solubility / mol/L in</u> <u>SO₂</u>
LiF	2.1 · 10 ⁻³	LiPF ₆	1.5 · 10 ⁻²
LiBr	4.9 · 10 ⁻³	LiSbF ₆	2.8 · 10 ⁻⁴
Li ₂ SO ₄	2.7 · 10 ⁻⁴	LiBF ₂ (C ₂ O ₄)	1.4 · 10 ⁻⁴
LiB(C ₂ O ₄) ₂	3.2 · 10 ⁻⁴	CF ₃ SO ₂ NLiSO ₂ CF ₃	1.5 · 10 ⁻²
Li ₃ PO ₄	-	LiBO ₂	2.6 · 10 ⁻⁴
Li ₃ AlF ₆	2.3 · 10 ⁻³	LiAlO ₂	4.3 · 10 ⁻⁴
LiBF ₄	1.7 · 10 ⁻³	LiCF ₃ SO ₃	6.3 · 10 ⁻⁴
LiAsF ₆	1.4 · 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 rechargeable battery cells known from the prior art

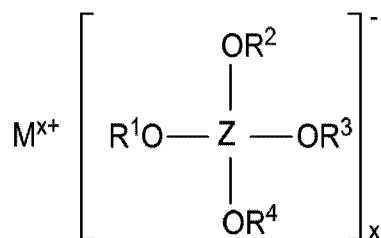
- exhibits improved electrical performance data, in particular high energy density;
- has a stable coating layer on the negative electrode, whereby the coating layer capacity should be low and no further reductive electrolyte decomposition should occur on the negative electrode during further operation;
- comprises an SO₂-based electrolyte, which contributes to the deposition of metallic lithium being as uniform as possible;
- 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;
- has a wide electrochemical window, so that no oxidative electrolyte decomposition occurs at the positive electrode;
- exhibits improved overcharging and deep discharging 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 having a discharge element, at least one negative electrode having

a discharge element, a housing and an electrolyte. The negative electrode comprises metallic lithium as an active material, at least in the charged state of the rechargeable battery cell.

- 5 The electrolyte is based on SO_2 and comprises at least one first conducting salt. Said first conducting salt has the formula (I).



Formula (I)

10

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 R^1 , R^2 , R^3 and R^4 are selected independently of one another from the group formed by $\text{C}_1\text{-C}_{10}$ alkyl, $\text{C}_2\text{-C}_{10}$ alkenyl, $\text{C}_2\text{-C}_{10}$ alkynyl, $\text{C}_3\text{-C}_{10}$ cycloalkyl, $\text{C}_6\text{-C}_{14}$ aryl and $\text{C}_5\text{-C}_{14}$ heteroaryl. The central atom Z is either aluminum or bo-

15 ron.

20

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

25 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 inven-

tion 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.

5 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.

10 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.

15 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-butylnyl, 2-n-butylnyl, isobutylnyl, 1-pentylnyl, 1-hexynyl, 1-heptynyl, 1-octynyl, 1-nonylnyl, 1-decynyl, and the like.

20 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.

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, pyranlyl, thiopyranlyl 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.

35 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.

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 .

Negative electrode

The active material of the negative electrode is metallic lithium. This means that lithium is also the active metal of the rechargeable battery. Said lithium is deposited on the discharge element of the negative electrode when the rechargeable battery cell is charged. This means that the negative electrode also comprises a discharge element in addition to the metallic lithium. 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. When the rechargeable battery cell is discharged, the metallic lithium is converted into lithium ions, wherein the lithium ions migrate from the negative electrode to the positive electrode. If the positive electrode is designed as an intercalation electrode, the lithium ions in the uncharged state of the battery cell are located at least partly in a host matrix of the active material of the positive intercalation electrode.

15

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

An advantageous development of the rechargeable battery cell according to the invention provides that the electronically conductive discharge element of the negative electrode is free of metallic lithium in the discharged state of the rechargeable battery cell. Metallic lithium is deposited on the electronically conductive discharge element of the negative electrode when charging the battery cell. The metallic lithium is essentially completely dissolved when discharging and enters the host matrix of the active material of the positive electrode in the form of ions.

25

A further advantageous development of the battery cell according to the invention provides that the electronically conductive discharge element of the negative electrode already comprises metallic lithium before the first charging of the rechargeable battery cell occurs. Further metallic lithium is deposited on the electronically conductive discharge element when the battery cell is charged. The metallic lithium is completely or only partially dissolved when discharging and enters the host matrix of the active material of the positive electrode in the form of ions. On the one hand, the metallic lithium, which is already located on the discharge element, can be applied to the discharge element before the battery cell is assembled, and can be built into the battery cell together with it. On the other

35

hand, the metallic lithium can be deposited on the discharge element of the negative electrode before the battery cell is operated, that is, before the first charging and discharging by a preceding initialization charging process.

5 A further advantageous development of the battery cell according to the invention provides that the electronically conductive discharge element of the negative electrode is free of metallic lithium before the battery cell is charged for the first time. Metallic lithium is deposited on the electronically conductive discharge element when the battery cell is charged. The metallic lithium is completely or only partially dissolved when discharging and enters
10 the host matrix of the active material of the positive electrode in the form of ions.

A further advantageous development of the battery cell according to the invention provides that the discharge element of the negative electrode is at least partially formed from a lithium-storing material. In such a development, when the battery cell is being charged,
15 part of the lithium resulting from the electrode reaction is initially stored in the electronically conductive discharge element made of the lithium-storing material. As the battery cell continues to be charged, metallic lithium is then deposited on the electronically conductive discharge element. The metallic lithium is completely or only partially dissolved when discharging and enters the host matrix of the active material of the positive electrode in the
20 form of ions.

The lithium-storing material can, for example, be the insertion material carbon, in particular in the form of the carbon allotrope graphite. It can also be a material which forms an alloy with lithium, such as lithium-storing metals and metal alloys (for example, Si, Ge, Sn,
25 SnCo_xC_y , SnSi_x and the like, here preferably silicon) or oxides of lithium-storing metals and metal alloys (for example, SnO_x , SiO_x , oxidic glasses of Sn, Si and the like) or a lithium intercalation material that does not comprise carbon, such as lithium titanates, in particular $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Conversion materials such as transition metal oxides can also be used as lithium-storing materials.

30

A further advantageous development of the battery cell according to the invention provides that the discharge element of the negative electrode is designed as a planar discharge element 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
35 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 in the charged state of the battery cell, 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, 25 mAh/cm².

Furthermore, there is also the possibility for the discharge element of the negative electrode 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, that is, metallic lithium, can be deposited into the pores of the metal structure. The amount of active material deposited 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 used in organic lithium cells. A further advantageous embodiment provides that the area-specific capacity of the negative electrode in the charged state of the battery cell 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.

A further advantageous development of the battery cell according to the invention provides that the discharge element includes a 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.

Electrolyte

Advantageous developments of the rechargeable battery cell with regard to the SO_2 -based electrolyte are described below.

In a further advantageous embodiment of the rechargeable battery cells, 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; preferably from C_2 - C_4 alkyl; particularly preferably from the alkyl groups 2-propyl, methyl and ethyl;
- C_2 - C_6 alkenyl; preferably from C_2 - C_4 alkenyl; particularly preferably from the alkenyl groups ethenyl and propenyl;
- C_2 - C_6 alkynyl; preferably from C_2 - C_4 alkynyl;
- C_3 - C_6 cycloalkyl;
- phenyl; and
- C_5 - C_7 heteroaryl.

In the case of this advantageous embodiment of the SO_2 -based electrolyte, the term " C_1 - C_6 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.

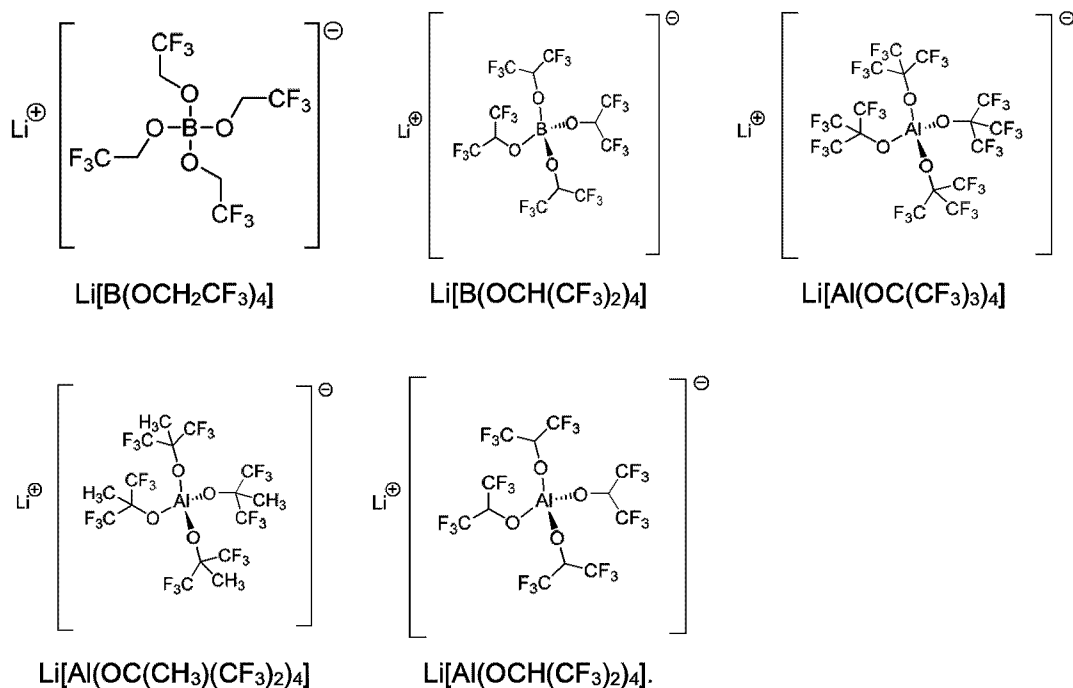
In the case of this advantageous embodiment of the SO₂-based electrolyte, the term "C₃-C₆ cycloalkyl" includes cyclic saturated hydrocarbon groups having three to six carbon atoms. These include in particular cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

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, vinyl ethylene carbonate and its derivatives, methylethylene 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, 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 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 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 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 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 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,
- (ii) 0.6 to 95% by weight of the first conducting salt,
- 5 (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.

Positive electrode

10

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

15 An advantageous development of the rechargeable battery cell according to the invention provides that the positive electrode can be charged at least up to an upper potential of 4.0 volts, preferably up to a potential of 4.4 volts, more preferably of at least a potential of 4.8 volts, more preferably at least up to a potential of 5.2 volts, more preferably at least up to a potential of 5.6 volts and most preferably at least up to a potential of 6.0 volts.

20 In a further advantageous development of the rechargeable battery cell according to the invention, the positive electrode comprises at least one active material. Said material can store ions of the active metal and release and take up the ions of the active metal during operation of the battery cell.

