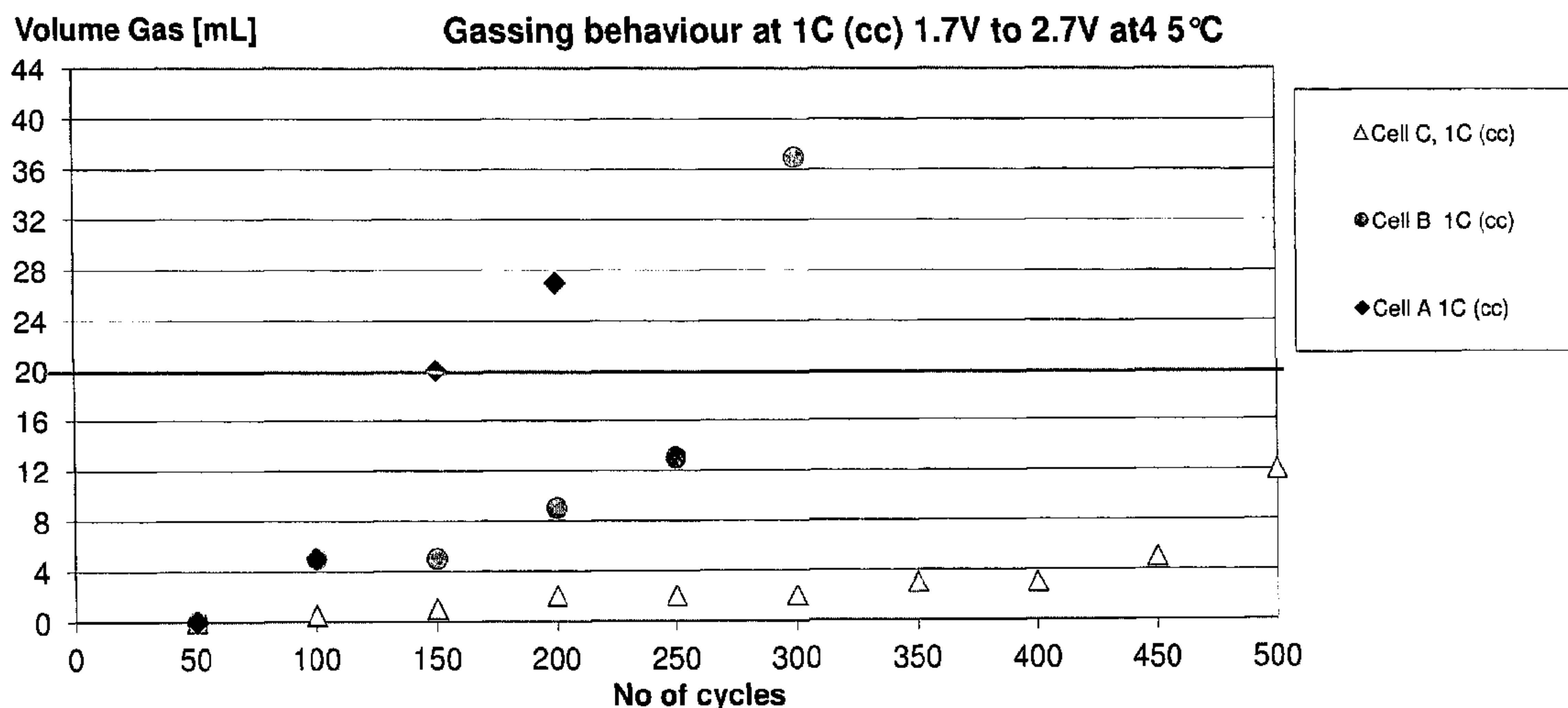




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(72) Inventeurs/Inventors:
LAUMANN, ANDREAS, DE;
HOLZAPFEL, MICHAEL, DE;
WENDRICH, GENOVEFA, DE
(73) Propriétaire/Owner:
JOHNSON MATTHEY PLC., GB
(74) Agent: SMART & BIGGAR

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(57) **Abrégé/Abstract:**

The present invention relates to a doped lithium titanium spinel with formula $\text{Li}_{4-y}\text{K}'_y\text{Ti}_{5-z}\text{K}''_z\text{O}_{12-x}\text{A}_x$ (I), wherein A is on or more anions selected from the group consisting I, N, Br, Cl, F, K', K'' are each one or more cations selected from the group consisting of Na, K, Cd, Se, Te, S, Sb, As, P, Pb, Bi, Hg, Si, C and $0 < x, y, z < 0.4$. Further, the present invention relates to an electrode comprising a layer of such lithium titanium spinel and a secondary non-aqueous electrolyte battery with such an electrode.

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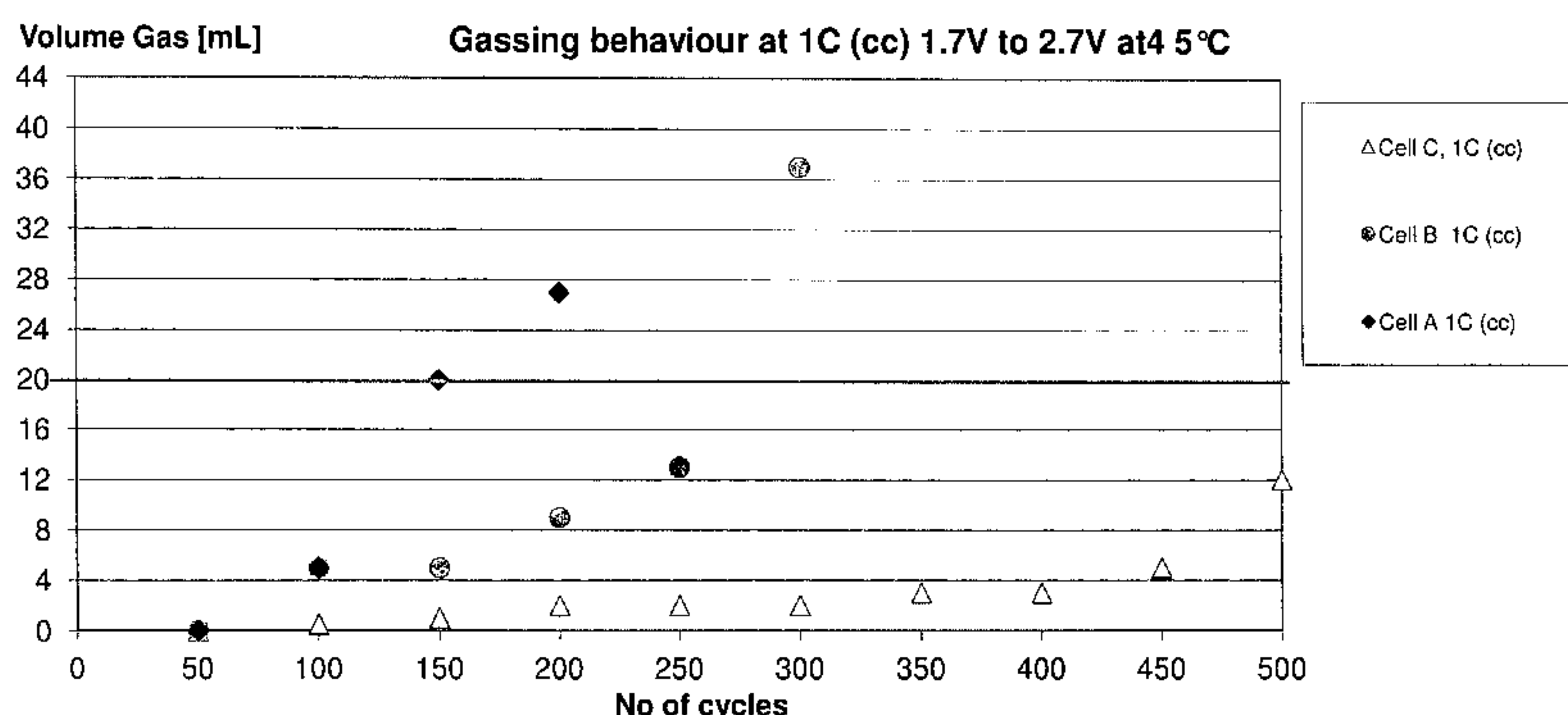
(71) Applicant: SÜD-CHEMIE IP GMBH & CO. KG
[DE/DE]; Lenbachplatz 6, 80333 München (DE).(72) Inventors: LAUMANN, Andreas; Nymphenburgerstr.
106, 80636 München (DE). HOLZAPFEL, Michael;
Friedhofstr. 21, 77694 Kehl (DE). WENDRICH, Genov-
efa; Lärchenstr. 9, 84051 Essenbach (DE).(74) Agent: STOLMÁR & PARTNER; Blumenstr. 17, 80331
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Figure 1



