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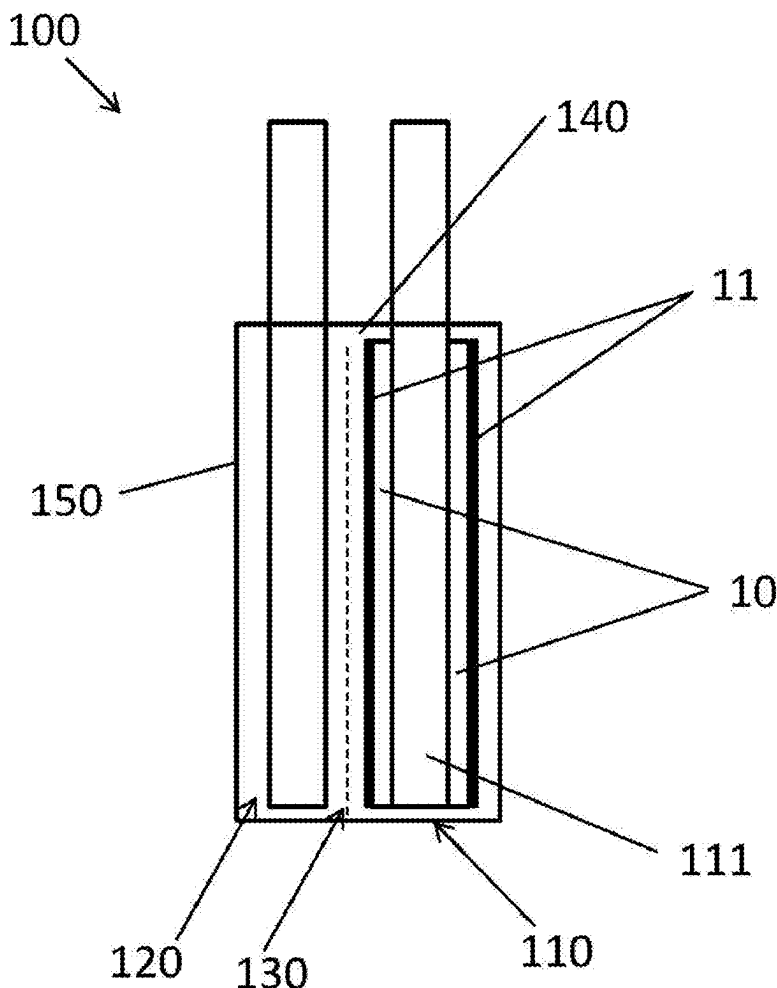
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ABSTRACT

The present disclosure relates to an anode for an electro-chemical energy storage device, at least comprising a silicon-carbon composite material in the amount of ≥ 45 wt.-% to ≤ 90 wt.-%, relating to the anode, graphite in the amount of ≥ 5 wt.-% to ≤ 47 wt.-%, relating to the anode; carbon nanotubes in the amount of >0 wt.-% to <1 wt.-%, relating to the anode; and a binder, in particular a polymer binder, in particular in the amount of 2.5 wt.-% to 8 wt.-%, relating to the anode.