25 In a further advantageous development of the rechargeable battery cell according to the invention, the positive electrode comprises at least one intercalation compound. In the sense of the present invention, the term "intercalation compound" refers to a sub-category of the insertion materials described above. Said intercalation compound acts as a host matrix, which has vacancies that are interconnected. The ions of the active metal can dif-
 30 fuse 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.

35 In a further advantageous development of the rechargeable battery cell according to the invention, the positive electrode comprises at least one conversion compound as the ac-

5 tive material. In the sense of the present invention, the term "conversion compounds" refers to materials which form other materials during electrochemical activity; that is, chemical bonds are broken and re-established during charging and discharging of the battery cell. Structural changes occur in the matrix of the conversion compound during the absorption or release of the ions of the active metal.

In a further advantageous development of the rechargeable battery cell according to the invention, the active material has the composition $\text{Li}_x\text{M}'_y\text{M}''_z\text{O}_a$, wherein

- 10 – M' is at least one metal selected from the group formed by the elements Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn;
- M'' is at least one element 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;
- 15 – x and y independently of one another are numbers greater than 0;
- z is a number greater than or equal to 0; and
- a is a number greater than 0.

The indices y and z in the composition $\text{Li}_x\text{M}'_y\text{M}''_z\text{O}_a$ relate to the totality of metals and elements that are represented by M' and M'', respectively. If, for example, M' comprises two metals M'¹ and M'², the following applies to the index y: $y=y_1+y_2$, wherein y₁ and y₂ represent the indices of the metals M'¹ and M'². The indices x, y, z and a must be chosen such that there is charge neutrality within the composition. Examples of compounds in which M' comprises two metals are lithium nickel manganese cobalt oxides of the composition $\text{Li}_x\text{Ni}_{y_1}\text{Mn}_{y_2}\text{Co}_z\text{O}_a$ with M'¹=Ni, M'²=Mn and M''=Co. Examples of compounds in which z=0, that is, which have no further metal or element M'', are lithium cobalt oxides $\text{Li}_x\text{Co}_y\text{O}_a$.

For example, if M'' comprises two elements, on the one hand, a metal M''¹ and on the other hand, phosphorus as M''², the following applies to the index z: $z=z_1+z_2$, wherein z₁ and z₂ represent the indices of the metal M''¹ and of phosphorus (M''²). The indices x, y, z and a must be chosen such that there is charge neutrality within the composition. Examples of compounds in which M'' comprises a metal M''¹ and phosphorus as M''² are lithium iron manganese phosphates $\text{Li}_x\text{Fe}_y\text{Mn}_{z_1}\text{P}_{z_2}\text{O}_4$ with M'=Fe, M''¹=Mn and M''²=P and z₂=1. In a further composition, M'' can comprise two non-metals, for example, fluorine as M''¹ and sulfur as M''². Examples of such compounds are lithium iron fluorosulfates $\text{Li}_x\text{Fe}_y\text{F}_{z_1}\text{S}_{z_2}\text{O}_4$ with M'=Fe, M''¹=F and M''²=P.

A further advantageous development of the rechargeable battery cell according to the invention provides that M' consists of the metals nickel and manganese and M" is cobalt. These can be compositions of the formula $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_w\text{O}_2$ (NMC), that is, lithium nickel
manganese cobalt oxide having the structure of layered oxides. Examples of these lithium
 5 nickel manganese cobalt oxide active materials are $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111), $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811). Further compounds of lithium nickel manganese cobalt oxide can have the composition $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$, $\text{LiNi}_{0.5}\text{Mn}_{0.25}\text{Co}_{0.25}\text{O}_2$, $\text{LiNi}_{0.52}\text{Mn}_{0.32}\text{Co}_{0.16}\text{O}_2$, $\text{LiNi}_{0.55}\text{Mn}_{0.30}\text{Co}_{0.15}\text{O}_2$, $\text{LiNi}_{0.58}\text{Mn}_{0.14}\text{Co}_{0.28}\text{O}_2$,
 10 $\text{LiNi}_{0.64}\text{Mn}_{0.18}\text{Co}_{0.18}\text{O}_2$, $\text{LiNi}_{0.65}\text{Mn}_{0.27}\text{Co}_{0.08}\text{O}_2$, $\text{LiNi}_{0.7}\text{Mn}_{0.2}\text{Co}_{0.1}\text{O}_2$, $\text{LiNi}_{0.7}\text{Mn}_{0.15}\text{Co}_{0.15}\text{O}_2$, $\text{LiNi}_{0.72}\text{Mn}_{0.10}\text{Co}_{0.18}\text{O}_2$, $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$, $\text{LiNi}_{0.86}\text{Mn}_{0.04}\text{Co}_{0.10}\text{O}_2$, $\text{LiNi}_{0.90}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$, $\text{LiNi}_{0.95}\text{Mn}_{0.025}\text{Co}_{0.025}\text{O}_2$ or a combination thereof. Positive electrodes for rechargeable battery cells having a cell voltage of over 4.6 volts can be produced using these compounds.

15 A further advantageous development of the rechargeable battery cell according to the invention provides that the active material is a metal oxide which is rich in lithium and manganese (lithium and manganese-rich oxide material). These materials can be described with the following formulas: $\text{Li}_x\text{Mn}_y\text{M}''_z\text{O}_a$. M' of the formula $\text{Li}_x\text{M}'_y\text{M}''_z\text{O}_a$ described above thus represents the metal manganese (Mn). The index x here is greater than or equal to 1,
 20 the index y is greater than the index z or greater than the sum of the indices $z_1+z_2+z_3$ etc. For example, if M" comprises two metals M"¹ and M"² with the indices z_1 and z_2 (for example, $\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}\text{O}_2$ with M"¹=Ni $z_1=0.175$ and M"²=Co $z_2=0.1$), the following applies for the index y: $y > z_1+z_2$. The index z is greater than or equal to 0 and the index a is greater than 0. The indices x, y, z and a must be chosen such that there is charge neutrality within the composition. Metal oxides which are rich in lithium and manganese can
 25 also be described by the formula

$m\text{Li}_2\text{MnO}_3 \cdot (1-m)\text{LiM}'\text{O}_2$ with $0 < m < 1$. Examples of such compounds are

$\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}\text{O}_2$, $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ or $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$.

30 A further advantageous development of the rechargeable battery cell according to the invention provides that the composition has the formula $\text{Li}_x\text{M}'_y\text{M}''_z\text{O}_4$. These compounds are spinel structures. For example, M' can be cobalt, and M" manganese. In this case, the active material is lithium cobalt manganese oxide (LiCoMnO_4). LiCoMnO_4 can be used to produce positive electrodes for rechargeable battery cells having a cell voltage of over 4.6
 35 volts. This LiCoMnO_4 is preferably free of Mn^{3+} . In a further example, M' can be nickel and M" can be manganese. In this case, the active material is lithium nickel manganese oxide

(LiNiMnO₄). The molar proportions of the two metals M' and M'' can vary. Lithium nickel manganese oxide can, for example, have the composition LiNi_{0.5}Mn_{1.5}O₄.

In a further advantageous development of the rechargeable battery cell according to the invention, the positive electrode comprises at least one active material which constitutes a conversion compound. Conversion compounds undergo a solid-state redox reaction during the absorption of the active metal, for example, lithium or sodium, in which the crystal structure of the material changes. This occurs by breaking and recombining chemical bonds. Completely reversible reactions of conversion compounds can be, for example, as follows:



Examples of conversion compounds are FeF₂, FeF₃, CoF₂, CuF₂, NiF₂, BiF₃, FeCl₃, FeCl₂, CoCl₂, NiCl₂, CuCl₂, AgCl, LiCl, S, Li₂S, Se, Li₂Se, Te, I and LiI.

In a further advantageous development of the battery cell according to the invention, the compound has the composition Li_xM'_yM''_{z1}M''_{z2}O₄, wherein M''₂ is phosphorus and z₂ has the value 1. The compound having the composition Li_xM'_yM''_{z1}M''_{z2}O₄ is a lithium metal phosphate. In particular, this compound has the composition Li_xFe_yMn_{z1}P_{z2}O₄.

Examples of lithium metal phosphates are lithium iron phosphate (LiFePO₄) or lithium iron manganese phosphates (Li(Fe_yMn_z)PO₄). An example of a lithium iron manganese phosphate is the phosphate of the composition Li(Fe_{0.3}Mn_{0.7})PO₄.

Lithium metal phosphates of other compositions can also be used for the battery cell according to the invention.

A further advantageous development of the rechargeable battery cell according to the invention provides that the positive electrode comprises at least one metal compound. This metal compound is selected from the group that is formed by a metal oxide, a metal halide and a metal phosphate. The metal of this metal compound is preferably a transition metal of the atomic numbers 22 to 28 of the periodic table of the elements, in particular cobalt, nickel, manganese or iron.

A further advantageous development of the rechargeable battery cell according to the invention provides that the positive electrode comprises at least one metal compound which has the chemical structure of a spinel, a layered oxide, a conversion compound or a polyanionic compound.

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

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
 10 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
 15 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
 20 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
 25 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 .

30

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
 35 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/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 positive 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 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.

30

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:

35

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 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 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 (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-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 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 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.

- 5 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;

- 15 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 the potential profile in volts [V] during two charge/discharge cycles as a function of the percentage charge of a test full cell having metallic lithium as the active material of the negative electrode, wherein the charge and discharge current is 0.1 mA/cm²;

Figure 7: shows the potential profile in volts [V] during two charge/discharge cycles as a function of the percentage charge of a test full cell having metallic lithium as the active material of the negative electrode, wherein an initialization cycle was performed before the two charge/discharge cycles and the charge and discharge current is 0.1 mA/cm²;

- Figure 8: shows the potential profile in volts [V] during two charge/discharge cycles as a function of the percentage charge of a test full cell having metallic lithium as the active material of the negative electrode, wherein an external pressure was applied to the cell, an initialization cycle was performed before the two charge/discharge cycles and the charge and discharge current is 0.1 mA/cm²;
- Figure 9: shows a negative electrode obtained after dismantling the second test full cell from Experiment 1;
- Figure 10: shows the potential profile in volts [V] during two charge/discharge cycles as a function of the percentage charge of a test full cell having metallic lithium as the active material of the negative electrode, wherein an initialization cycle was performed before the two charge/discharge cycles and the charge and discharge current is 0.5 mA/cm²;
- Figure 11: shows the potential profile in volts [V] during two charge/discharge cycles as a function of the percentage charge of a test full cell having metallic lithium as the active material of the negative electrode, wherein an initialization cycle was performed before the two charge/discharge cycles and the charge and discharge current is 1.0 mA/cm²;
- Figure 12: shows the cycle efficiency in % as a function of the number of cycles of a test full cell having metallic lithium as the active material of the negative electrode, wherein the charge and discharge current is 1.0 mA/cm²;
- Figure 13: shows the cycle efficiencies in % as a function of the number of cycles of three test full cells having metallic lithium as the active material of the negative electrode, wherein two test full cells comprised electrolyte 1 and one test full cell comprised a reference electrolyte;
- Figure 14: shows the conductivity in [mS/cm] of electrolyte 1 as a function of the concentration of compound 1;

Figure 15: shows the conductivity in [mS/cm] of electrolyte 3 as a function of the concentration of compound 3; and

Figure 16: shows the conductivity in [mS/cm] of 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 LiCoMnO₄.