(57) Abstract: The present invention relates to a doped lithium titanium spinel with formula $I Li_{4-y} K'_y Ti_{5-z} K''_z O_{12-x} A_x$ (I), wherein A is on or more anions selected from the group consisting of I, N, Br, Cl, F, K', K'' are each one or more cations selected from the group consisting of Na, K, Cd, Se, Te, S, Sb, As, P, Pb, Bi, Hg, Si, C and $0 < x, y, z < 0.4$. Further, the present invention relates to an electrode comprising a layer of such lithium titanium spinel and a secondary non-aqueous electrolyte battery with such an electrode.

WO 2013/072059 A1

Standard secondary lithium ion batteries contain usually carbon-based anodes, mostly made of graphite. Carbon operates at a potential of 0 to 200 mV vs. Li/Li⁺. At these potentials no electrolyte solvent and salt known up to date is thermodynamically stable. Lithium batteries using graphite anodes can work with several thousand of cycles since during the first cycle the electrolyte at the solid liquid interface is reduced and the resulting species (polymeric species, lithium alkoxide carbonates, lithium alkoxides, lithium carbonate, lithium fluoride and lithium fluorophosphates) are forming a layer being insoluble in the electrolyte and electronically isolating but conductive for Li⁺. During this first cycle a part of the reduction products are also obtained as gases (CO, CO₂, H₂, CH₄, C₂H₄ etc.). Thus, generally speaking lithium ion batteries are submitted to this first slow formation cycle whereupon the layer (Solid Electrolyte Interface, SEI) is formed and gases are released only when the battery is hermetically sealed. During the following cycles the gas formation is low enough to permit thousands of cycles without excessive gas formation.

It appears that in the case of lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ or lithium titanium spinel) as active anode material the
aforedescribed situation appears to be different and more
5 complex.

The use of lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$, or lithium titanium spinel for short, in particular as a substitute for graphite as anode material in rechargeable lithium-ion batteries was
10 proposed some time ago.

The advantages of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ compared with graphite are in particular its better cycle stability, its better thermal rating and the higher operational reliability. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a
15 relatively constant potential difference of 1.56 V compared with lithium and achieves several 1000 charge/discharge cycles with a loss of capacity of < 20%.

Thus lithium titanate has a clearly more positive potential
20 than graphite which has previously usually been used as anode in rechargeable lithium-ion batteries.

However, the higher potential also results in a lower voltage difference. Together with a reduced capacity of 175 mAh/g
25 compared with 372 mAh/g (theoretical value) of graphite, this leads to a clearly lower energy density compared with lithium-ion batteries with graphite anodes.

However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a long life and is non-toxic and is
30 therefore also not to be classified as posing a threat to the environment. Also doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$, wherein the titanium sites have been doped with metals has been proposed in CN 101877407.

Upon using lithium titanate as an anode, the formation of gas during the formation cycle was also observed. However, gassing can continue even after the formation and eventually last for hundreds and thousands of the cycles. This causes major problems in the so-called battery packs since the gassing in the hermetically sealed battery packs ends in blowing up the packs and finally destroying the battery packs after several hundreds of cycles. (see Jin et al. Argonne National Laboratory Presentation, May 9 to 13, 2011). This phenomenon leads also to a power fade mechanism as was shown for example in lithium titanium spinel/LiMn₂O₄ cells (Belharouak I., et al., 28th International Battery Seminar & Exhibit, Fort Lauderdale, Florida, March 15, 2011).

Lithium titanate shows as already described above a plateau at 1.56 V versus Li/Li⁺ and generally the lower potential limit for operation is set to 1.0 V vs. Li/Li⁺ (sometimes 1.2 V or even 1.5 V). At these potential it is believed that the electrolyte is stable and thus would not be reduced during its lifetime. As a result, lithium titanate is said to be an anode material which does not form an SEI. However, it was observed that there is indeed a reduction of electrolyte components taking place on the surface of lithium titanate. The gas formation of these cells is a major problem and a serious drawback for the lifetime of secondary ion lithium batteries containing lithium titanium spinel as anode material.

The gas formed is mainly, or to a large part, hydrogen which is also a safety risk. Possible sources of this hydrogen are remaining physisorbed humidity within the cell (in anode, separator, cathode or electrolyte) which is reduced to hydrogen, remaining chemisorbed water within the lithium titanate (LTO) itself, protons of the solvent molecules of the electrolyte. Various mechanisms may contribute to this effect:

The surface of LTO contains Ti-OH groups which show dehydroxylation behaviour similar to that of TiO_2 . Moreover, these surface groups may react with CO_2 to form surface carbonates. TiO_2 is known for its photocatalytic effects in various applications, e.g. the cleavage of water into H_2 and O_2 by sun-light or the decomposition of organic matter by sun-light. It can be assumed that the catalytic effect of TiO_2 surfaces can also be active without sun-light, even though with much reduced kinetics. In this case the amount of hydrogen formed should be proportional to the surface area of the LTO. Indeed, higher amounts of gas formed for fine particle materials can be found than for materials with a lower BET surface.

Further it is fairly impossible to prepare 100 % of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. Therefore, a small excess of lithium salt (as for example Li_2CO_3 or LiOH) is used to ensure that all TiO_2 will react (and rutile can almost be not detected by XRD), so that an excess of TiO_2 cannot interfere in the gas formation.

Also an interference of soluble metal species originating from the cathode materials is one further possible source gassing phenomena:

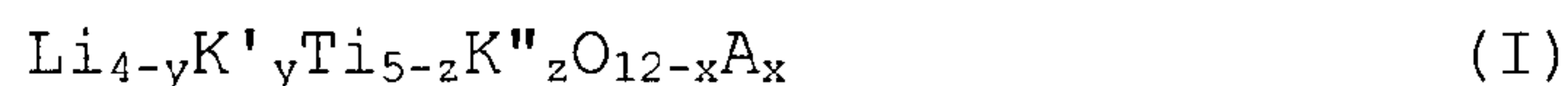
LiMn_2O_4 and, to a lesser amount, LiFePO_4 are known to release soluble Mn and Fe species into the electrolyte during operation as cathode active material. These soluble metal species can be reduced at the low potential of the anode (graphite and lithium titanate) to insoluble species as low-valent oxides or even metal on the surface of the anode material. Even for LiMeO_2 -based materials as LiCoO_2 , NMC and NCA such dissolution of metal traces cannot be excluded. See

also Dedryvère et al., JPCC 2009 (cited above), where a possible anodic reduction and deposition of organic species - which were oxidized on the cathode beforehand - is discussed.

- 5 The redeposited metal adds to the triple interphase lithium titanate, Al and electrolyte, at a potential of 1.0V vs. Li/Li⁺ and could increase hydrogen formation by a catalytic effect.

Therefore, the problem to be solved by the present invention was
 10 to provide a material suitable as an active electrode material based on lithium titanium spinel which does not show a gassing or at least a retarded or minimized gassing over the working lifetime of an electrode containing this active material.