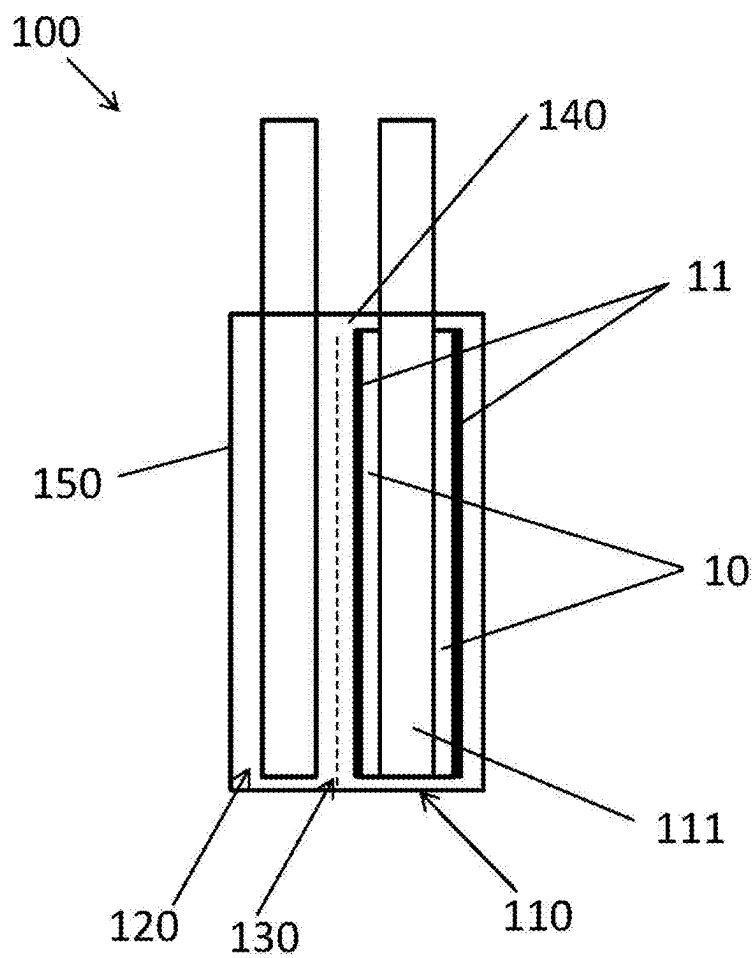


Fig.1

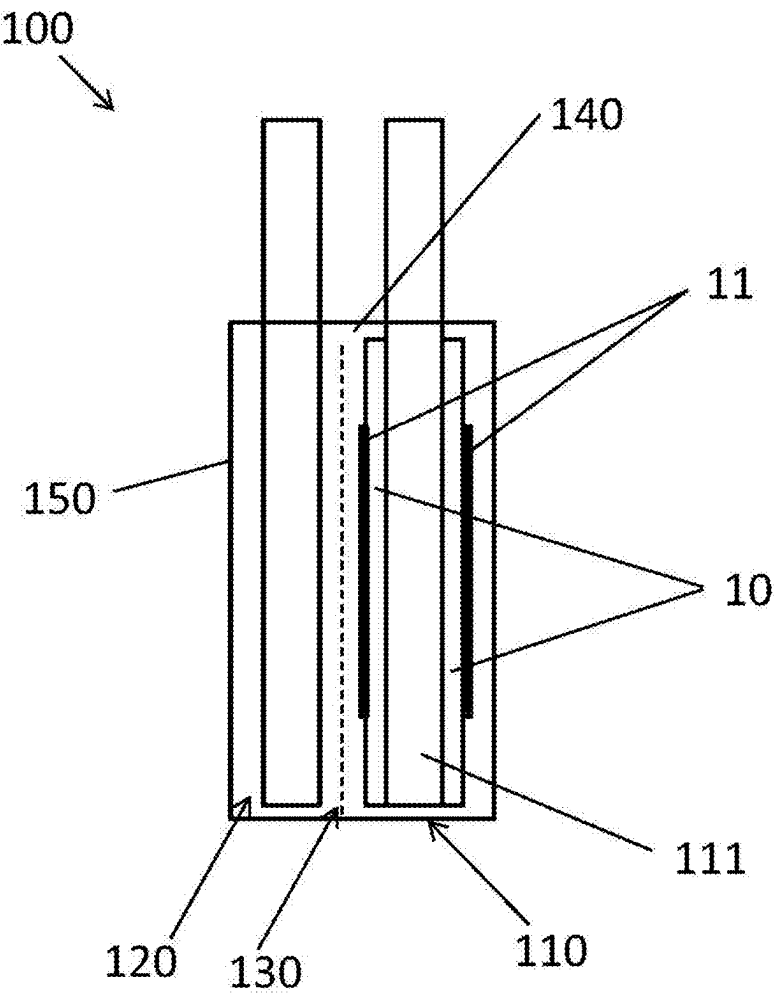


Fig.2

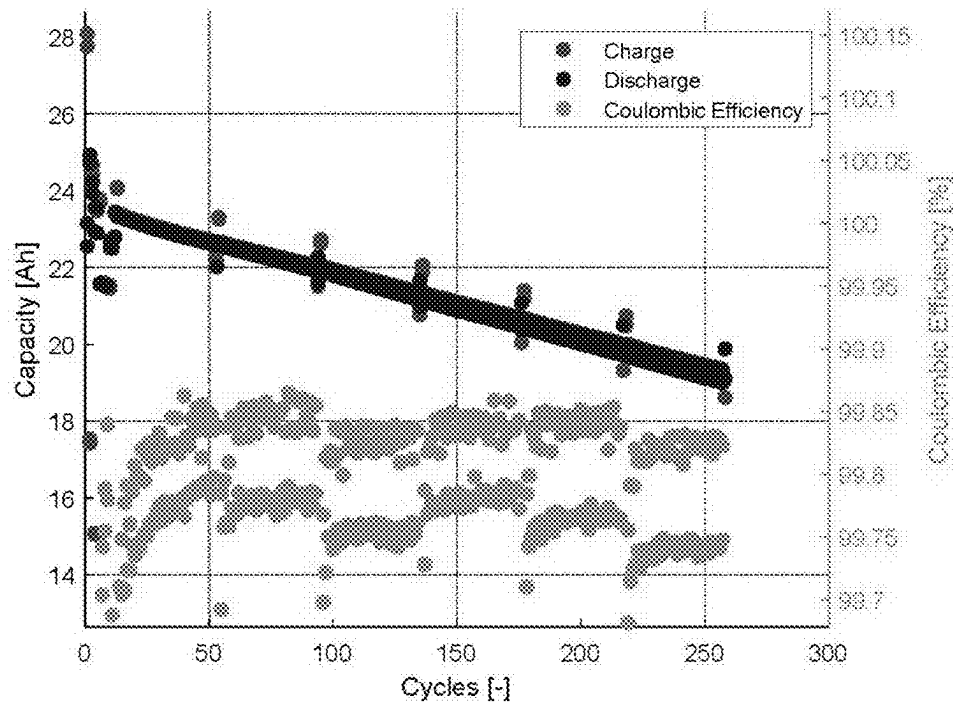


Fig.3

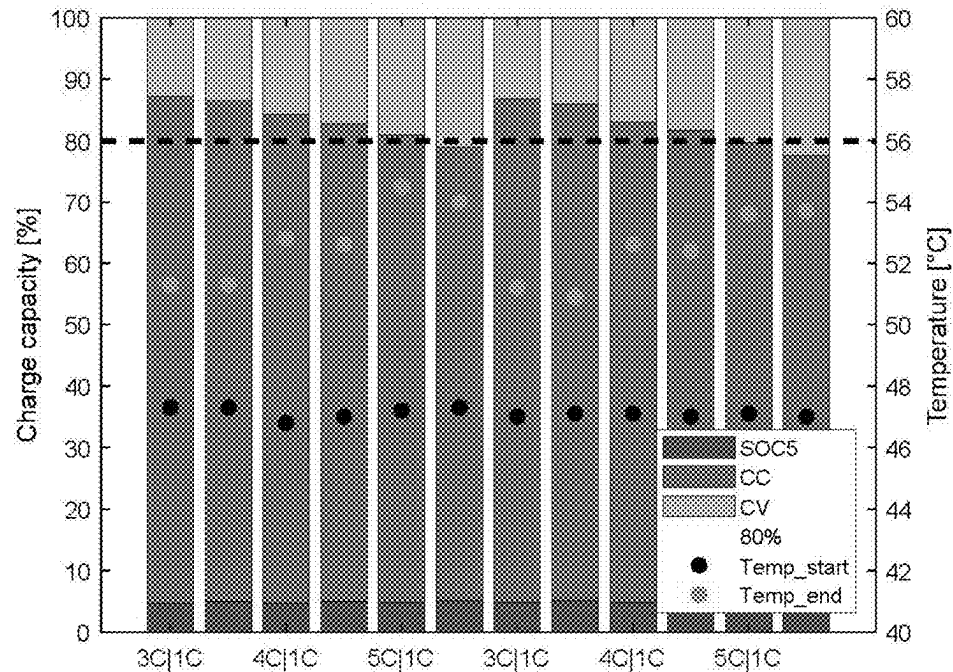


Fig.4

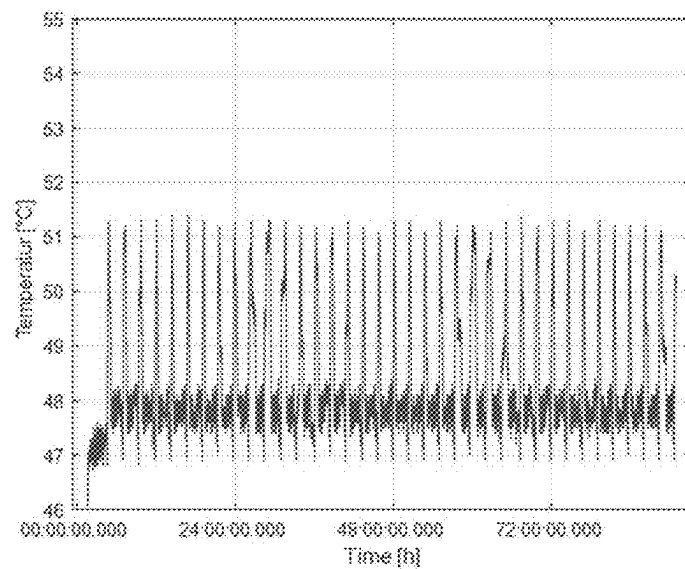


Fig.5

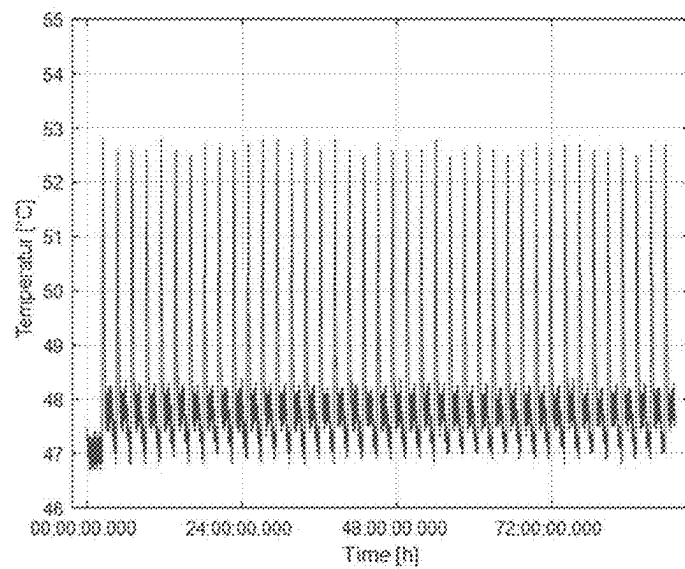


Fig.6

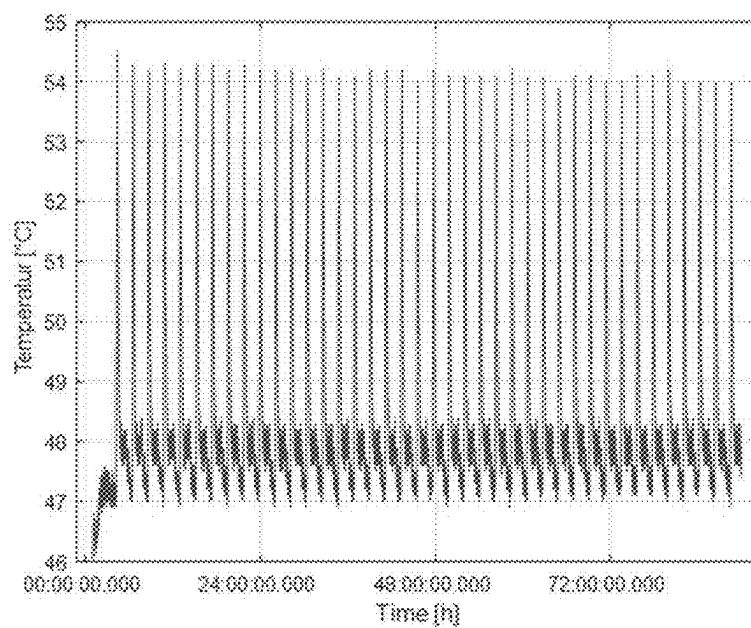


Fig.7

ANODE FOR AN ELECTROCHEMICAL ENERGY STORAGE DEVICE

[0001] The present invention leads to an anode for an electrochemical energy storage device, such as for a secondary battery. In particular, the present invention relates to an anode for an electrochemical storage device which comprises a silicon carbon composite material. The present invention further relates to an electrochemical energy storage device comprising such an anode.

[0002] Electrochemical energy storage devices are widely known in the art. Particularly in view of the advancing electrification of vehicles, electrochemical energy storage devices are becoming increasingly important. With this regard, especially the charging time becomes more important to gain better acceptance in the market.

[0003] Due to the rapidly increasing importance of electrochemical energy storage device, in particular Li-ion batteries, there is a continuous need for further development and improvement in the field of formation of such devices. Based on the above it is an object of the present invention to overcome at least one disadvantage of the prior art, at least partially. It is particularly an object of the present invention to provide an electrochemical energy storage device which shows fast charging times. It is further an object of the present invention to provide an electrochemical energy storage device which shows good cycling stability and long lifetime.