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 so that it fills its pores uniformly 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 lithium as an active material.

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 housing wall. 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 [V3]). 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 [V4], [V5] and [V6]:

[V4] „I. Krossing, *Chem. Eur. J.* **2001**, 7, 490;

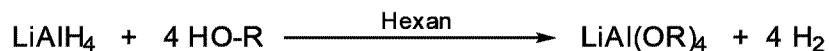
[V5] S. M. Ivanova et al., *Chem. Eur. J.* **2001**, 7, 503;

[V6] Tsujioka et al., *J. Electrochem. Soc.*, **2004**, 151, A1418“

30

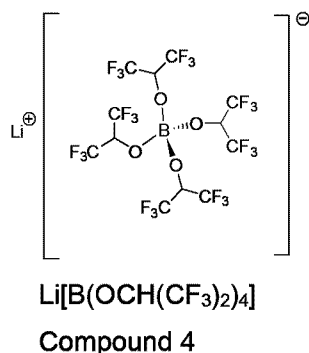
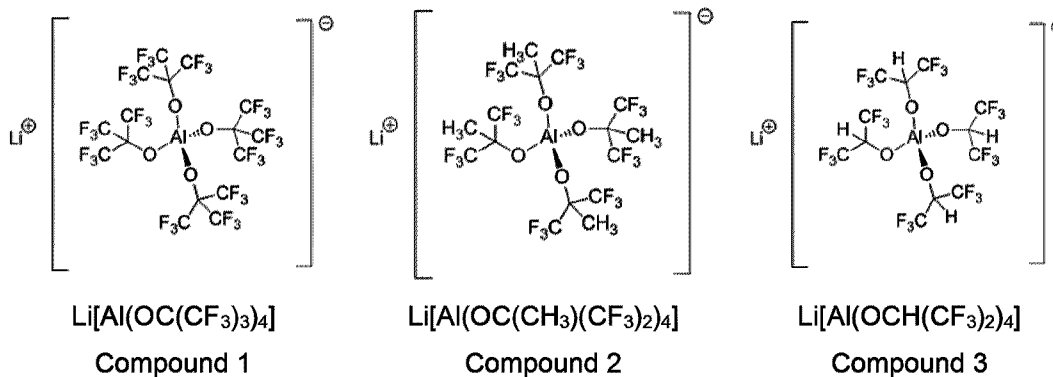
These four different, first conducting salts according to formula (I) are referred to below as compounds 1, 2, 3 and 4. They come from the family of polyfluoroalkoxyaluminates and were prepared in hexane according to the following reaction equation, starting from LiAlH₄ and the corresponding alcohol 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 active material of the positive electrode is named in the respective experiment. The negative electrodes comprised metallic lithium as the active material, which was deposited on the discharge element of the negative electrode or was already present. The discharge element of the positive and negative electrodes was made of nickel. The test full cells were each filled with the electrolyte required for the experiments, that is, ei-
 20 ther 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.

25

Example 4: Measurement in test full cells

Coating layer capacity:

The capacity consumed in the first cycle to form a coating layer on the negative electrode is an important criterion for the quality of a battery cell. This coating layer is formed on the
 30 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 (coating layer capacity), so that the test full cell has less cyclic capacity available for the subsequent cycles. The coating layer capacity in % of the theory that was used to form the coating layer on the negative elec-
 35 trode is calculated according to the following formula:

$$\text{Coating layer capacity [in \% of the theory]} = (Q_{\text{lad}} (x \text{ mAh}) - Q_{\text{ent}} (y \text{ mAh})) / Q_{\text{NEL}}$$

Q_{lad} describes the amount of charge specified in the respective experiment in mAh; Q_{ent} describes the amount of charge in mAh that was obtained when the test full cell was subsequently discharged. Q_{NEL} is the theoretical capacity of the negative electrode used. The theoretical capacity is calculated, for example, in the case of graphite, to a value of 372 mAh/g.

The nominal capacity is obtained by subtracting the coating layer capacity ($=Q_{\text{lad}} (x \text{ mAh}) - Q_{\text{ent}} (y \text{ mAh})$) from the theoretical capacity of the positive electrode.

Discharge capacity:

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 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 called I/U charging. This process is repeated depending on the desired number of cycles.

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 voltage/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.

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 battery is preferably discharged at a current rate of C/2 and at a temperature of 22°C. The discharge capacity is obtained from the discharge current and the time until the criteria for ending the discharge are fulfilled. The associated figures show mean values for the

discharge capacities 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 ratio of the discharge capacity Q_{ent} and the charge capacity Q_{lad} results in the cycle efficiency $Z = Q_{\text{ent}} / Q_{\text{lad}}$. The charge capacity is specified by the charge parameters. The

5 discharge capacity is determined for each cycle as described above.

Experiment 1: Cycles of test full cells using a charge and discharge current of 0.1 mA/cm²

Experiments in test full cells according to Example 3 were performed using metallic lithium
 10 as an active material of the negative electrode. The test full cells were filled with electrolyte 1 described in Example 2. The positive electrodes comprised lithium nickel manganese cobalt oxide as an active material. Two charge/discharge cycles were performed and the discharge capacities were determined. Two charge/discharge cycles were performed directly with the first test full cell. An initialization cycle was performed with the second test
 15 full cell before the two charge/discharge cycles. Metallic lithium was deposited for 3 min at 12 mA and further until the end of the charge at 0.1 mA/cm². This was followed by a discharge. The two charge/discharge cycles then started. The influence of external pressure was examined using the third test full cell. For this purpose, the housing of the test full cell was pressed together in a defined manner from the outside at a pressure of approx. 50
 20 N/cm². An initialization cycle was then performed as described for the second full test cell, followed by two charge/discharge cycles. The test full cells were charged at a current of 0.1 mA/cm² up to a potential of 4.4 volts and until a charge capacity of 8 mAh/cm² was reached. The discharge then took place at a current of 0.1 mA/cm² until a potential of 2.9 volts was reached.

25 Figures 6, 7 and 8 each show the potential in volts of the three test full cells during charging and discharging as a function of the charge in %, which is related to the maximum charge. The cycle efficiencies of the two cycles shown are also depicted for each test full cell in the figures.

30 All three test full cells show a similar potential profile in cycle 1 and cycle 2. The cycle efficiencies are over 90% for all test full cells and are somewhat better for the test full cells in which an initialization cycle was performed.

Experiment 2: Morphology of lithium deposition

The second test full cell from Experiment 1 was dismantled after a few cycles to determine the morphology of the deposited metallic lithium. Figure 9 shows this negative electrode in which a homogeneous and compact lithium deposition can be seen. No punctiform lithium deposits can be seen, rather, the entire electrode is evenly covered. This advantageous deposition of lithium indicates a good cycle stability of lithium in the electrolyte 1 used.

Experiment 3: Cycles of test full cells using a charge and discharge current of 0.5 mA/cm² and 1.0 mA/cm²

Two further test full cells were produced as described in Experiment 1 in order to investigate charging and discharging at higher currents. Two charge/discharge cycles were performed using a charge and discharge current of 0.5 mA/cm² with the first test full cell. The charge and discharge current was 1.0 mA/cm² in the second test full cell. Said cell was charged and discharged 21 times. An initialization cycle was performed for both test full cells before the charge/discharge cycles. The test full cells were charged at a current of 0.5 mA/cm² or 1.0 mA/cm² up to a potential of 4.4 volts and until a charge capacity of 8 mAh/cm² was reached. The discharge then took place at a current of 0.5 mA/cm² or 1.0 mA/cm² until a potential of 2.9 volts was reached.

Figures 10 and 11 each show the potential in volts of the two test full cells during charging and discharging as a function of the charge in %, which is related to the maximum charge. The cycle efficiencies of the two cycles shown are also depicted for each test full cell in Figures 10 and 11. Both full cells show a similar potential profile in cycle 1 and cycle 2. The cycle efficiencies are over 97% for both test full cells and are somewhat better for the test full cell operated at a current of 1 mA/cm². Further cycles were performed with this test full cell (1 mA/cm²). Figure 12 shows the cycle efficiency in % as a function of the number of cycles. The cycle efficiency shows a stable profile and approx. 95% is still achieved in cycle 21.

Experiment 4: Cycle efficiencies of test full cells having electrolyte 1 compared to test full cells having a reference electrolyte

In order to compare the cycle efficiencies of test full cells having electrolyte 1 with a test full cell having a reference electrolyte, test full cells having a reference electrolyte were first produced. The test full cells comprised lithium iron phosphate as the active material of the positive electrode and metallic lithium as the active material of the negative electrode. The test full cell comprised a reference electrolyte of the composition $\text{LiAlCl}_4 \times 6\text{SO}_2$. To prevent corrosion of lithium, that is, the loss in said electrolyte, fast charging and discharging rates of 7.5 mAh/cm^2 were selected. The test full cells were charged at this rate to a potential of 3.6 V and then discharged to a potential of 2.5 V . For comparison, the second test full cell from Experiment 1 (charge/discharge current 0.1 mA/cm^2) and the second test full cell from Experiment 3 (charge/discharge current 1 mA/cm^2), were used, both of which comprised electrolyte 1. Figure 13 shows the cycle efficiencies in % as a function of the number of cycles of the first four charge/discharge cycles of the test full cell using a charge/discharge current of 0.1 mA/cm^2 , the first seven charge/discharge cycles of the test full cell using a charge/discharge current of 1 mA/cm^2 and the first seven charge/discharge cycles of the test full cell having the reference electrolyte. The cycle efficiencies of the test full cells having electrolyte 1 show a very stable profile. The first test full cell achieves a cycle efficiency of 98% after four cycles, the second test full cell a cycle efficiency of 92% after seven cycles. The test full cell having the reference electrolyte shows much worse behavior. It achieves a cycle efficiency of only approx. 68% in cycle 7.

Experiment 5: Determination of the conductivities of electrolytes 1, 3 and 4

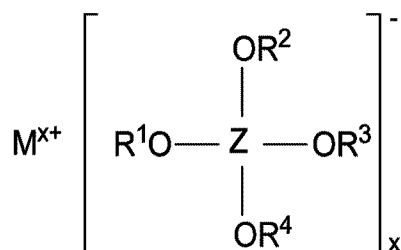
To determine the conductivity, electrolytes 1, 3 and 4 were prepared using different concentrations of compounds 1, 3 and 4. The conductivities of the electrolytes were determined using a conductive measurement method for each concentration of the various compounds. After temperature control, a two-electrode sensor was held touching in the solution and measured in a measuring range of $0\text{--}50 \text{ mS/cm}$. During the measurements, it was noted that the sensor can react with the SO_2 -containing electrolyte solution. Figure 14 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 $0.6 \text{ mol/L} - 0.7 \text{ mol/L}$ having a value of approx. 37.9 mS/cm . In comparison, the organic

electrolytes known from the prior art, such as LP30 (1 M LiPF_6 / EC-DMC (1:1 weight)) have a conductivity of only approx. 10 mS/cm.