- 15 In one aspect, the present invention relates to a lithium titanium spinel compound of formula (I)



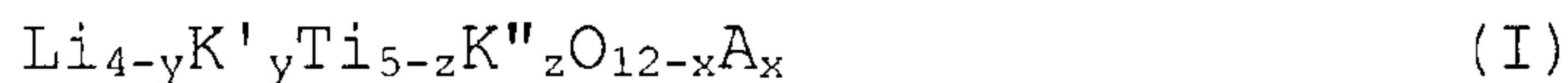
20 wherein

A is one or more anion(s) selected from the group consisting of I, N, Br, Cl, F,

- 25 K', K'' are each one or more cation(s) selected from the group consisting of Na, K, Cd, Se, Te, S, Sb, As, P, Pb, Bi, Hg, Si, C

and $0 \leq x, y, z \leq 0.4$.

In another aspect, the present invention relates to a doped lithium titanium spinel according to formula I



5 wherein K'' is one or more cation selected from the group consisting of S, Sb, As and P, and $0.01 \leq z \leq 0.1$.

In another aspect, the present invention relates to a doped lithium titanium spinel according to formula I

10



wherein K'' is one or more cation selected from the group consisting of Sb, As and P, and $0.02 \leq z \leq 0.07$.

15

In another aspect, the present invention relates to a doped lithium titanium spinel according to formula I



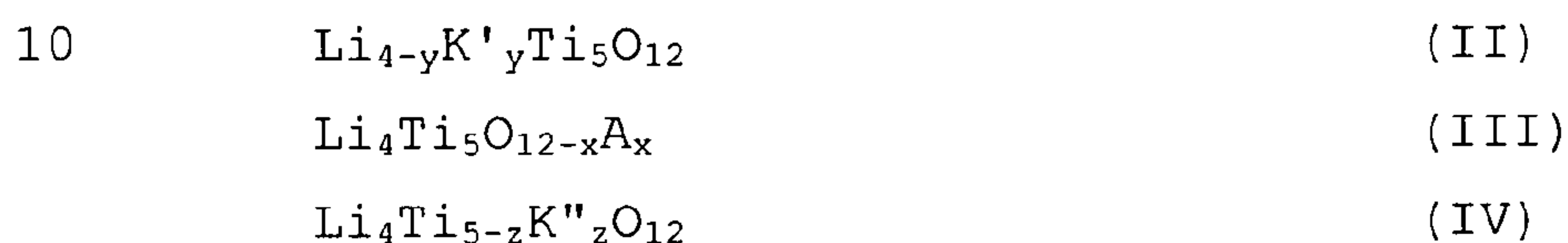
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wherein $0.02 \leq z \leq 0.07$.

The doping of the lithium titanium spinel according to the present invention can take place for the cations at the lithium positions
25 and/or the titanium positions or for the anions at the oxygen positions in the spinel crystal lattice.

In some embodiments of the invention, a doping is present not only at one of these positions but at two or even at three of these positions at the same time.

5 Further specific formulae of these aforementioned embodiments are in one aspect of the present invention compounds with formulae (II) to (IV) where doping occurs only at one position:



15 wherein $0 < x, y, z \leq 0.4$ and A, K', K'' are defined as in the foregoing.

In preferred embodiments of the present invention the amount of doping at the specific sites is $x = 0$, $z = 0$ and $y = 0.01$ to 0.2 . In further embodiments the values are $x = 0$, $y = 0$ and $z = 0.01$ to 0.2 , preferably z is in the range of 0.01 to 0.1 and still more preferred z is in the range of 0.02 to 0.07 .

In still further embodiments of the present invention the spinels with the above-mentioned formulae have the following dopant concentrations: $x = 0$, $z = 0$, $y = 0.01$ to 0.2 , preferably y is in the range of 0.01 to 0.1 and more preferred from 0.02 to 0.07 . In a further embodiment $x = 0.01$ to 0.2 , preferably 0.01 to 0.1 and more preferred from 0.02 to 0.07 and y and z are 0 .

30

In other aspects of the invention, doping is present at two positions described by formulae (V) to (VII):





5 with $0 < x, y, z \leq 0.4$ and A, K' and K'' defined as in the foregoing.

The lithium titanium spinels according to the formulae mentioned above have dopant concentration of $x = 0$ and y, z are in the range from 0.01 to 0.12, preferably from 0.01 to 10 0.1 and more preferred from 0.02 to 0.07, or $y = 0$ and y, z are in the ranges from 0.01 to 0.2, preferably from 0.01 to 0.1 and more preferred from 0.02 to 0.07. Alternatively $z = 0$ and x, y are in the range from 0.01 to 0.2, preferably from 0.01 to 0.1 and more preferred from 0.02 to 0.07.

15 Generally speaking, dopant concentrations for x, y and z in the range from 1000 to 20000 ppm are preferred for the purpose of the present invention, in more specific embodiments, the dopant concentration is 1000 to 8000 ppm, in still other 20 embodiments 2000 to 7500 ppm.

Surprisingly it was found that the doping according to the invention with dopants generally being considered as catalyst poisons does not lead to the drawbacks described for 25 transition metal doping of lithium titanate, like significant loss of reversible electric power generating capacity during a first charge-discharge cycle, or a loss in capacity as described in US 2011/0067230 and the presence of increased gassing during cycling.

30 Instead no loss of reversible electric power generating capacity during a first charge-discharge cycle and no loss in capacity compared to pure lithium titanate has been observed

with the compounds of the present invention when used as active anode material in secondary lithium ion batteries.

Also a significant loss in gassing compared to non-doped lithium titanate has been observed. It appears that the dopants can suppress the formation of hydrogen from the sources discussed above.

In embodiments of the invention K', K'' are each one or more cation(s) selected from the group consisting of wherein K', K'' are each one or more cation(s) selected from the group consisting of Na, K, Cd, S, Sb, As, P, Te, Se, C. Preferably K'' is selected from the group consisting of S, Sb, As, P, Te, Se, C, preferably Sb, As, P and C, still more preferred Sb, As and P.

In specific embodiments of the invention, the compound has the formula $\text{Li}_4\text{Ti}_{5-z}\text{Sb}_z\text{O}_{12}$. Specific compounds represented by this formula are $\text{Li}_4\text{Ti}_{4,99}\text{Sb}_{0,01}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,98}\text{Sb}_{0,02}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,975}\text{Sb}_{0,025}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,95}\text{Sb}_{0,05}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,9}\text{Sb}_{0,1}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,85}\text{Sb}_{0,15}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,8}\text{Sb}_{0,2}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,75}\text{Sb}_{0,25}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,5}\text{Sb}_{0,5}\text{O}_{12}$. Especially preferred are $\text{Li}_4\text{Ti}_{4,98}\text{Sb}_{0,02}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,975}\text{Sb}_{0,025}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,95}\text{Sb}_{0,05}\text{O}_{12}$.

The doped lithium titanate according to the invention is phase-pure. The term "phase-pure" or "phase-pure lithium titanate" means according to the invention that no rutile phase can be detected in the end-product by means of XRD measurements within the limits of the usual measurement accuracy. In other words, the lithium titanate according to the invention is essentially rutile-free in this embodiment. The term "essentially" is understood such as that minor traces of rutile which might almost not be detected by standard XRD measurements are present in the product.

In still further embodiments of the invention the doped lithium titanium spinel is additionally doped with a further metal or transition metal selected from the group consisting of Fe, Co, V, Cr, Mn, Mg, Sc, Y, Zn, Al, Ga, Pt, Pd, Ru, Rh, Au, Ag, Cu or several of these which provides novel compounds with enhanced capacity when used as active electrode materials.