[0004] This object is solved by an anode for an electrochemical energy storage device having the features of claim 1. This object is further solved by an electrochemical energy storage device having the features of claim 11. Preferred embodiments of the invention are described in the dependent claims and the following description, each of which may individually or in combination represent an aspect of the invention unless explicitly excluded. Where a feature is shown in combination with another feature, this is for simplified illustration of the invention only and is in no way intended to imply that this feature cannot be a further feature of the invention without the other feature.

[0005] Described is an anode for an electrochemical energy storage device, at least comprising

[0006] a silicon-carbon composite material in the amount of ≥ 45 wt.-% to ≤ 90 wt.-%, relating to the anode;

[0007] graphite in the amount of ≥ 5 wt.-% to ≤ 47 wt.-%, relating to the anode;

[0008] carbon nanotubes in the amount of > 0 wt.-% to < 1 wt.-%, relating to the anode; and

[0009] a binder, in particular a polymer binder, in particular in the amount of ≥ 3 wt.-% to 8 wt.-%, relating to the anode.

[0010] The above-named components may sum up to 100 wt.-% relating to the anode.

[0011] Such an anode shows significant improvements when used in an electrochemical energy storage device, especially in a lithium battery, like shown in more detail down below.

[0012] The predescribed materials, such as in particular the silicon-carbon composite material, graphite, carbon black, carbon nanotubes, all present in a binder, may form the anode and are provided on a metal foil, in order to form the final anode electrode for an electrochemical storage device.

[0013] The anode as described comprises a silicon-carbon composite material in the amount of ≥ 45 wt.-% to ≤ 90 wt.-%, and preferably a silicon content in the amount of ≥ 18 to ≤ 45 wt.-%, relating to the anode. Such a silicon carbon composite material may also be named silicon-carbon composite mixture.