Figures 15 (electrolyte 3) and 16 (electrolyte 4) show the conductivity values for electrolyte 3 and electrolyte 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.

Claims

1. A rechargeable battery cell (2, 20, 40) comprising an active metal, at least one positive electrode (4, 23, 44) having a discharge element (26), at least one negative electrode (5, 22, 45) having a second discharge element (27), a housing (1, 28) and an electrolyte, the negative electrode (5, 22, 45) comprising metallic lithium as an active material at least in the charged state of the rechargeable battery cell, and the electrolyte being based on SO₂ and comprising at least one first conducting salt which has the formula (I),



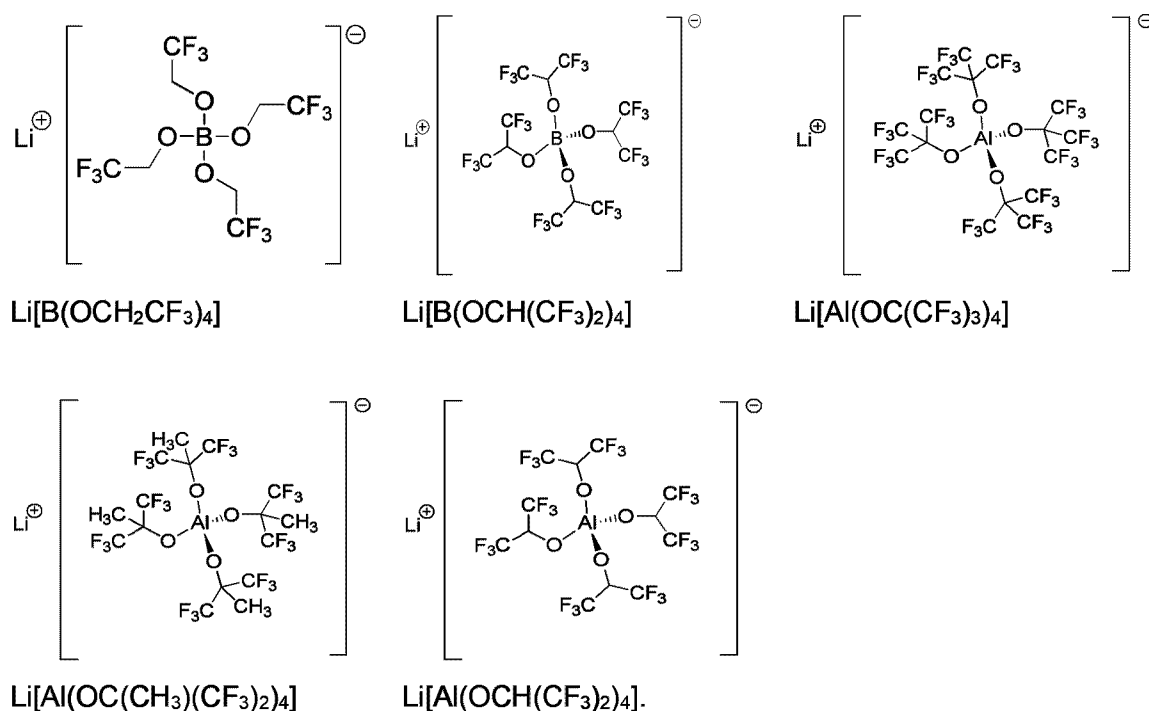
Formula (I)

- 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 metallic lithium is depositable on the discharge element (27) of the negative electrode (5, 22, 45) when the rechargeable battery cell is being charged.

3. The rechargeable battery cell (2, 20, 40) according to claim 1 or 2,
in which the metallic lithium is located on the discharge element (27) of the negative electrode (5, 22, 45) in the charged state of the rechargeable battery cell.
4. The rechargeable battery cell (2, 20, 40) according to any of claims 1 to 3,
in which the metallic lithium is already located on the discharge element (27) of the negative electrode (5, 22, 45) before the first charging of the rechargeable battery cell occurs.
5. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 4,
in which the discharge element (27) of the negative electrode (5, 22, 45) is designed
 - either planar in the form of a metal sheet or a metal foil, or
 - three-dimensional in the form of a porous metal structure.
6. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 6,
in which the discharge element (27) of the negative electrode (5, 22, 45) is formed at least partially from a lithium-storing material selected from the group formed by
 - Carbon,
 - a material which forms an alloy with lithium,
 - a lithium intercalation material that does not comprise carbon, and
 - a conversion material.
7. The rechargeable battery cell (2, 20, 40) according to claim 6,
in which the material which forms an active alloy with lithium is selected
 - from the group formed by lithium-storing metals and metal alloys consisting of Si, Ge, Sn, SnCo_xC_y and SnSi_x , or
 - from the group formed by oxides of lithium-storing metals and metal alloys.
8. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 7,
in which the positive electrode (4, 23, 44) comprises as active material at least one compound, said at least one compound has the composition $\text{Li}_x\text{M}'_y\text{M}''_z\text{O}_a$, wherein
 - M' is at least one metal selected from the group formed by the elements Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn;

- M'' is at least one element 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 and y independently of one another are numbers greater than 0;
 - z is a number greater than or equal to 0; and
 - a is a number greater than 0.
9. The rechargeable battery cell (2, 20, 40) according to claim 8, in which the compound has the composition $Li_xM'_yM''_zO_a$, in which M' is manganese and M'' is cobalt, and wherein x, y and z are equal to 1 and a is equal to 4.
10. The rechargeable battery cell (2, 20, 40) according to claim 8 or 9, in which the compound has the composition $Li_xM'_yM''_zO_a$, in which M' comprises nickel and manganese and M'' is cobalt and which has the formula $Li_xNi_{y1}Mn_{y2}Co_zO_a$.
11. The rechargeable battery cell (2, 20, 40) according to claim 8, in which the compound has the composition $Li_xM'_yM''^1_{z1}M''^2_{z2}O_4$, wherein M''^2 is phosphorus and $z2$ has the value 1.
12. The rechargeable battery cell (2, 20, 40) according to claim 11, in which the compound has the composition $Li_xM'_yM''^1_{z1}PO_4$, in which M' is iron and M''^1 is manganese.
13. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 12, 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_4 alkyl; 2-propyl, methyl and ethyl;
 - C_2 - C_6 alkenyl; C_2 - C_4 alkenyl; ethenyl and propenyl;
 - C_2 - C_6 alkynyl; C_2 - C_4 alkynyl;
 - C_3 - C_6 cycloalkyl;
 - phenyl; and
 - C_5 - C_7 heteroaryl.

14. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 13, in which at least one of the substituents R^1 , R^2 , R^3 and R^4 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 C_1 - C_4 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, phenyl and benzyl.
15. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 14, in which at least one of the substituents R^1 , R^2 , R^3 and R^4 of the first conducting salt is a CF_3 group or an OSO_2CF_3 group.
16. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 15, in which the first conducting salt is selected from the group formed by



17. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 16, wherein the electrolyte comprises at least one second conducting salt different from the first conducting salt according to formula (I).
18. The rechargeable battery cell (2, 20, 40) according to claim 17,

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 borate, a phosphate, an arsenate and a gallate.

19. The rechargeable battery cell (2, 20, 40) according to claim 17 or 18, in which the second conducting salt of the electrolyte is a lithium tetrahaloaluminate.
20. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 19, in which the electrolyte comprises at least one additive.
21. The rechargeable battery cell (2, 20, 40) according to claim 20, in which the additive of the electrolyte is selected from the group formed by vinylene carbonate and its derivatives, vinylethylene carbonate and its derivatives, methylethylene 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, 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.
22. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 21, 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.
23. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 22,

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.

24. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 23, in which the electrolyte comprises at least 0.1 mol SO₂ per mole of conducting salt.
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) comprises at least one metal compound which is selected from the group formed by a metal oxide, a metal halide and a metal phosphate, wherein the metal of the metal compound is a transition metal of atomic numbers 22 to 28 of the periodic table of the elements.
26. The rechargeable battery cell (2, 20, 40) according to any one of the claims 1 to 25, in which the positive electrode (4, 23, 44) comprises at least one metal compound which has the chemical structure of a spinel, a layered oxide, a conversion compound or a polyanionic compound.
27. The rechargeable battery cell (2, 20, 40) according to any one of the claims 1 to 26, in which the positive electrode (4, 23, 44) has a discharge element (34), 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.
28. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 27, in which the positive electrode (4, 23, 44) and/or the negative electrode (5) comprises at least one binder.
29. The rechargeable battery cell (2, 20, 40) according to claim 28, wherein the binder is 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 cellulose.

30. The rechargeable battery cell (2, 20, 40) according to claim 29, wherein the binder is present in a concentration of at most 20% by weight based on the total positive electrode weight.
31. The rechargeable battery cell (2, 20, 40) according to any one of claims 1 to 30, 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, 13, 21).