10 In particular, this object is achieved by the incorporation of metal ions Al, Mg, Ga, Fe, Co, Sc, Y, Mn, Ni, Cr, V or several of these ions, into the lattice structure. Aluminium is quite particularly preferred.

15 The synthesis of the doped lithium titanium spinels according to the invention is carried out either by conventional solid state synthesis by mixing and usually milling the starting materials and sintering at elevated temperatures or by sol-gel and even wet-chemical procedures. The dopant can also be introduced by physical means in the non-doped lithium titanate.

More specifically doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ according to the invention is obtained by means of a solid-state reaction between a titanium compound, typically TiO_2 , a lithium compound, typically Li_2CO_3 , and an oxide or hydroxide of the dopant element at high temperatures of over 750°C , as described in principle in: Cai et al. Int. J. Energy Research 2011, 35; 68-77 and Yi et al. J. Electrochem. Soc. 158 (3) A266-A274 (2011). Another possibility is the use of doped TiO_2 (Hashimoto et al. Jap. J. Appl. Phys. 2005, vol. 44, No. 12, pp 8269-8285) which gives access to doped lithium titanates where the titanium sites are doped. For the doping with anions, the (stoichiometric) use of corresponding Lithium salts like LiF, LiBr, LiCl and Li_2SO_4 has

been proven the most successful route (Yi et al, J. Phys. Chem Solids 71 (2010), 1236-1242). Doping with nitrogen was either carried out as proposed for TiO₂ by Hashimoto et al. in J. Appl. Phys. 44 (2), 8269-8285, 2005 or by the above mentioned
5 solid state reaction in the presence of hydrazine or urea compounds. S, N- and C-doping was also carried out in analogy to TiO₂ doping as described in Chen et al. Chem. Rev. 107, 2891-2959. S-doping can also be carried out in a solid state reaction using thiourea as sulfur source.

10

Alternatively, sol-gel processes for the preparation of doped Li₄Ti₅O₁₂ can also be used (DE 103 19 464 A1). Furthermore, preparation processes by means of flame spray pyrolysis are also known synthetic routes (Ernst, F.O. et al. Materials
15 Chemistry and Physics 2007, 101(2-3, pp. 372-378) as well as so-called "hydrothermal processes" in anhydrous media (Kalbac, M. et al., Journal of Solid State Electrochemistry 2003, 8(1) pp. 2-6).

20 The doped lithium titanium spinel according to the invention has a BET surface area (measured in accordance with DIN 66134) of 1-10 m²/g, preferably < 10 m²/g, still more preferably < 8 m²/g and quite particularly preferably < 5 m²/g. In a quite particularly preferred embodiment, typical values lie in the
25 range of 3-5 m²/g, more preferred 2-4 m²/g.

The primary particles (crystallites) of the doped lithium titanium spinel typically have a size of < 2 µm. It is important according to the invention that the primary
30 particles are small with the result that the current-carrying capacity and the cycle stability of an electrode containing the doped lithium titanium spinel according to the invention are particularly high.

In a further embodiment of the present invention, the particles of the doped lithium titanium spinel are coated with a carbon-containing layer to increase the conductivity of the doped lithium titanium spinel and to increase the rate capability of an electrode containing the doped lithium titanium spinel according to the invention as active material. Further, the processability of a carbon-coated lithium titanium spinel in the preparation of an electrode is improved compared to non-coated lithium titanium spinels.

10

The term "carbon-containing" is here understood to mean a pyrolytically obtained carbon material which forms by thermal decomposition of suitable precursor compounds. This carbon-containing material can also be described synonymously by the term "pyrolytic carbon".

15

The term "pyrolytic carbon" thus describes a preferably amorphous material of non-crystalline carbon. The pyrolytic carbon is, as already said, obtained from suitable precursor compounds by heating, i.e. by pyrolysis at temperatures of less than 1000°C, in other embodiments $\leq 850^{\circ}\text{C}$, in still further embodiments $\leq 800^{\circ}\text{C}$ and preferably $\leq 750^{\circ}\text{C}$.

20

At higher temperatures of in particular $>1000^{\circ}\text{C}$ an agglomeration of the particles of the lithium titanate spinel due to so-called "fusion" often occurs, which typically leads to a poor current-carrying capacity of the composite material according to the invention. It is important according to the invention in particular that a crystalline, ordered synthetic graphite does not form.

30

Typical precursor compounds for pyrolytic carbon are for example carbohydrates such as lactose, sucrose, glucose, starch, cellulose, glycols, polyglycols, polymers such as for

example polystyrene-butadiene block copolymers, polyethylene, polypropylene, aromatic compounds such as benzene, anthracene, toluene, perylene as well as all other compounds known to a person skilled in the art as suitable per se for the purpose
5 as well as combinations thereof. Particularly suitable mixtures are e.g. lactose and cellulose, all mixtures of sugars (carbohydrates) with each other. A mixture of a sugar such as lactose, sucrose, glucose, etc. and propanetriol is also preferred.

10

Either the layer of pyrolytic carbon can be deposited onto the particles of the doped lithium titanium spinel according to the invention compound by direct in-situ decomposition onto the particles brought into contact with the precursor compound
15 of pyrolytic carbon, or the carbon-containing layers are deposited indirectly via the gas phase, when a portion of the carbon precursor compound is first evaporated or sublimated and then decomposes. A coating by means of a combination of both decomposition (pyrolysis) processes is also possible
20 according to the invention.

The total carbon content of the carbon coated doped lithium titanium spinel according to the invention is preferably < 2 wt.-% relative to the total mass of composite material, still
25 more preferably < 1.6 wt.-%.

To synthesize such a carbon layer, typically, a slurry is formed from the doped lithium titanium spinel by adding an aqueous suspension (for example in the case of lactose, sucrose, cellulose etc) or a solution or the precursor per se
30 (for example benzene, toluene etc) in liquid form of one or more precursor compounds and the slurry is then usually first dried at a temperature of from 100 to 400°C.

The dried mixture can optionally also be compacted. The compacting of the dry mixture itself can take place as mechanical compaction e.g. by means of a roll compactor or a tablet press, but can also take place as rolling, build-up or
5 wet granulation or by means of any other technical method appearing suitable for the purpose to a person skilled in the art.

After the optional compacting of the mixture, in particular
10 the dried mixture, the mixture is sintered at $\leq 850^{\circ}\text{C}$, advantageously $\leq 800^{\circ}\text{C}$, still more preferably at $\leq 750^{\circ}\text{C}$, wherein the sintering takes place preferably under protective gas atmosphere, e.g. under nitrogen, argon, etc. Under the chosen conditions no graphite forms from the precursor
15 compounds for pyrolytic carbon, but a continuous layer of pyrolytic carbon which partly or completely covers the particles of the doped lithium titanium spinel compound does.

Although pyrolytic carbon still forms from the precursor
20 compound over a wider temperature range at higher sintering temperatures than described above, the particle size of the product formed increases through caking, which brings with it the disadvantages described above.

25 Nitrogen is used as protective gas during the sintering or pyrolysis for production engineering reasons, but all other known protective gases such as for example argon etc., as well as mixtures thereof, can also be used. Technical-grade nitrogen with low oxygen contents can equally also be used.
30 After heating, the obtained product can still be finely ground.

A further aspect of the present invention is an electrode, preferably an anode containing the lithium titanium spinel

according to the invention as active material. Typical further constituents of an electrode according to the invention (or in the so-called electrode formulation) are, in addition to the active material, also conductive carbon blacks as well as a
5 binder. According to the invention, however, it is even possible to obtain a usable electrode with active material containing or consisting of the lithium titanium spinel according to the invention without further added conductive agent (i.e. e.g. conductive carbon black), especially when
10 they are already carbon-coated. As already described before, the electrodes according to the invention using the doped lithium titanate according to the invention show a very low amount of gassing upon cycling.