[0014] The term carbon refers to a material or substance consisting of carbon or at least comprising carbon. In this regard, a carbon material may comprise high purity, amorphous and crystalline materials. A carbon may be an activated carbon, a pyrolyzed dried polymer gel, a pyrolyzed polymer cryogel, a pyrolyzed polymer xerogel, a pyrolyzed polymer aerogel, an activated dried polymer gel, an activated polymer cryogel, an activated polymer xerogel, an activated polymer aerogel, or a combination thereof. In a further embodiment, a carbon is producible by a pyrolysis of coconut shells or other organic waste. In this regard, a polymer is a molecule comprising two or more repeating structural units. A porous carbon offers the advantage that it is usually easy to produce, usually has low impurities and a large pore volume. As a result, a porous carbon exhibits good electrical conductivity and high mechanical and chemical stability. In one embodiment, the carbon material has a high micropore volume ratio like described in more detail below.

[0015] In one further embodiment, the carbon is a hard carbon material, a graphitic carbon, or an oxide containing compound. For example, the oxide containing compound is a silicon oxide (SiO_2). Alternatively, an oxide containing compound is a titanium oxide (TiO_2), a tin oxide (SnO_2), or other oxides. A hard carbon material is a non-graphitizable carbon material. A hard carbon offers the advantage that it remains amorphous at elevated temperatures (typically $> 1500^\circ \text{C}$.), whereas a “soft” carbon crystallizes and becomes graphite.

[0016] In one embodiment, the carbon may be a modified hard carbon. A modified hard carbon is a composite material comprising both a carbon, in particular a hard carbon, and a lithium alloy material. A lithium alloy material may be silicon, tin, germanium, nickel, aluminum, manganese, alumina (Al_2O_3), titanium, titanium oxide, sulphur, molybdenum, arsenic, gallium, phosphorus, selenium, antimony, bismuth, tellurium or indium or any other metal or metalloid capable of absorbing lithium.

[0017] The silicon portion may be a pure silicon or a material composition comprising silicon. For example, the silicon portion may be at least one alloy. An alloy may be a silicon-titanium alloy (Si-Ti), a silicon iron alloy (Si-Fe), a silicon nickel alloy (Si-Ni). In a further embodiment, the silicon portion may consist of P-dopants, As-dopants or N-dopants. A P-dopant is usually a phosphorus dopant, an As-dopant is usually an arsenic dopant and an N-dopant is usually a nitrogen dopant.

[0018] The presence of silicon in the silicon carbide composite material may be advantageous as in general, silicon comprises a significantly higher energy density than, e.g., graphite. For example, the energy density of silicon exceeds the energy density of graphite by a factor of ten.

[0019] It may further be provided that the anode comprises additionally to the described (first) silicon carbon composite material a further silicon-carbon composite material being different to the first silicon carbon composite material. In a further embodiment, the anode may comprise a further carbon and/or a further binder like described below. The at

least one further carbon and/or the at least one binder may be dissolved in an aqueous medium. A further carbon may be a hard carbon material or a graphitic carbon or an oxide containing compound.

[0020] The anode according to the invention further comprises graphite. Graphite is generally known as an anode material for lithium batteries, or lithium ion batteries, respectively. In general, graphite is a superior anode material and is known for a long time for lithium ion batteries, benefiting from its incomparable balance of relatively low cost, abundance, high energy density, power density, and very long cycle life. However, in prior art electrochemical energy storage devices, graphite is mostly present as the predominant material in terms of amount in the composition. In contrast to such an arrangement and according to the present invention, graphite is present in the anode in a comparably small amount, i.e. in an amount of ≥ 5 wt.-% to ≤ 47 wt.-%, relating to the anode.

[0021] It was surprisingly found that exchanging a huge amount of graphite by the carbon silicon composite material allows even improved characteristics compared to pure graphite or a huge amount of graphite.

[0022] Further, the anode as described comprises carbon nanotubes in an amount of >0 wt.-% to <1 wt.-%, relating to the anode. It was surprisingly found that adding carbon nanotubes can enhance the electrochemical properties of the anode and thus of the electrochemical energy storage device even further. In detail, especially the charging time can be further improved.

[0023] The carbon nanotubes can be described as an allotrope of carbon with a diameter in the range of ≥ 2 to 5 nanometer, for example, having a hollow structure and a high aspect ratio (length/diameter ratio) of about 200 to 5000. Carbon nanotubes such as single wall carbon nanotube (SW-CNT) can exhibit remarkable electrical conductivity. SW-CNT can be grown on silicon substrates using a chemical vapor deposition (CVD) method and represent electrically uniform arrays of single-walled carbon nanotubes. In some embodiments the single wall carbon nanotube as provided as suspension in water with some stabilizing polymers.

[0024] With regard to the suspension, these allow an especially easy processing as suspensions of carbon nanotubes in water for a very homogeneous solution.

[0025] It was shown that the advantages as described could be reached especially effectively in case the carbon nanotubes comprise single wall carbon nanotubes. However, it is also not excluded from the present invention that the carbon nanotubes are multi-wall carbon nanotubes.

[0026] Further, a binder is present in the anode as described, for example in the amount of 2.5 wt.-%, such as 3 wt.-%, to 8 wt.-%, relating to the anode. A binder in a manner known per se is a binding agent or binding material. A binder thus refers to a material that can hold together individual components, in particular particles, of a substance, for example a carbon and the silicon-carbon composite material. A binder is typically arranged such that when particles are brought together with a corresponding binder, a cohesive mass is formed which can be further shaped into a new form.

[0027] The binder may be configured to bind all compounds as present in the anode, such as in particular, the particularly porous carbon and the silicon content of the first silicon-carbon composite, the graphite and the carbon nano-

tubes. In a further embodiment, the binder is adapted to bind further materials to at least one of the respective silicon-carbon composites. Thus, a binder is generally arranged to hold together the components of the silicon-carbon composite mixture and optionally further carbon materials of the electrode which may be formed as an anode.

[0028] The anode may comprise at least one further binder. This results in the advantage that carbon increases the conductivity of the electrode and thus provides improved conductivity. The at least one further binder further supports the mechanical stability.

[0029] The anode may comprise at least two binders, wherein a first binder is arranged to bind the particularly porous carbon and the silicon-carbon portion of the first silicon-carbon composite and the particularly porous carbon and the silicon portion of the at least one further silicon-carbon composite, and wherein the at least one further binder is arranged to bond the first silicon-carbon composite to the at least one further silicon-carbon composite.

[0030] Optionally, the silicon-carbon composite material comprises at least one further binder adapted to bond the first material component and the at least one further material component together.