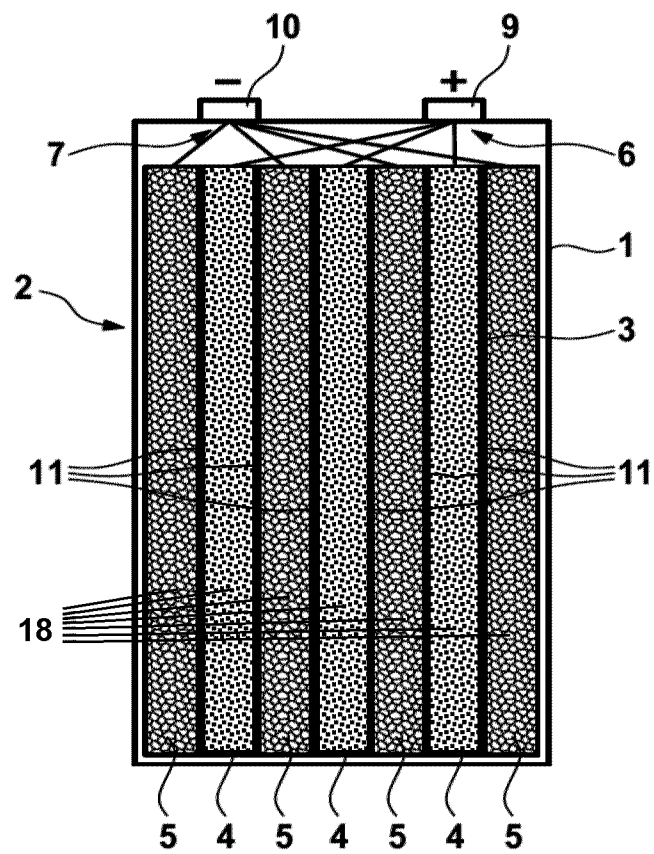


Fig. 1

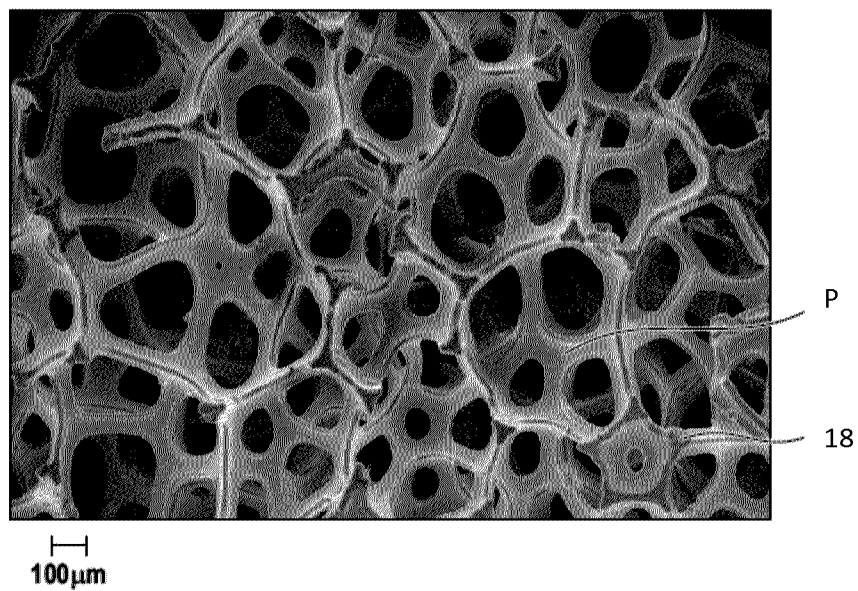


Fig. 2

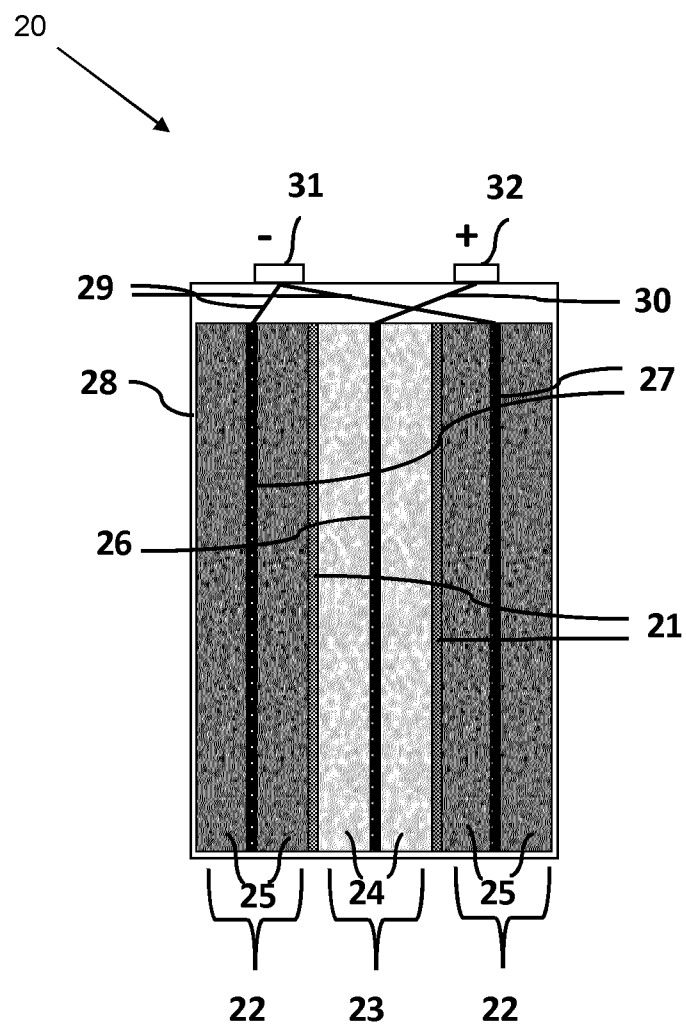


Fig. 3

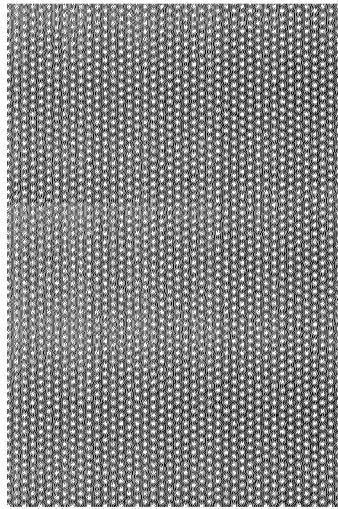