15 Any binder known per se to a person skilled in the art can be used as binder, such as for example polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF), polyvinylidene difluoride hexafluoropropylene copolymers (PVDF-HFP), ethylene-propylene-diene terpolymers (EPDM),
20 tetrafluoroethylene hexafluoropropylene copolymers, polyethylene oxides (PEO), polyacrylonitriles (PAN), polyacryl methacrylates (PMMA), carboxymethylcelluloses (CMC), and derivatives and mixtures thereof.

25 Typical proportions of the individual constituents of the electrode material are preferably 90 parts by weight active material, e.g. of the lithium titanium spinel according to the invention, 5 parts by weight conductive carbon and 5 parts by weight binder. A different formulation likewise advantageous
30 within the scope of the present invention consists of 90 - 96 parts by weight active material and 4 - 10 parts by weight binder. The electrode comprises besides the support layer at least one layer consisting of or comprising the active material.

In further embodiments of the present invention the electrode is made such that the concentration of the doping agent (the dopant) in the layer consisting of or comprising lithium titanium spinel according to the invention is a gradient over the thickness of the layer. It is preferred that the concentration is highest at the surface and lowest at the support layer (usually an aluminium or titanium foil) but the other way round, i.e the inverse gradient is also within the scope of the present invention.

In a still further embodiment, the electrode containing a layer of doped lithium titanium spinel according to the invention further comprises at least one second layer of undoped lithium titanium spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$. This layer is either arranged on the layer of doped lithium titanium spinel or below. In still further embodiments also several layers of doped lithium titanium spinel and undoped lithium titanium spinel typically alternating may be envisaged.

A further object of the present invention is a secondary lithium-ion battery pack containing an electrode according to the invention as anode, with the result that the battery pack shows very reduced gassing over the lifetime of the battery. The use of such lithium-ion batteries according to the invention is thus also possible in particular in cars with simultaneously smaller dimensions of the electrode or the battery as a whole.

In developments of the present invention, the secondary lithium-ion battery according to the invention has as exemplary cathode/anode pairs $\text{LiFePO}_4 // \text{Li}_{4-y}\text{K}'_y\text{Ti}_{5-z}\text{K}''_z\text{O}_{12-x}\text{A}_x$ with a single cell voltage of approx. 2.0 V, which is well suited as substitute for lead-acid cells or $\text{LiCo}_a\text{Mn}_b\text{Fe}_c\text{PO}_4 //$

$\text{Li}_{4-y}\text{K}'_y\text{Ti}_{5-z}\text{K}''_z\text{O}_{12-x}\text{A}_x$ and further $\text{LiMn}_{2-a}\text{Ni}_{0+b}\text{O}_4$ $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$
(wherein x , y and z are as defined further above and $0 < a$ and
 $b \leq 0.7$) with increased cell voltage and improved energy
density.

5

The invention is explained in further detail by way of figures
and examples which should not be construed as limiting the
scope of the present invention.

10 Figure 1 shows the gassing of a doped lithium titanium spinel
according to the invention and of a non doped lithium
titanium spinel.

Figure 2 shows the cycling characteristics of an electrode
15 comprising $\text{Li}_4\text{Ti}_{4.75}\text{Sb}_{0.25}\text{O}_{12}$ as active material

General

20 1. Measurement methods

The BET surface area was determined according to DIN 66134.

The particle-size distribution was determined according to DIN
25 66133 by means of laser granulometry with a Malvern
Mastersizer 2000.

XRD spectra are received on an X-ray diffractometer Bruker D4
on $\text{CuK}[\alpha]$ radiation with Sol-X detector. All samples obtained
30 give well-defined spectra correspond to cubic structure (Space
Group Fd-3m (227)). Small amounts of residual TiO_2 (0.5%) are
present in most of the samples.

2. Experimental:

2.1 Preparation of doped lithium Titanium Spinel

5

LiOH·H₂O, Li₂CO₃ and TiO₂ in anatase or rutile form are used below as primary starting products. The water content in the case of commercially available LiOH·H₂O (from Merck) varies from batch to batch and was determined prior to synthesis.

10

2.1.1 Preparation of Li₄Ti_{5-z}Sb_zO₁₂

2.1.1.1 Solid State Method 1

15

a) Li₄Ti_{5-z}Sb_zO₁₂ samples were prepared by a solid state method from Sb₂O₃, TiO₂ and Li₂CO₃. Optionally the starting materials were milled (e.g. by a ball-mill, a jet-mill etc.) in a liquid medium (e.g. isopropanol) to form a slurry and dried. Optionally, the dry mixture can be granulated before sintering. In another embodiment the starting materials are only mixed and afterwards granulated. The dried and mixed reactant mixture was heated at 850°C for 24 h in air and then cooled down to room temperature. The resultant product was analyzed by X-Ray diffractometry measurements and Scanning Electron Microscopy (SEM). The typical size of the primary particles was around 200 nm. The particle size distribution measurements (including secondary particles, i.e. agglomerates) for the below mentioned compounds was: d₁₀₀: 7,5 µm, d₉₀: 4,7 µm, d₅₀: 2,3 µm, d₁₀: 0,9µm.

20

25

30

The following antimony doped lithium titanium spinels were synthesized by using 0,5 mol Li_2CO_3 , (1-a) mol TiO_2 and a/2 mol Sb_2O_3 :

5 $\text{Li}_4\text{Ti}_{4,99}\text{Sb}_{0,01}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,98}\text{Sb}_{0,02}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,975}\text{Sb}_{0,025}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,95}\text{Sb}_{0,05}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,9}\text{Sb}_{0,1}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,85}\text{Sb}_{0,15}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,8}\text{Sb}_{0,2}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,75}\text{Sb}_{0,25}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,5}\text{Sb}_{0,5}\text{O}_{12}$.

2.1.1.2 Solid State Method 2

10

b) $\text{Li}_4\text{Ti}_{5-z}\text{Sb}_z\text{O}_{12}$ samples were prepared by a solid state method from Sb-doped TiO_2 (prepared beforehand by the reaction of pure TiO_2 and Sb_2O_3 in the required amounts and reacted at 800°C for 24 h) and Li_2CO_3 . The starting materials were optionally milled in a liquid medium to form a slurry and dried. Optionally, the dry mixture can be granulated before sintering. The dried and mixed reactant mixture was heated at 850°C for 24 h in air and then cooled down to room temperature. The resultant product was analyzed by X-Ray diffractometry measurements and Scanning Electron Microscopy (SEM). The typical size of the primary particles was around 200 nm.

25 The following antimony doped lithium titanium spinels were synthesized by using 0,5 mol Li_2CO_3 , 5 mol Sb-doped TiO_2 :

$\text{Li}_4\text{Ti}_{4,99}\text{Sb}_{0,01}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,98}\text{Sb}_{0,02}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,975}\text{Sb}_{0,025}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,95}\text{Sb}_{0,05}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,9}\text{Sb}_{0,1}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,85}\text{Sb}_{0,15}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,8}\text{Sb}_{0,2}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,75}\text{Sb}_{0,25}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,5}\text{Sb}_{0,5}\text{O}_{12}$.