[0031] For example, the binder is a styrene-butadiene rubber/carboxymethylcellulose (SBR/CMC) mixture, a polyacrylic acid (PAA) and/or a lithium polyacrylic (LiPAA) or a sodium polyacrylic (NaPAA). In an alternative embodiment, the binder is formed as a fluoropolymer such as a polytetrafluoroethylene (PTFE), a perfluoroalkoxy polymer resin (PFA), a fluorinated ethylene propylene (FEP), a polyethylene tetrafluoroethylene (ETFE), a polyvinyl fluoride (PVF), a polyethylene chlorotrifluoroethylene (ECTFE), a (polyvinylidene fluoride (PCDF), a (polychlorotrifluoroethylene (PCTFE), a trifluoroethanol, or combinations of at least one of these materials with at least one other material. In a further embodiment, a binder is a polyimide or a copolymer of polyacrylic acid and styrene-butadiene. However, it is especially preferred that the binder is a styrene-butadiene rubber/carboxymethylcellulose (SBR/CMC) mixture, a polyacrylic acid (PAA) and/or a lithium polyacrylic (LiPAA) or a sodium polyacrylic (NaPAA).

[0032] Generally, the binder may use in an organic solution or in a water-based solution.

[0033] An anode as described shows the advantage of outstanding charging times which allow charging the electrochemical energy storage device from a very low state of charge to a very high state of charge in a very short time. This improves the acceptance in the market significantly.

[0034] Especially, thinking about secondary batteries as used in vehicles, the charging time is a significant factor which may improve acceptance of electrically driven vehicles. Therefore, especially improving charging times is an important characteristic of secondary batteries for vehicles, such as cars. However, of course it should be noted that the anode as described here and consequently the electrochemical energy storage device is not limited to use in vehicles.

[0035] Apart from the above and additionally to charging times, further characteristics of the anode are not deteriorated, such as long lifetime, high cycling stability and resistance against damages.

[0036] The silicon-carbon composite mixture may be composed such that the silicon-carbon composite mixture has an electrode density ranging from 0.09 g/cm^3 to 1.5

g/cm³, or from 1.1 g/cm³ and 1.3 g/cm³. This offers the advantage that the particles comprise better contact with each other and thus the conductivity of the resulting electrode is improved.

[0037] Especially, the silicon-carbon composite mixture has an electrical conductivity ranging from 0.3 S/cm to 2 S/cm, or from 0.5 S/cm and 1.2 S/cm. This offers the advantage that the resistance of the electrode is reduced, thus allowing a faster reaction of the Li-ions with the silicon-carbon composite mixture. Hence, a charging speed of the lithium-ion cell may be increased.

[0038] Preferably, the silicon-carbon composite material has a silicon content in the amount of ≥ 18 wt.-% to ≤ 55 wt.-%, relating to the silicon-carbon composite material. The silicon content of the total mass of the silicon-carbon composite material is usually between 18 wt.-% and 40 wt.-%, especially between 26 wt.-% and 36 wt.-%. According to a further embodiment the silicon content of the total mass of the silicon-carbon composite material is usually between 30 wt.-% and 50 wt.-%, especially between 37 wt.-% and 46 wt.-%. These embodiments may improve charging process in particular in regard to charging times in a very efficient manner.

[0039] It may further be preferred that the silicon-carbon composite material has a carbon scaffold with pores, wherein the pores have a total pore volume of ≥ 0.5 cm³/g. Typically, the porous carbon has a pore space, also referred to as a pore volume, wherein the pore space is a group of voids (pores) in the carbon that is fillable with a gas or fluid. This embodiment on the one hand significantly may reduce weight of the anode and thus of the electrochemical energy storage device.

[0040] This embodiment may be of outermost importance especially in case the anode and thus the electrochemical energy storage device is used in mobile applications, such as in vehicles. Apart from that, the electrochemical properties may also be improved. With this regard, A porous arrangement offers the advantage that it is usually easy to produce, usually has low impurities and a large pore volume. As a result, a porous carbon exhibits good electrical conductivity and high mechanical and chemical stability.

[0041] Preferably, the silicon-carbon composite material is present in a bimodal particle size distribution. It is particularly preferred that a first particle size Dv50 is in the range of ≥ 1 μ m to ≤ 6 μ m and wherein a second particle size Dv50 is in the range of ≥ 6 μ m to ≤ 20 μ m.

[0042] The particle size distribution can be measured as known in the art. For example, the particle size distribution can be measured by laser light scattering of the particles in suspension, or a powder time-of-flight methodology, or other methods known in the art. The particle size distribution can be expressed as the number particle distribution or volume particle distribution, as known in the art. Accordingly, the particle size distribution can be expressed as Dvx, where D represents particle diameter, v represents the value corresponding to volume basis, and x represents the cumulative percentage of particles. For example, Dv1, Dv10, Dv50, Dv90, and Dv99 are the diameter at which 1%, 10%, 50%, 90%, and 99% of the plurality of particles in the given volume distribution reside below the named micron size. The particle size distribution is bounded by the DO (smallest particle in the distribution) and Dv100 (maximum size of the largest particle); the Dv50 is the volume average particle size. The particle size distribution can be described in terms

of one of more modes present in the particle size distribution, where the concept of mode is known in the art, for example is a maxima in the distribution. Particle size distributions can be monomodal or multimodal such as bimodal or trimodal. Modes within multimodal particle size distributions can comprise distinct local maxima within the particle distribution and/or shoulders that can be resolved from the first and/or second derivative(s) of the particle size distribution.

[0043] The present disclosure offers the advantage that the bimodal distribution of the composite enables a higher packing density and improved electrical conductivity of an anode electrode.

[0044] In a further embodiment, the bimodal silicon-carbon composite comprises at least one further carbon and/or at least one further binder. This results in the advantage that carbon increases the conductivity of the electrode and thus provides improved conductivity. The at least one further binder further supports the mechanical stability. A further carbon may be a hard carbon material or a graphitic carbon or a metal oxide. For example, the oxide containing compound is a silicon oxide (SiO₂). Alternatively, a metal oxide is a titanium oxide (TiO₂), a tin oxide (SnO₂) or other metal oxide. A hard carbon material is a non-graphitizable carbon material. A hard carbon offers the advantage that it remains amorphous at elevated temperatures (typically $>1500^{\circ}$ C., whereas a “soft” carbon crystallizes and becomes graphite.

[0045] In one embodiment, the at least one further carbon and/or the at least one further binder is dissolved in an aqueous medium.

[0046] In a further embodiment, the multimodal silicon-carbon composite material is composed such that the silicon-carbon composite material has an electrode density of 0.9 g/cm³ to 1.5 g/cm³, in particular between 1.1 g/cm³ and 1.3 g/cm³. This offers the advantage that the particles comprise better contact with each other and thus the conductivity of the resulting electrode is improved.

[0047] Alternatively, it may also be advantageous that the silicon-carbon composite material is present in a monomodal particle size distribution. With this regard, it may be particularly preferred that the particle size Dv50 is in the range of ≥ 7 μ m to <12 μ m. This embodiment efficiently reduces or avoids side reactions, as comparably large particles have a smaller surface area.