Fig. 4



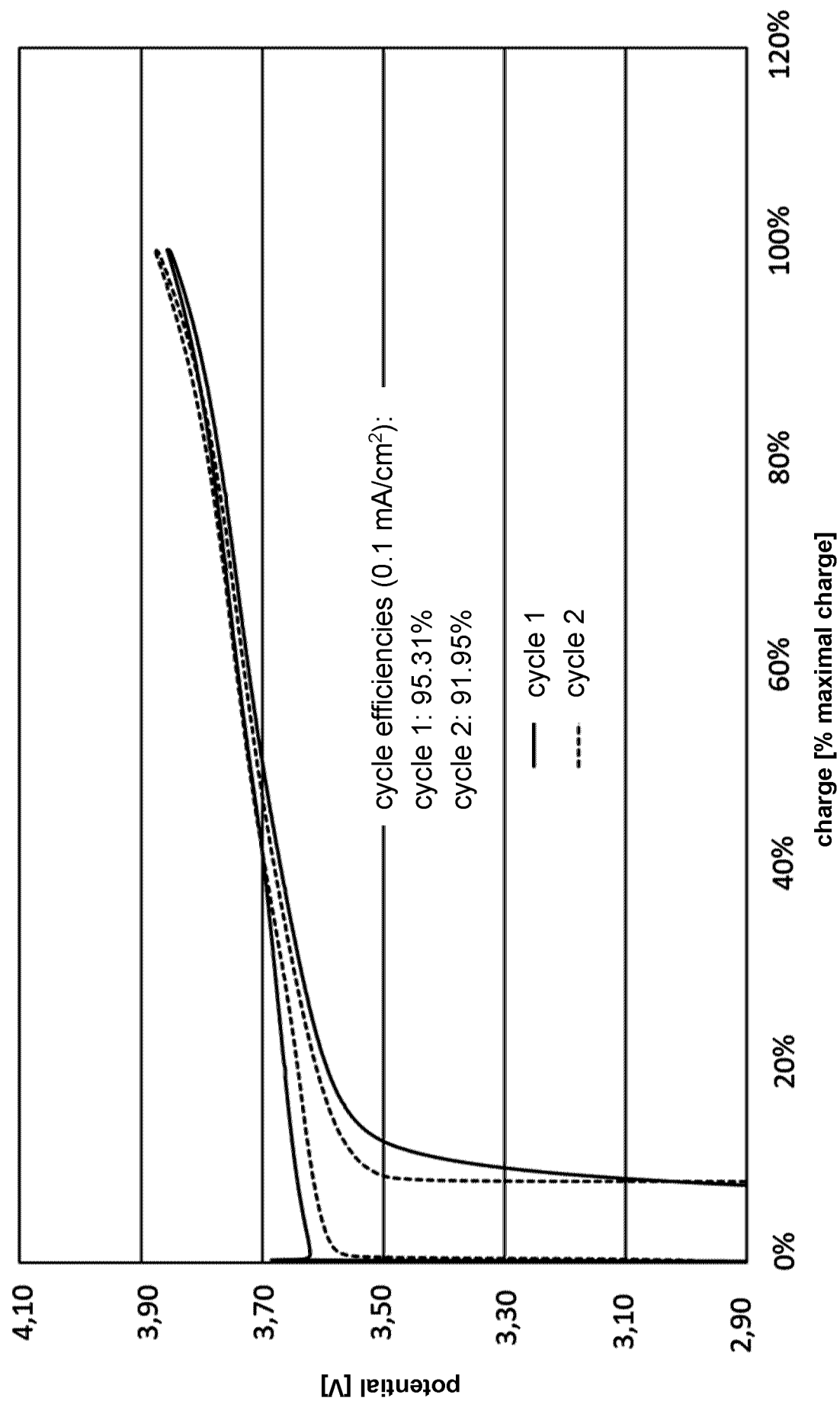


Fig. 6

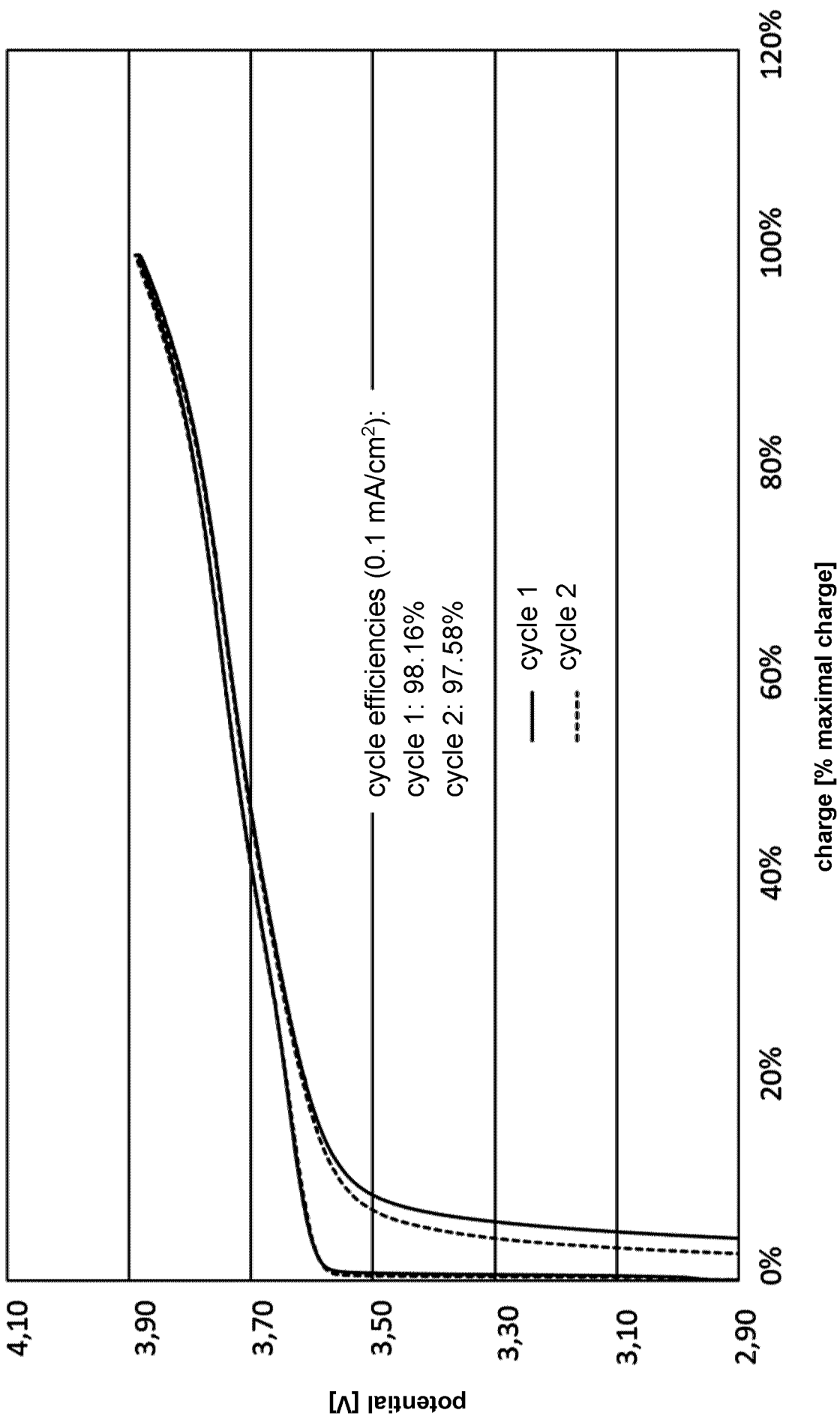


Fig. 7

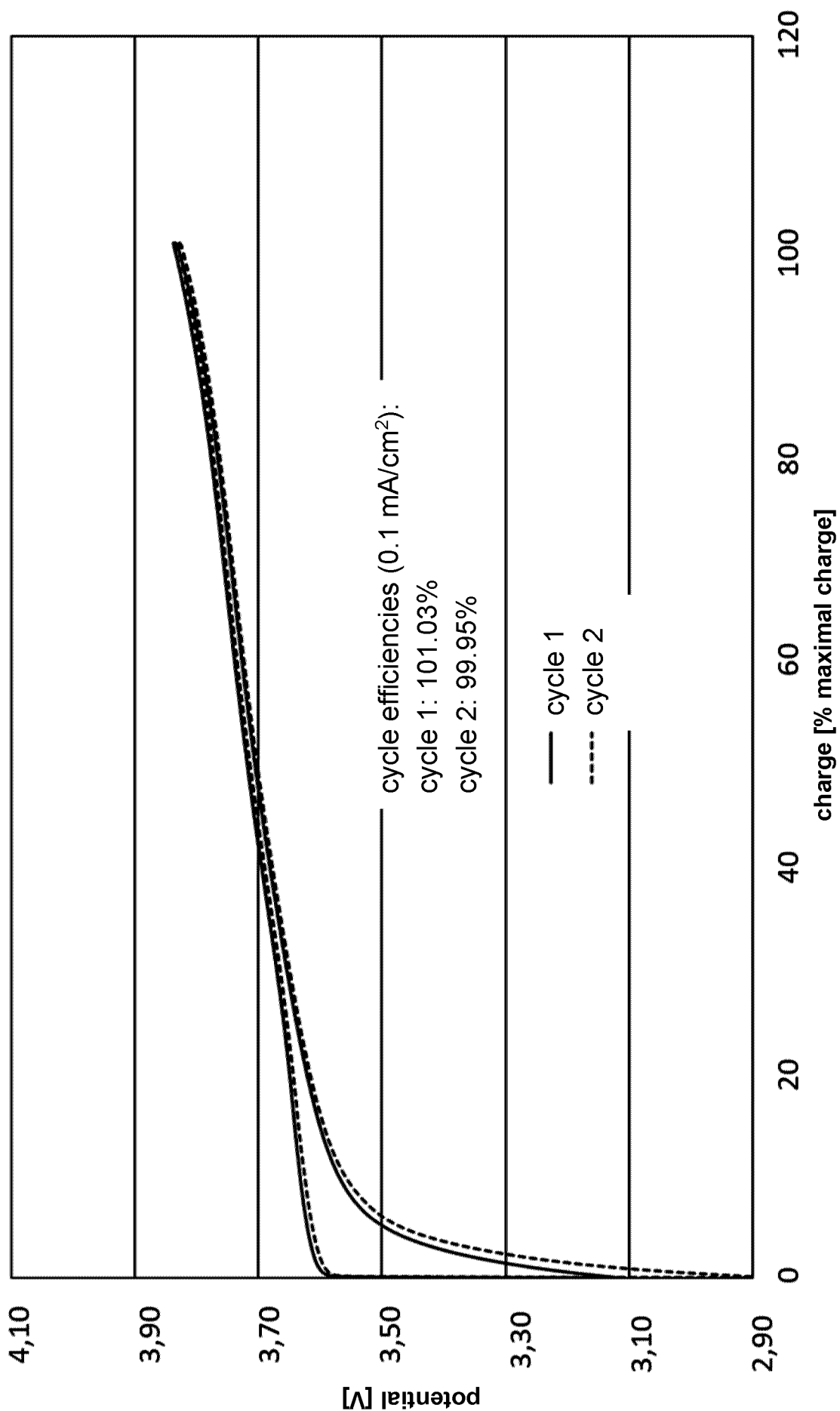


Fig. 8



Fig. 9

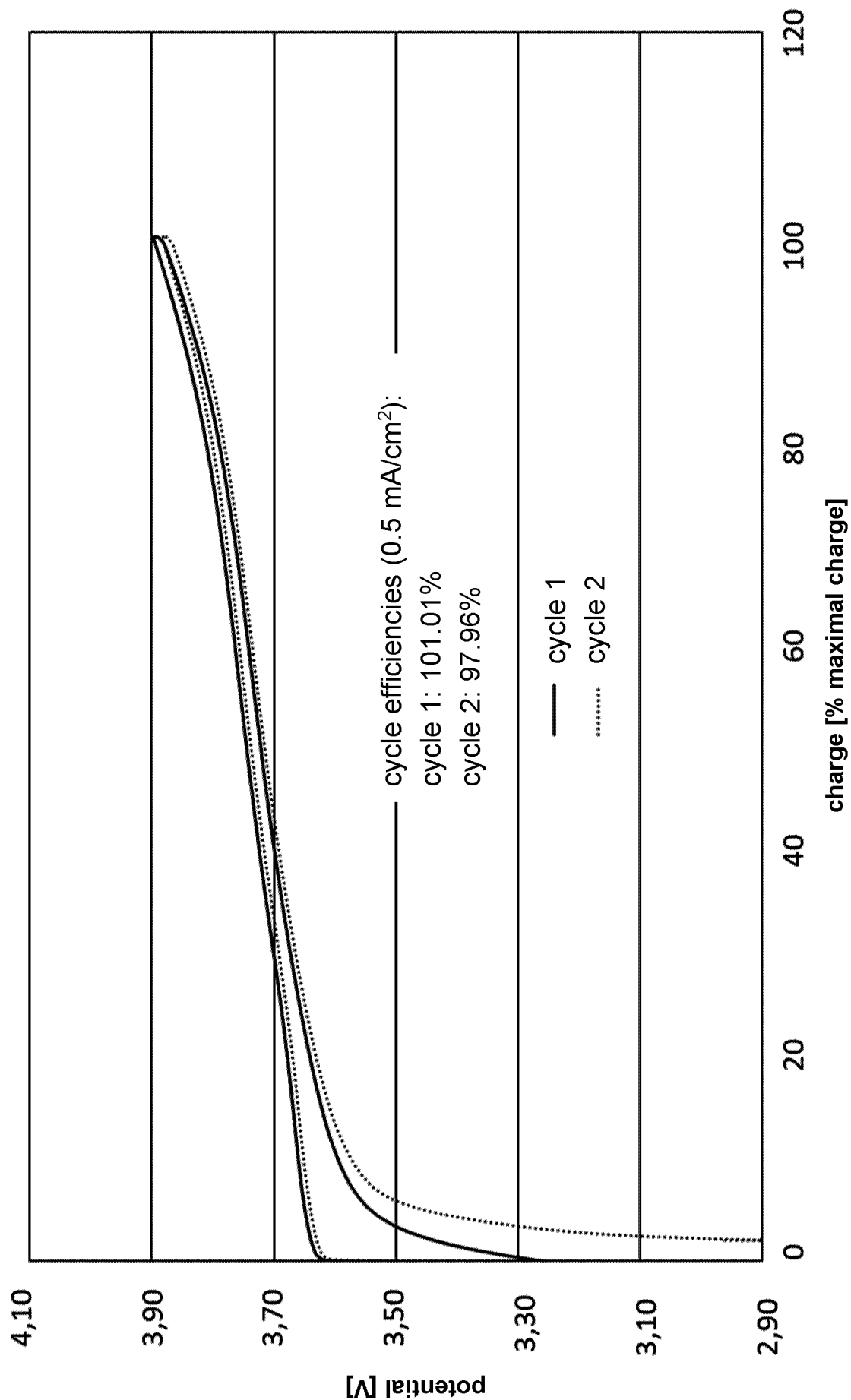