30

2.1.1.3 Combined Hydrothermal/Solid State Method

c) Further $\text{Li}_4\text{Ti}_{5-z}\text{Sb}_z\text{O}_{12}$ samples were prepared by a modified solid state method including a hydrothermal step from Sb-

doped TiO_2 (prepared beforehand by the reaction of pure TiO_2 and Sb_2O_3 in the required amounts and reacted at 800°C for 24 h) and Li_2CO_3 by first preparing a $\text{Li}_2\text{TiO}_3/\text{Ti}_{1-z}\text{Sb}_z\text{O}_2$ composite, alternatively a $\text{Li}_2\text{Ti}_{1-z}\text{Sb}_z\text{O}_3/\text{TiO}_2$ or still a $\text{Li}_2\text{Ti}_{(1-z)/2}\text{Sb}_z\text{O}_3/\text{Ti}_{(1-z)/2}\text{Sb}_z\text{O}_2$ composite as described for the non-doped composite in DE 10 2008 050 692.3 A1 by reaction of the Sb-doped TiO_2 in a LiOH solution. Alternatively, TiO_2 and Sb_2O_3 in the required stoichiometric amounts are reacted in LiOH solutions. The obtained composite was filtered, dried at 100°C to 200°C (or spray-dried) and then calcined at $750 \pm 20^\circ\text{C}$, preferably at $T \leq 750^\circ\text{C}$. The particle size distribution measurements (including secondary particles, i.e. agglomerates) for the below mentioned compounds was: d_{100} : $50\mu\text{m}$, d_{90} : $25\mu\text{m}$, d_{50} : $9\mu\text{m}$, d_{10} : $0,6\mu\text{m}$.

The following antimony doped lithium titanium spinels were synthesized by this method:

$\text{Li}_4\text{Ti}_{4,99}\text{Sb}_{0,01}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,975}\text{Sb}_{0,025}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,95}\text{Sb}_{0,05}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,9}\text{Sb}_{0,1}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,8}\text{Sb}_{0,2}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,75}\text{Sb}_{0,25}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,5}\text{Sb}_{0,5}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,3}\text{Sb}_{0,7}\text{O}_{12}$.

2.1.2 Preparation of $\text{Li}_4\text{Ti}_{5-z}\text{Cd}_z\text{O}_{12}$

$\text{Li}_4\text{Ti}_{5-z}\text{Cd}_z\text{O}_{12}$ samples were prepared by a solid state method from CdO , TiO_2 and Li_2CO_3 . The starting materials were ball-milled or mixed in an isopropanol liquid medium to form a slurry and dried. Optionally, the dry mixture can be granulated before sintering. The dried and mixed reactant mixture was heated at 850°C for 24 h in air and then cooled down to room

temperature. The resultant product was analyzed by X-Ray diffractometry measurements and Scanning Electron Microscopy (SEM).

- 5 The following cadmium doped lithium titanium spinels were synthesized by using 0,5 mol Li_2CO_3 , (1-a) mol TiO_2 and a mol CdO :

10 $\text{Li}_4\text{Ti}_{4,99}\text{Cd}_{0,01}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,95}\text{Cd}_{0,05}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,9}\text{Cd}_{0,1}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,8}\text{Sb}_{0,2}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,75}\text{Cd}_{0,25}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,5}\text{Cd}_{0,5}\text{O}_{12}$.

2.1.3 Preparation of $\text{Li}_4\text{Ti}_{5-z}\text{P}_z\text{O}_{12}$

$\text{Li}_4\text{Ti}_{5-z}\text{P}_z\text{O}_{12}$ samples were prepared by a solid state method from
 15 P_2O_5 (alternatively $(\text{NH}_4)_4\text{P}_2\text{O}_5$ or $(\text{NH}_4)_4\text{P}_2\text{O}_7$ were used), TiO_2 and Li_2CO_3 . The starting materials were ball-milled or mixed in an isopropanol liquid medium to form a slurry and dried. Optionally, the dry mixture can be granulated before sintering. The dried and mixed reactant mixture was heated at
 20 850°C for 24 h in air and then cooled down to room temperature. The resultant product was analyzed by X-Ray diffractometry measurements and Scanning Electron Microscopy (SEM).

- 25 The following phosphorus doped lithium titanium spinels were synthesized by using 0,5 mol Li_2CO_3 , (1-a) mol TiO_2 and a/2 mol P_2O_5 (or one of the abovementioned salts):

30 $\text{Li}_4\text{Ti}_{4,99}\text{P}_{0,01}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,9}\text{P}_{0,1}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,8}\text{P}_{0,2}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,75}\text{P}_{0,25}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,5}\text{P}_{0,5}\text{O}_{12}$.

2.1.4 Preparation of $\text{Li}_4\text{Ti}_{5-z}\text{As}_z\text{O}_{12}$

$\text{Li}_4\text{Ti}_{5-z}\text{As}_z\text{O}_{12}$ samples were prepared by a solid state method from As_2O_3 , TiO_2 and Li_2CO_3 . The starting materials were ball-milled
5 or mixed in an isopropanol liquid medium to form a slurry and dried. Optionally, the dry mixture can be granulated before sintering. The dried and mixed reactant mixture was heated at 850°C for 24 h in air and then cooled down to room temperature. The resultant product was analyzed by X-Ray
10 diffractometry measurements and Scanning Electron Microscopy (SEM).

The following arsenic doped lithium titanium spinels were synthesized by using 0,5 mol Li_2CO_3 , (1-a) mol TiO_2 and a/2 mol
15 As_2O_3 :

$\text{Li}_4\text{Ti}_{4,99}\text{As}_{0,01}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,98}\text{As}_{0,02}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,95}\text{As}_{0,05}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,9}\text{As}_{0,1}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,85}\text{As}_{0,15}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,8}\text{As}_{0,2}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,75}\text{As}_{0,25}\text{O}_{12}$,
20 $\text{Li}_4\text{Ti}_{4,5}\text{As}_{0,5}\text{O}_{12}$.

2.1.5 Preparation of $\text{Li}_4\text{Ti}_{5-z}\text{Bi}_z\text{O}_{12}$

$\text{Li}_4\text{Ti}_{5-z}\text{Bi}_z\text{O}_{12}$ samples were prepared by a wet chemical method as follows:

25 tetra-butyl titanate was dissolved in de-ionized water under cooling for the formation of a white precipitate $\text{TiO}(\text{OH})_2$ which was then dissolved by nitric acid to form a limpid titanyl nitrate solution. Stoichiometric amounts of lithiumacetate and
30 bismuth nitrate were added to the solution. The solution was evaporated to dryness and the resulting solid was dried, milled in a planetary mill and calcined at 900°C for 12h in air. The resultant product was analyzed by X-Ray

diffractometry measurements and Scanning Electron Microscopy (SEM).

The following bismuth doped lithium titanium spinels were
5 synthesized by this method:

$\text{Li}_4\text{Ti}_{4,99}\text{Bi}_{0,01}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,95}\text{Bi}_{0,05}\text{O}_{12}$, $\text{Li}_4\text{Ti}_{4,75}\text{Bi}_{0,25}\text{O}_{12}$,
 $\text{Li}_4\text{Ti}_{4,5}\text{Bi}_{0,5}\text{O}_{12}$.

10

2.1.6 Preparation of $\text{Li}_{4-y}\text{Na}_y\text{Ti}_5\text{O}_{12}$

$\text{Li}_{4-y}\text{Na}_y\text{Ti}_5\text{O}_{12}$ samples were prepared by a solid state method from K_2CO_3 , TiO_2 and Li_2CO_3 . The starting materials were optionally
15 ball-milled or mixed in an ethanol liquid medium to form a slurry and dried. Optionally, the dry mixture can be granulated before sintering. The dried and mixed reactant mixture was heated at 850°C for 24 h in air and then cooled down to room temperature. The resultant product was analyzed
20 by X-Ray diffractometry measurements and Scanning Electron Microscopy (SEM).

The following sodium doped lithium titanium spinels were
25 synthesized by using 0,5-b mol Li_2CO_3 , b mol Na_2CO_3 , 1 mol TiO_2 :

$\text{Li}_{3,99}\text{Na}_{0,01}\text{Ti}_5\text{O}_{12}$, $\text{Li}_{3,95}\text{Na}_{0,05}\text{Ti}_5\text{O}_{12}$, $\text{Li}_{3,9}\text{Na}_{0,1}\text{Ti}_5\text{O}_{12}$, $\text{Li}_{3,8}\text{Na}_{0,2}\text{Ti}_5\text{O}_{12}$,
 $\text{Li}_{3,75}\text{Na}_{0,25}\text{Ti}_5\text{O}_{12}$, $\text{Li}_{3,5}\text{Na}_{0,5}\text{Ti}_5\text{O}_{12}$.