[0048] It may further be preferred that the surface area of the silicon-carbon composite material is less than 30 m²/g. The surface area is measured according to the BET measurement which is a term for an analytical method for determining the size of surfaces, in particular porous solids, by means of gas adsorption. In a further embodiment, the BET surface area is between 4 m²/g and 25 m²/g.

[0049] This offers the advantage that the resistance of the electrode is reduced, thus allowing a faster reaction of the Li-ions with the multimodal Si—C-composite material. Hence, a charging speed of the lithium-ion cell may be further increased.

[0050] The anode may further comprise carbon black in an amount of ≥ 0.5 wt.-% to ≤ 2 wt.-%, relating to the anode. The provision of carbon black may improve the electrical properties of the anode even further. As an example, carbon black delivers superior conductivity in the anode, which in turn yields a number of performance and cost benefits for lithium-ion batteries, for example.

[0051] In a particularly preferred embodiment, the anode may comprise

[0052] a silicon-carbon composite material in the amount of ≥ 65 wt.-% to ≤ 80 wt.-%, relating to the anode, and a silicon content in the amount of ≥ 26 wt.-% to ≤ 32 wt.-%, relating to the silicon carbide composite material (10);

[0053] graphite in the amount of ≥ 9 wt.-% to ≤ 29 wt.-%, such as to 23 wt.-%, relating to the anode;

[0054] carbon nanotubes in the amount of > 0.01 wt.-% to < 0.1 wt.-%, relating to the anode;

[0055] carbon black in the amount of > 0.5 wt.-%, such as > 1.5 wt.-%, to < 3 wt.-%, relating to the anode; and

[0056] a binder in the amount of > 2.5 wt.-%, such as > 3 wt.-%, to < 8 wt.-%, relating to the anode.

[0057] In one further embodiment the anode electrode has a density comprising E greater than 0.01, such as greater than 0.05 or greater than 0.1 wherein E is defined as $1 - (\text{tap density for composite mixture}) / (\text{mass averaged tap density for individual fractions})$, wherein density is the electrode density as measured in an electrode composed of ≥ 70 wt % composite, 20 wt % graphite, and 2 wt % Super C65, and 8% PAA.

[0058] The tap density of particulate silicon-carbon composite material(s) and silicon-carbon composite mixture can be measured as known in the art. For example, tap density can be measured with a PT-TD300 Tap Density Tester, wherein a known mass of powder is loaded into a graduated cylinder, for example until filling the graduated cylinder to $\frac{1}{2}$ to $\frac{3}{4}$ of its total capacity, the cylinder is loaded into the testing device, and the loaded cylinder tapped for a fixed number of taps (e.g., 250 taps) and the new tapped volume recorded, and this tapping process repeated until the point where the measured volume is no longer changing, for example within 2% of the previous reading.

[0059] In one further embodiment for the determination of E measurement of electrode properties of the silicon-carbon composite mixture and the individual fractions comprising each mode are measured under otherwise identical conditions.

[0060] Accordingly, one embodiment provides an anode comprising:

[0061] a) a first silicon-carbon composite material comprising:

[0062] i. a porous carbon scaffold comprising micropores and mesopores and a total pore volume no less than $0.5 \text{ cm}^3/\text{g}$;

[0063] ii. a silicon content from 30% to 70% by mass, relating to the silicon-carbon composite material;

[0064] iii. a plurality of particles comprising a Dv50 of $\geq 6 \mu\text{m}$ to $20 \mu\text{m}$;

[0065] b) at least one further silicon-carbon composite material comprising:

[0066] i. at least one further carbon scaffold comprising micropores and mesopores and a total pore volume no less than $0.5 \text{ cm}^3/\text{g}$;

[0067] ii. a silicon content from 30% to 70% by mass, relating to the silicon-carbon composite material;

[0068] iii. a plurality of particles comprising a Dv50 of $1 \mu\text{m}$ to $6 \mu\text{m}$; and

[0069] c) 10% to 90% by mass of the first silicon-carbon composite material and 10% to 90% of the at least one further silicon-carbon composite material, relating to the silicon-carbon composite material.

[0070] One additional embodiment provides an anode comprising:

[0071] a) a first silicon-carbon composite material comprising:

[0072] i. a porous carbon scaffold comprising micropores and mesopores and a total pore volume no less than $0.5 \text{ cm}^3/\text{g}$;

[0073] ii. a silicon content from 30% to 70% by mass, relating to the silicon-carbon composite material;

[0074] iii. a plurality of particles comprising a Dv50 of $6 \mu\text{m}$ to $20 \mu\text{m}$;

[0075] b) at least one further silicon-carbon composite material comprising:

[0076] i. at least one further carbon scaffold comprising micropores and mesopores and a total pore volume no less than $0.5 \text{ cm}^3/\text{g}$;

[0077] ii. a silicon content from 30% to 70% by mass, relating to the silicon-carbon composite material;

[0078] iii. a plurality of particles comprising a Dv50 of $1 \mu\text{m}$ to $6 \mu\text{m}$;

[0079] c) 10% to 90% by mass of the first silicon-carbon composite material and 10% to 90% of the at least one further silicon-carbon composite material;

[0080] d) a surface area of less than $30 \text{ m}^2/\text{g}$;

[0081] e) E greater than 0.01, wherein E is defined as $1 - (\text{tap density for composite mixture}) / (\text{mass averaged tap density for individual fractions})$; and

[0082] f) for the determination of E measurement of tap density of the silicon-carbon composite mixture and the individual fractions comprising each mode are measured under otherwise identical conditions.

[0083] Another embodiment provides an anode comprising:

[0084] a) a first silicon-carbon composite material comprising:

[0085] i. a porous carbon scaffold comprising micropores and mesopores and a total pore volume no less than $0.5 \text{ cm}^3/\text{g}$;

[0086] ii. a silicon content from 30% to 70% by mass, relating to the silicon-carbon composite material;

[0087] iii. a plurality of particles comprising a Dv50 of $6 \mu\text{m}$ to $20 \mu\text{m}$;

[0088] b) at least one further silicon-carbon composite material comprising:

[0089] i. at least one further carbon scaffold comprising micropores and mesopores and a total pore volume no less than $0.5 \text{ cm}^3/\text{g}$;

[0090] ii. a silicon content from 30% to 70% by mass, relating to the silicon-carbon composite material;

[0091] iii. a plurality of particles comprising a Dv50 of $1 \mu\text{m}$ to $6 \mu\text{m}$;

[0092] c) 10% to 90% by mass of the first silicon-carbon composite material and 10% to 90% of the at least one further silicon-carbon composite material;

[0093] d) a surface area of less than $30 \text{ m}^2/\text{g}$; and

[0094] e) E greater than 0.01, wherein E is defined as $1 - (\text{conductivity for composite material}) / (\text{mass averaged conductivity for individual fractions})$.