Fig. 10

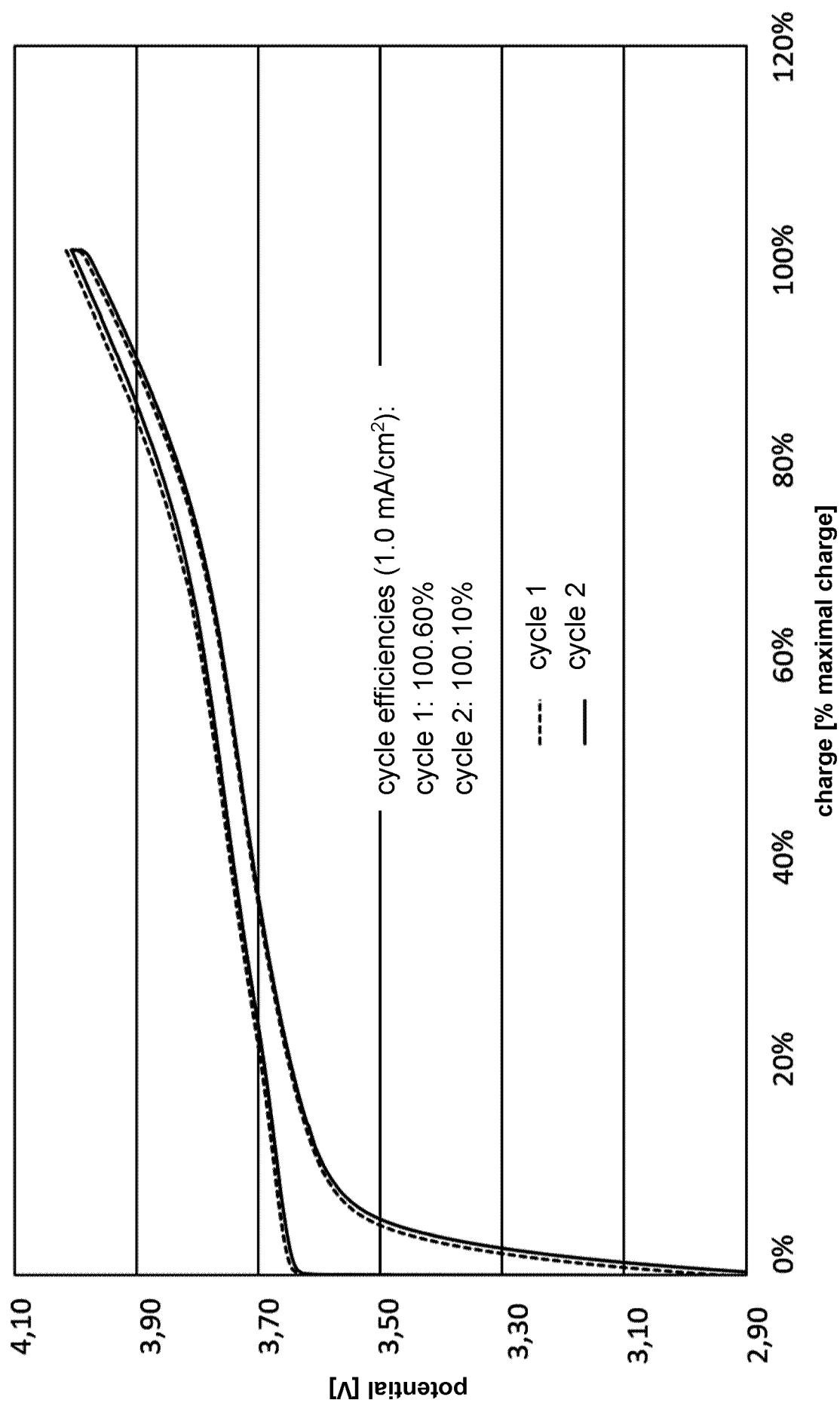


Fig. 11

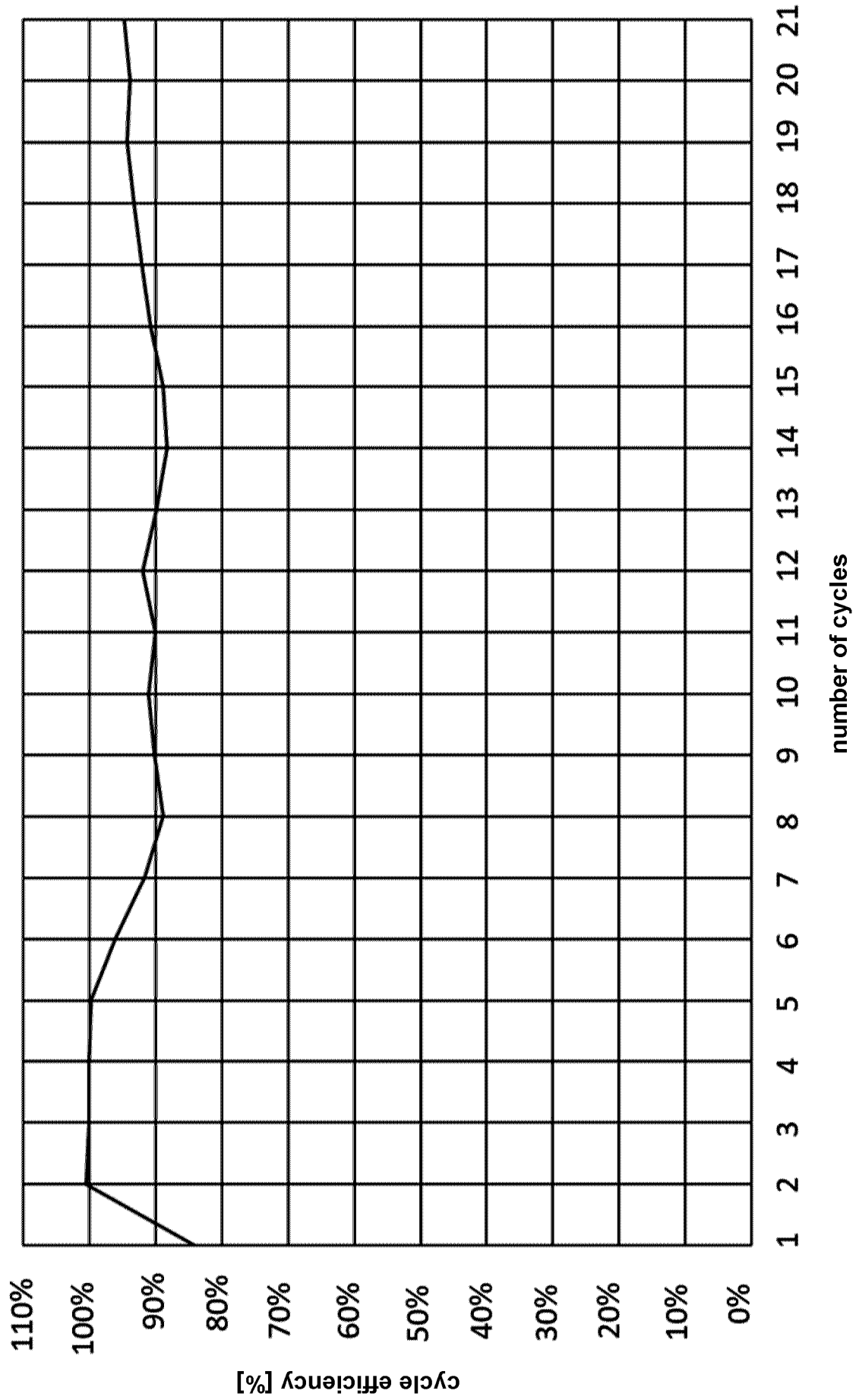


Fig. 12

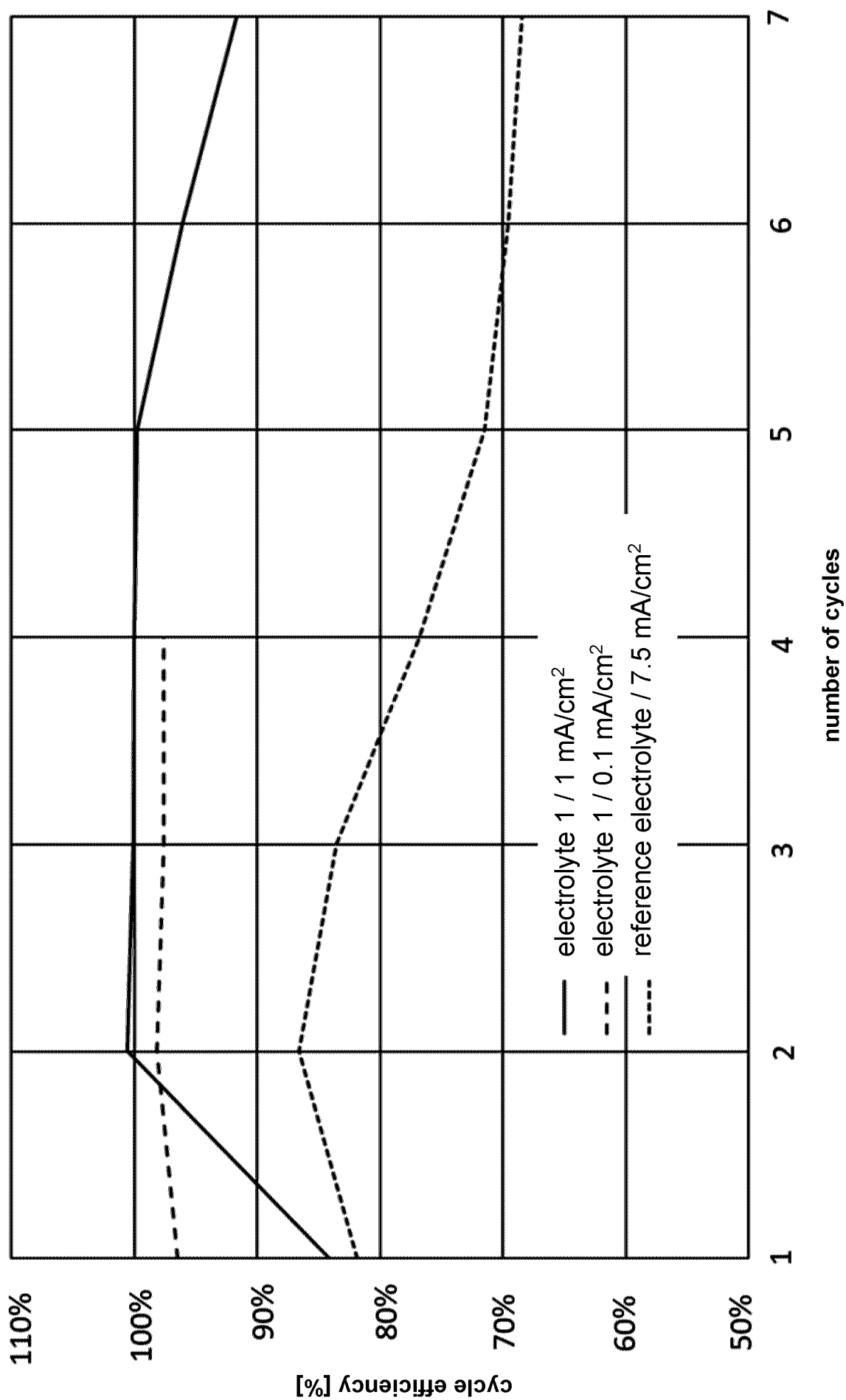


Fig. 13