30 *2.1.7 Preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{Cl}_x$*

a) solid state

Li₄Ti₅O_{12-x}Cl_x samples were prepared by a solid state method from LiCl, TiO₂ and Li₂CO₃. The starting materials were ball-milled. Optionally, the dry mixture can be granulated before sintering. The reactant mixture was heated at 850°C for 24 h
 5 in air and then cooled down to room temperature. The resultant product was analyzed by X-Ray diffractometry measurements and Scanning Electron Microscopy (SEM).

The following chlorine doped lithium titanium spinels were
 10 synthesized by using 0,5-b mol Li₂CO₃, 1 mol TiO₂ and b mol LiCl:

Li₄Ti₅O_{11,99}Cl_{0,01}, Li₄Ti₅O_{11,95}Cl_{0,05}, Li₄Ti₅O_{11,93}Cl_{0,07},
 Li₄Ti₅O_{11,9}Cl_{0,1}, Li₄Ti₅O_{11,8}Cl_{0,2}, Li₄Ti₅O_{11,75}Cl_{0,25}, Li₄Ti₅O_{11,7}Cl_{0,3},
 15 Li₄Ti₅O_{11,6}Cl_{0,4}, Li₄Ti₅O_{11,5}Cl_{0,5}.

20 b) Sol-gel

Cl-doped lithium titanium spinels were prepared by evaporating sol synthesized from commercial Titanium (III) chloride solution, Lithiumoxalate, dehydrated ethanol and 2 N HCl (1:
 25 0,8:2,2 : 0,21 mol ratio). The sol was evaporated at different temperatures below 100°C. The powders obtained from the sol were sintered at 700°C for 10 h. The resultant product was analyzed by X-Ray diffractometry measurements and Scanning Electron Microscopy (SEM).

30

The following chlorine doped lithium titanium spinels were synthesized by this method:

$\text{Li}_4\text{Ti}_5\text{O}_{11,99}\text{Cl}_{0,01}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,95}\text{Cl}_{0,05}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,9}\text{Cl}_{0,1}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,8}\text{Cl}_{0,2}$,
 $\text{Li}_4\text{Ti}_5\text{O}_{11,75}\text{Cl}_{0,25}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,5}\text{Cl}_{0,5}$.

5

2.1.8 Preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{Br}_x$

$\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{Br}_x$ samples were prepared by a solid state method from
 LiBr, TiO_2 and Li_2CO_3 . The starting materials were ball-milled
 10 or mixed. Optionally, the mixture can be granulated before
 sintering. The dried and mixed reactant mixture was heated at
 850°C for 24 h in air and then cooled down to room
 temperature. The resultant product was analyzed by X-Ray
 diffractometry measurements and Scanning Electron Microscopy
 15 (SEM).

The following bromine doped lithium titanium spinels were
 synthesized by using 0,5-b mol Li_2CO_3 , 1 mol TiO_2 and b mol
 LiBr:

20

$\text{Li}_4\text{Ti}_5\text{O}_{11,99}\text{Br}_{0,01}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,95}\text{Br}_{0,05}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,93}\text{Br}_{0,07}$,
 $\text{Li}_4\text{Ti}_5\text{O}_{11,9}\text{Br}_{0,1}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,85}\text{Br}_{0,15}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,8}\text{Br}_{0,2}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,75}\text{Br}_{0,25}$,
 $\text{Li}_4\text{Ti}_5\text{O}_{11,7}\text{Br}_{0,3}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,6}\text{Br}_{0,4}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,5}\text{Br}_{0,5}$.

25

2.1.9 Preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{F}_x$

$\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{Br}_x$ samples were prepared by a solid state method from
 LiF, TiO_2 and Li_2CO_3 . The starting materials were ball-milled or
 30 mixed. Optionally, the mixture can be granulated before
 sintering. The dried and mixed reactant mixture was heated at
 850°C for 24 h in air and then cooled down to room
 temperature. The resultant product was analyzed by X-Ray

diffractometry measurements and Scanning Electron Microscopy (SEM).

The following fluorine doped lithium titanium spinels were
5 synthesized by using 0,5-b mol Li_2CO_3 , 1 mol TiO_2 and b mol LiF :

$\text{Li}_4\text{Ti}_5\text{O}_{11,99}\text{F}_{0,01}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,95}\text{F}_{0,05}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,93}\text{F}_{0,07}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,9}\text{F}_{0,1}$,
 $\text{Li}_4\text{Ti}_5\text{O}_{11,85}\text{F}_{0,15}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,8}\text{F}_{0,2}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,75}\text{F}_{0,25}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,7}\text{F}_{0,3}$,
10 $\text{Li}_4\text{Ti}_5\text{O}_{11,6}\text{F}_{0,4}$, $\text{Li}_4\text{Ti}_5\text{O}_{11,5}\text{F}_{0,5}$.

2.1.10 Preparation of $\text{Li}_4\text{Ti}_{5-z}\text{Sb}_z\text{O}_{12-x}\text{F}_x$

$\text{Li}_4\text{Ti}_{5-z}\text{Sb}_z\text{O}_{12-x}\text{F}_x$ samples were prepared by a solid state method
15 from LiF , Sb_2O_3 , TiO_2 and Li_2CO_3 . The starting materials were ball-milled in an ethanol liquid medium to form a slurry and dried. Optionally, the dry mixture can be granulated before sintering. The dried and mixed reactant mixture was heated at 900°C for 24 h in air and then cooled down to room
20 temperature. The resultant product was analyzed by X-Ray diffractometry measurements and Scanning Electron Microscopy (SEM).

The following antimony/fluorine doped lithium titanium spinels
25 were synthesized by using 0,5-b mol Li_2CO_3 , 1-a mol TiO_2 , a/2 mol Sb_2O_3 and b mol LiF :

$\text{Li}_4\text{Ti}_{4.99}\text{Sb}_{0,01}\text{O}_{11,99}\text{F}_{0,01}$, $\text{Li}_4\text{Ti}_{4.98}\text{Sb}_{0,02}\text{O}_{11,95}\text{F}_{0,05}$,
 $\text{Li}_4\text{Ti}_{4.95}\text{Sb}_{0,05}\text{O}_{11,93}\text{F}_{0,07}$, $\text{Li}_4\text{Ti}_{4.9}\text{Sb}_{0,1}\text{O}_{11,9}\text{F}_{0,1}$, $\text{Li}_4\text{Ti}_{4.85}\text{Sb}_{0,15}\text{O}_{11,85}\text{F}_{0,15}$,
30 $\text{Li}_4\text{Ti}_{4.8}\text{Sb}_{0,2}\text{O}_{11,8}\text{F}_{0,2}$, $\text{Li}_4\text{Ti}_{4.5}\text{Sb}_{0,5}\text{O}_{11,75}\text{F}_{0,25}$, $\text{Li}_4\text{Ti}_{4.99}\text{Sb}_{0,01}\text{O}_{11,7}\text{F}_{0,3}$,
 $\text{Li}_4\text{Ti}_{4.99}\text{Sb}_{0,01}\text{O}_{11,6}\text{F}_{0,4}$, $\text{Li}_4\text{Ti}_{4.75}\text{Sb}_{0,25}\text{O}_{11,5}\text{F}_{0,5}$.