[0095] With regard to manufacturing the silicon carbon composite material, an embodiment provides a method to manufacture a silicon-carbon composite mixture comprising the steps:

- [0096] a) providing a porous carbon scaffold;
 - [0097] b) comminution the porous carbon scaffold to produce at least two particulate fractions, comprising:
 - [0098] i. a first porous carbon composite material comprising a plurality of particles with $Dv50=6\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$;
 - [0099] ii. at least one additional porous carbon composite material comprising a particle size distribution with $Dv50=1\text{ }\mu\text{m}$ to $6\text{ }\mu\text{m}$;
 - [0100] c) impregnation of silicon into the pores of the at least two particulate fractions of porous carbon composite materials by chemical vapor infiltration; and
 - [0101] d) blending of the first particulate silicon-carbon composite material and the at least one additional particulate silicon-carbon composite material.
- [0102] Yet another embodiment provides a method to manufacture a silicon-carbon composite mixture comprising the steps:
- [0103] a) providing a porous carbon scaffold
 - [0104] b) comminution the porous carbon scaffold to produce at least two particulate fractions, comprising:
 - [0105] i. a first porous carbon composite material comprising a plurality of particles with $Dv50=6\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$;
 - [0106] ii. at least one additional porous carbon composite material comprising a particle size distribution with $Dv50=1\text{ }\mu\text{m}$ to $6\text{ }\mu\text{m}$;
 - [0107] c) impregnation of silicon into the pores of the at least two particulate fractions of porous carbon composite materials by chemical vapor infiltration; and
 - [0108] d) applying a coating onto the surface of the at least two particulate fractions of the porous silicon-carbon composite by chemical vapor deposition; and
 - [0109] e) blending of the first particulate silicon-carbon composite material and the at least one additional particulate silicon-carbon composite material.
- [0110] Thus, generally, the silicon-carbon composite material may be manufactured by infiltrating a porous carbon material with silicon, such as with SiH_4 and/or other gases, such as trimethylaluminum.
- [0111] One specific embodiment provides a method of manufacturing an anode electrode comprising a silicon-carbon composite mixture as described herein, comprising the steps:
- [0112] a) mixing the silicon-carbon composite mixture with at least one carbon, such as graphite, and carbon nanotubes to create a mixture,
 - [0113] b) combining the mixture and a binder solution in a twin screw extruder, thereby forming an electrode paste,
 - [0114] c) applying the electrode paste to a conductor thereby producing at least one electrode,
 - [0115] d) drying the at least one electrode at a temperature of 100°C . to 140°C .
- [0116] Following the above, in a first step, a porous carbon scaffold material is produced. In preferred embodiments, the carbon scaffold is prepared according to US Publication No. 2017/0015559. In preferred embodiments, the porous carbon scaffold carbon is an amorphous carbon comprising nitrogen. The use of nitrogen (N) improves the conductivity of the amorphous carbon.
- [0117] In preferred embodiments, the porous carbon scaffold comprises micropores, mesopores, and/or macropores, wherein micropores are defined as pores with diameter less

than 2 nm, mesopores are defined as pores with diameter of 2 nm to 50 nm, and macropores are defined as pores with diameter greater than 50 nm. As used herein, the percentage “microporosity,” “mesoporosity” and “macroporosity” refers to the percent of micropores, mesopores and macropores, respectively, as a percent of total pore volume. For example, a carbon scaffold having 90% microporosity is a carbon scaffold where 90% of the total pore volume of the carbon scaffold are micropores.

[0118] In a further step, the polymer gel may be pyrolyzed in nitrogen at a temperature of 700°C . to 950°C . to obtain a silicon-carbon composite material.

[0119] In a further step, the silicon-carbon composite material is comminuted by grinding to produce at least two silicon-carbon composites having at least two fractions, in particular one of the at least two silicon-carbon composites comprises a particle size distribution with a percentile of $Dv50=6\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$ and another fraction comprises a particle size distribution with a percentile of $Dv50=1\text{ }\mu\text{m}$ to $6\text{ }\mu\text{m}$. Such comminution can be accomplished as known in the art, for example abrasion type milling processes such particle size reduction using a hammer mill, ball mill, jet mill, or other abrasion type mill.

[0120] The two or more fractions of silicon-carbon composites each comprise a porous carbon scaffold with certain properties, for example properties as disclosed in US Publication No. 2017/0170477.

[0121] With regard to further advantages and technical features of the anode, it is referred to the electrochemical energy storage device, to the vehicle as well as to the examples and the figures.

[0122] Further described is an electrochemical energy storage device, comprising

[0123] an anode like described above;

[0124] a cathode;

[0125] a separator disposed between the cathode and the anode; and

[0126] an electrolyte comprising lithium ions.

[0127] The general arrangement of the electrochemical energy storage device may be chosen as generally known in the art. However, an important characteristic of such a device is that it comprises an anode as described in more details above.

[0128] Further to the anode, the electrochemical energy storage device, or an electrochemical cell of the latter, comprises a cathode. The cathode may generally be formed as known in the art for lithium batteries.

[0129] Generally, the cathode may comprise a single crystal (SC) form, a polycrystalline form (PC) or a mixture of single crystal (SC) and polycrystalline (PC) form of layered transition metal oxide materials having the general formula $\text{Li}_{1-x}\text{TM}_{1-x}\text{O}_2$ with TM being Ni, Co, Mn, Al, Zr, Ti, Nb, W. The amount of these metals is preferably as follows: Ni=0.7 to 0.95, Co=0.01 to 0.15, Mn=0.01 to 0.1, Al=0 to 0.03, Zr=0 to 0.01, Nb, Ti, W=0 to 0.02, wherein x may be any value between 0 and 0.05. Further, in case a mixture of single crystal (SC) and polycrystalline (PC) form is present, the mixture ratio may be 20 to 35 wt % SC and 65 to 80% PC.

[0130] In particular, the cathode comprises lithium nickel manganese cobalt oxide, wherein the lithium nickel manganese cobalt oxide is present in a mixture of a polycrystalline form and a single crystal form. According to this embodiment, the electrochemical properties of the electrochemical

energy storage device may be improved even further, in particular with regard to cycling behavior and in particular with regard to charging time.