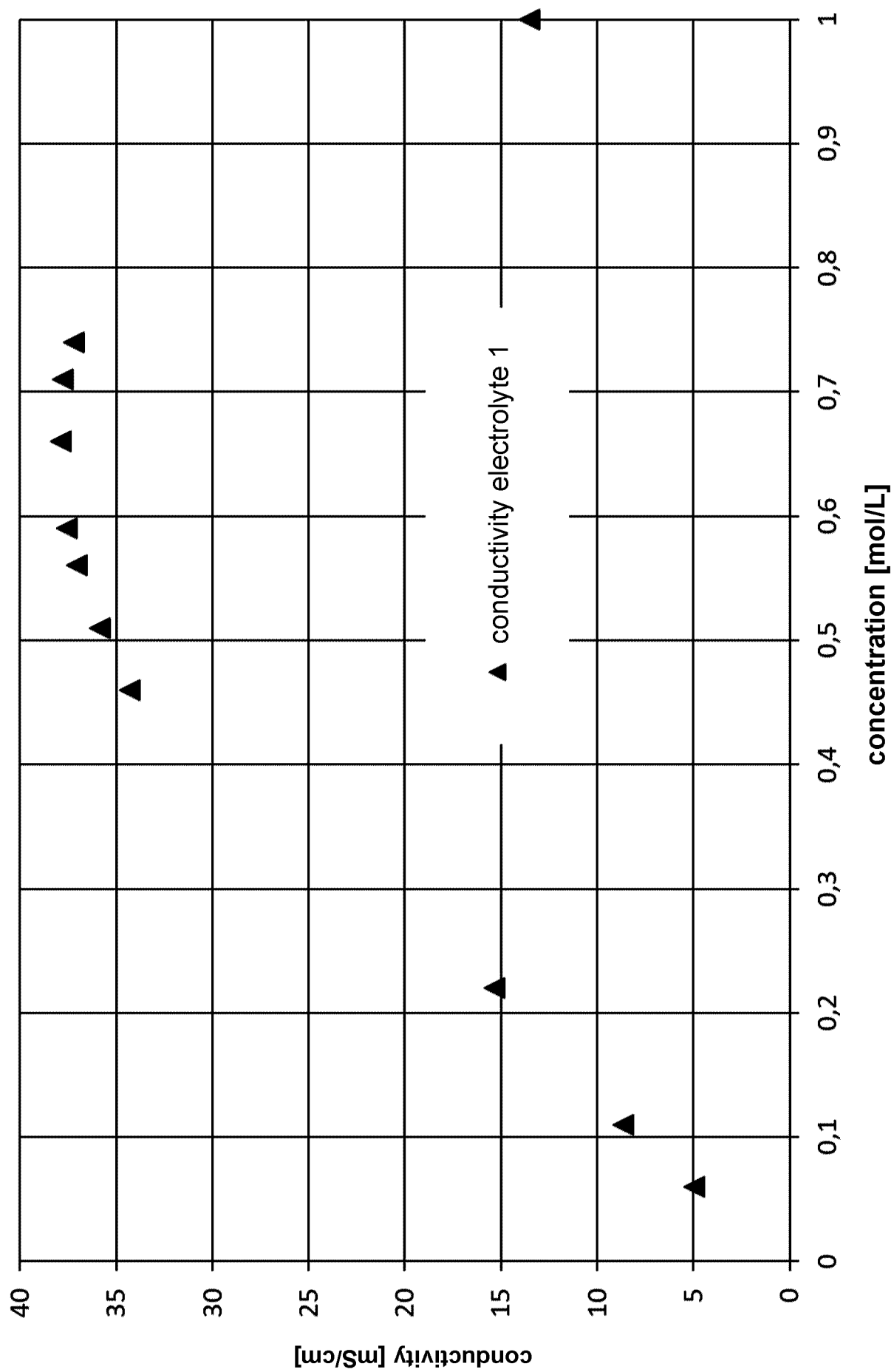


Fig. 14

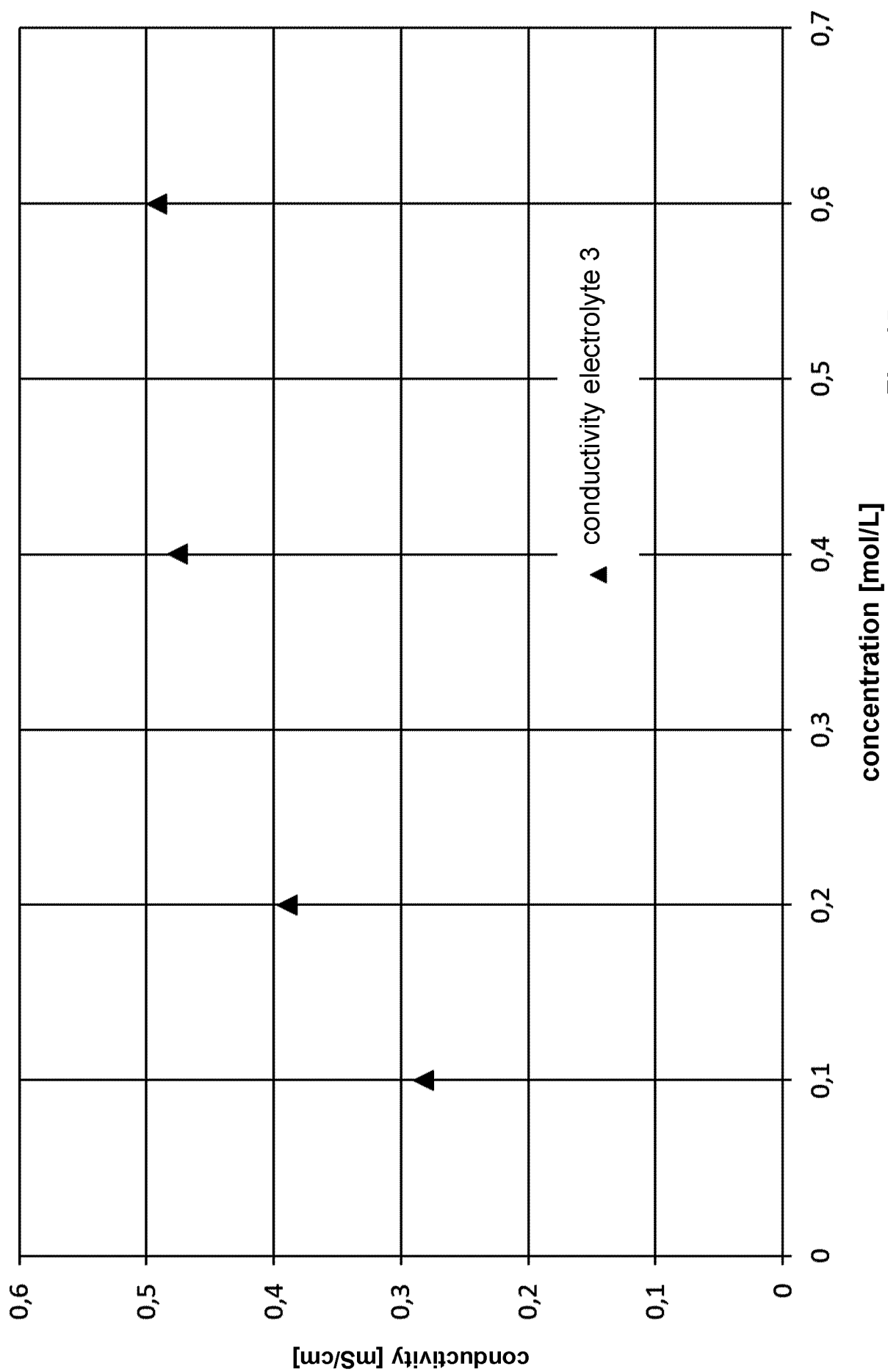


Fig. 15

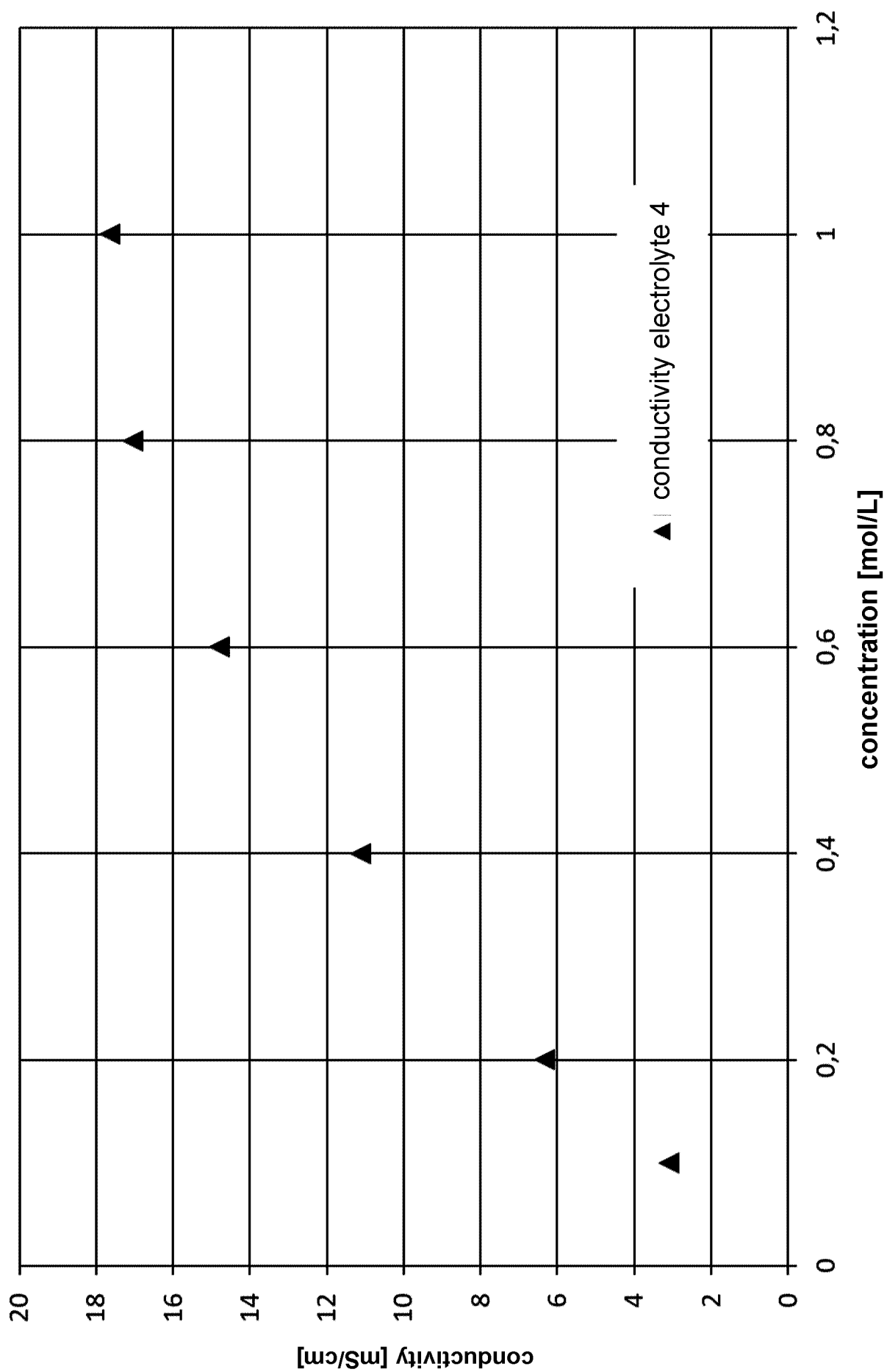
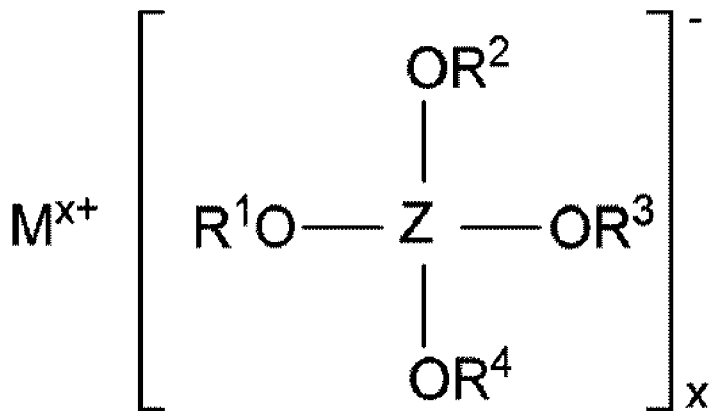


Fig. 16



Formula (I)