2.1.11 Preparation of $\text{Li}_{4-y}\text{Na}_y\text{Ti}_{5-z}\text{Sb}_z\text{O}_{12-x}\text{Br}_x$

$\text{Li}_{4-y}\text{Na}_y\text{Ti}_{5-z}\text{Sb}_z\text{O}_{12-x}\text{Br}_x$ samples were prepared by a solid state method from LiBr, Sb_2O_3 , Na_2CO_3 , TiO_2 and Li_2CO_3 . The starting materials
 5 were ball-milled in an ethanol liquid medium to form a slurry and dried. Optionally, the dry mixture can be granulated before sintering. The dried and mixed reactant mixture was heated at 900°C for 24 h in air and then cooled down to room temperature. The resultant product was analyzed by X-Ray diffractometry
 10 measurements and Scanning Electron Microscopy (SEM).

The following antimony/bromine doped lithium titanium spinels were synthesized by using 0,5-b-c mol Li_2CO_3 , b mol Na_2CO_3 , 1-a mol TiO_2 , a/2 mol Sb_2O_3 and c mol LiBr:

15

$\text{Li}_{3,99}\text{Na}_{0,01}\text{Ti}_{4,99}\text{Sb}_{0,01}\text{O}_{11,99}\text{Br}_{0,01}$, $\text{Li}_{3,9}\text{Na}_{0,1}\text{Sb}_{0,02}\text{O}_{11,95}\text{Br}_{0,05}$,
 $\text{Li}_{3,8}\text{Na}_{0,2}\text{Sb}_{0,05}\text{O}_{11,93}\text{Br}_{0,07}$, $\text{Li}_{3,5}\text{Na}_{0,5}\text{Sb}_{0,1}\text{O}_{11,9}\text{Br}_{0,1}$,
 $\text{Li}_{3,99}\text{Na}_{0,01}\text{Sb}_{0,15}\text{O}_{11,85}\text{Br}_{0,15}$, $\text{Li}_{3,75}\text{Na}_{0,25}\text{Sb}_{0,2}\text{O}_{11,8}\text{Br}_{0,2}$,
 $\text{Li}_{3,6}\text{Na}_{0,4}\text{Sb}_{0,5}\text{O}_{11,75}\text{Br}_{0,25}$, $\text{Li}_{3,9}\text{Na}_{0,1}\text{Sb}_{0,01}\text{O}_{11,7}\text{Br}_{0,3}$,
 20 $\text{Li}_{3,99}\text{Na}_{0,01}\text{Sb}_{0,01}\text{O}_{11,6}\text{Br}_{0,4}$, $\text{Li}_{3,99}\text{Na}_{0,01}\text{Sb}_{0,25}\text{O}_{11,5}\text{Br}_{0,5}$.

2.2 Manufacture of the Electrode

Standard electrode compositions contained 90 wt.-% active
 25 material, 5 wt.-% Super P carbon black and 5 wt.-% PVDF (polyvinylidene fluoride).

Slurries were produced by first producing a 10 wt.-% PVDF 21216 solution in NMP (N-methylpyrrolidone) with a conductive additive
 30 (Super P carbon black), which was then further diluted with NMP, and finally adding the respective active material. The resulting viscous suspension was deposited by

means of a coating knife onto an aluminium foil which was dried under vacuum at 80°C. Discs with a diameter of 1.3 cm were cut out from this foil, weighed and rolled to approx. 50 µm. The thickness and the density of the electrodes were then measured. The electrodes were then dried overnight in vacuum at 120°C in a Büchi dryer. Corresponding cells were then assembled in a glovebox under argon. The active-mass content of the electrode was 4.1 mg/cm².

10

The measured potential window was 1,0 V - 2,7 V (against Li⁺/Li). EC (ethylene carbonate):DMC (dimethylene carbonate) 1:1 (vol.) with 1M LiPF₆ was used as electrolyte.

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The specific charge-discharge capacity which is achieved at low rates of roughly 165 to 170 Ah/kg is close to the theoretical value.

20

The capacity and the cycle stability of the doped Li₄Ti₅O₁₂ according to the invention in a typical half cell compared with metal lithium are remarkably good at the C rate with an average decline ("fading") of the order of 0.03%/cycle.

25

2.2. Determination of the capacity and current-carrying capacity

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The capacity and current-carrying capacity were measured with the standard electrode composition.

The electrochemical measurements were made in hermetically sealed titanium-based two electrode cells. Electrodes of 1.3 cm in diameter were prepared using 90 % active material

(loading 4.1 mg/cm^2), 5 % carbon black can 5 % poly(vinylidene difluoride) PVdF binder on Al foil. Before the cells were assembled in an argon-filled glove-box, the thin films of electrode material on the Al-foil were dried at 105°C under vacuum. The electrolyte was 1 M LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 molar ratio). Lithium metal was used as counter electrode and glass fibre as separator. The voltage window was between 1.0 and 2.0 V vs. Li/Li^+ . For the first two cycles, the cells were charged/discharged at 10/C. Then, the cells were first charged or discharged at a constant current (CC-mode) of 1C/1D until the voltage reached 1.0 V and 2.0 V, respectively, and then the voltage was held at the cut-off potential until the current reached C/50 and D/50, respectively (CV-mode).

15

Figure 2 shows the specific capacity of an electrode containing 4.1 g active mass ($\text{Li}_4\text{Ti}_{4.75}\text{Sb}_{0.25}\text{O}_{12}$) and shows an excellent stability over 320 cycles.

20 3. Gassing experiments

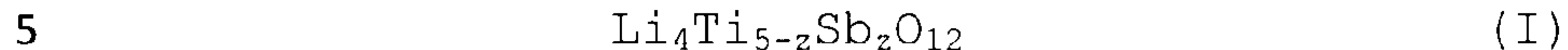
Two sealed cell packs, i.e. a secondary lithium ion batteries according to the present invention with an cathode/anode pair $\text{LiFePO}_4//\text{Li}_4\text{Ti}_{4.975}\text{Sb}_{0.025}\text{O}_{12}$ (cell C) and $\text{LiFePO}_4//\text{Li}_4\text{Ti}_{4.99}\text{Sb}_{0.01}\text{O}_{12}$ (cell B) with a single cell voltage of approx. 2.0 V and as a comparative example a cell pack, with an cathode/anode pair $\text{LiFePO}_4//\text{Li}_4\text{Ti}_5\text{O}_{12}$ (cell A) also with a single cell voltage of approx. 2.0 V were cycled from 1.7 to 2.7 V at 45°C over 500 cycles and the gas evolving from the battery pack was measured. The measurement was carried out in such a way that the battery packs are placed after 50 cycles each in a vessel filled with water and the increase in water volume due to the increase in

volume of the hermetically sealed battery pack caused by gassing was measured.

As can be seen from figure 1, cell A with the non doped lithium
5 titanium spinel as active material for the anode showed
significant gassing already at 100 cycles and increasing
exponentially up to 200 cycles. Cell B with a small antimony
doping of the lithium titanium spinel showed significant
gassing from 150 cycles on, i.e the gassing can be slowed down
10 by using a doped lithium titanium spinel. Cell C showed
significant gassing only at 500 cycles demonstrating the effect
of increasing the amount of the dopant in the lithium titanium
spinel.

Claims

1. Doped lithium titanium spinel according to formula I



wherein $0.02 \leq z \leq 0.07$.

2. Doped lithium titanium spinel according to claim 1, which is
10 additionally doped with a further metal or transition metal
selected from the group consisting of Fe, Cr, Mn, Zn, Al, Ga,
Pt, Pd, Ru, Rh, Au, Ag and Cu.

3. Doped lithium titanium spinel according to claim 1 or 2 in
15 the form of particles which are coated with a carbon-
containing layer.

4. Electrode comprising a layer containing the doped lithium
titanium spinel according to any one of claims 1 to 3.

20

5. Electrode according to claim 4, wherein the concentration of
the doping agent in the lithium titanium spinel forms a
gradient over the thickness of the layer.

- 25 6. Electrode according to claim 4 or 5, further comprising a
layer of undoped lithium titanium spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

7. Secondary non-aqueous electrolyte battery with the electrode
according to any one of claims 4 to 6.

Figure 1