[0131] With regard to the separator, the latter may generally as well be formed as known in the prior art. Preferably, the separator may comprise a trilayer polymer.

[0132] Such a polymer may for example comprise an inorganic coating, such as Al_2O_3 , BaTiO_3 .

[0133] It may further be preferred that the separator is laminated to the anode. This allows the advantage to improve stacking of electrodes, as the separator is already fixed on the anode electrode.

[0134] The electrolyte may comprise at least one compound selected from the group consisting of fluoroethylene carbonate, propylene carbonate, ethylene carbonate, lithium hexafluorophosphate, and lithium bis(fluorosulfonyl)imide. It could be shown that such electrolytes show superior properties when used in lithium batteries. In general, the electrolyte may comprise a mixture of LiPF_6 and LiFSi , wherein the electrolyte may be based on fluoroethylenecarbonate (FEC) based. It may exemplarily comprise 1 to 10 wt.-% FEC, 0 to 20 wt.-% ethylene carbonate (EC), 0 to 30 wt.-% propylene carbonate (PC), each relating to the electrolyte, and optional additional additives.

[0135] An electrochemical energy storage device as described above comprising an anode as described shows the advantage of outstanding charging times which allow charging the electrochemical energy storage device from a very low state of charge to a very high state of charge in a very short time. This improves the acceptance in the market significantly.

[0136] Especially, thinking about secondary batteries as used in vehicles, the charging time is a significant factor which may improve acceptance of electrically driven vehicles.

[0137] Apart from the above and additionally to charging times, further characteristics of the anode are not deteriorated, such as long lifetime, high cycling stability and resistance against damages.

[0138] With regard to further advantages and technical features of the electrochemical energy storage device, it is referred to the anode, to the vehicle as well as to the examples and the figures.

[0139] Further described is an electrically driven vehicle, comprising an electric engine and an electrochemical energy storage device for supplying electrical energy to the electric engine, characterized in that the electrochemical energy storage device is formed like described before.

[0140] The vehicle may generally be any vehicle which is electrically driven. In particular, the electrically driven vehicle may be a fully electrically driven vehicle or a so-called hybrid vehicle. However, it may be preferred that the electrically driven vehicle is a fully electrically driven land vehicle, such as a car, a bus or a truck.

[0141] Such a vehicle comprises an electric engine and an electrochemical energy storage device for supplying electrical energy to the electric engine.

[0142] The electric engine may generally be arranged as known in the art, for example, the electrically driven engine may be a permanent synchronous machine as electric motor or an asynchronous machine as electric motor. Of course, both engines may be present and may be supplied with electrical energy from the electrochemical energy storage device. The latter is designed as defined above.

[0143] An anode as described and thus a respective electrochemical energy storage device shows the advantage of outstanding charging times which allow charging the electrochemical energy storage device from a very low state of charge to a very high state of charge in a very short time. This improves the acceptance in the market significantly.

[0144] Especially, thinking about secondary batteries as used in vehicles, the charging time is a significant factor which may improve acceptance of electrically driven vehicles. Therefore, especially improving charging times is an important characteristic of secondary batteries for vehicles. However, of course it should be noted that the anode as described here and consequently the electrochemical energy storage device is not limited to use in vehicles.

[0145] Apart from the above and additionally to charging times, further characteristics of the anode are not deteriorated, such as long lifetime, high cycling stability and resistance against damages.

[0146] With regard to further advantages and technical features of the vehicle, it is referred to the anode, to the electrochemical energy storage device as well as to the examples and the figures.

[0147] Generally, single or a plurality of features and in particular amounts of respective compounds may be transferred between single embodiments.

[0148] In the following, the invention is explained by way of example with reference to the accompanying drawing and the accompanying examples by way of preferred embodiments, wherein the features shown below may each individually or in combination constitute an aspect of the invention:

[0149] FIG. 1 shows an exemplary electrochemical storage device with a manufactured anode comprising a silicon-carbon composite material;

[0150] FIG. 2 shows an exemplary electrochemical storage device according to a further embodiment with an anode comprising a silicon-carbon composite material;

[0151] FIG. 3 shows the capacity and the coulombic efficiency over a plurality of charging cycles of an electrochemical energy storage device according to the invention;

[0152] FIG. 4 shows the temperature which arises in the electrochemical energy storage device and the charge capacity for different charging parameters according to the invention;

[0153] FIG. 5 shows the temperature profile of an electrochemical energy storage device according to the invention obtained at a C-rate of 3 C;

[0154] FIG. 6 shows the temperature profile of an electrochemical energy storage device according to the invention obtained at a C-rate of 4 C; and

[0155] FIG. 7 shows the temperature profile of an electrochemical energy storage device according to the invention obtained at a C-rate of 5 C.

[0156] In the figures, identical reference numbers identify similar elements. The sizes and relative positions of elements in the figures are not necessarily drawn to scale and some of these elements are enlarged and positioned to improve figure legibility. Further, the particular shapes of the elements as drawn are not intended to convey any information regarding the actual shape of the particular elements, and have been solely selected for ease of recognition in the figures.

[0157] FIG. 1 shows a sectional view of an exemplary electrochemical storage device 100 with an anode 110, also called anode electrode, comprising a silicon-carbon composite material 10.

[0158] The electrochemical storage device 100 is formed as a lithium-ion-battery cell. The electrochemical storage device 100 comprises at least one anode 110, at least one cathode 120 and a separator 130 disposed between the cathode 120 and the anode 110. The cathode 120 preferably comprises a transition metal oxide.

[0159] Furthermore, an electrolyte 140 comprising lithium ions is provided in a cell housing 150 of the electrochemical storage device 100. The electrochemical storage device 100 can be formed as a lithium-ion-battery cell in a pouch form. Thus, the cell housing 150 may be formed as an aluminum bag. The anode 110, the cathode 120 and the separator 130 are arranged in the cell housing 150, too.

[0160] It is noted that FIG. 1 shows a simplified sectional view. The anode 110, the cathode 120 and the separator 130 are usually formed as multiple layers which are wound or folded in order to optimize packaging and in order to increase the possible surface area of the electrolyte 140. In the shown example, only one layer of the components is visible for illustrational purpose.

[0161] The anode 110 is coated on both sides with a silicon-carbon composite material 10. The surface coating 11 of the silicon-carbon composite material 10 is performed on surface areas of the silicon-carbon composite material 10 which are not in contact with a current collector 111 of the anode 110.

[0162] By utilizing an anode 110 with the silicon-carbon material 10 the electrical properties, especially with regard to charging times, is significantly enhanced.

[0163] In FIG. 2 a further exemplary electrochemical storage device 100 is shown. The electrochemical storage device 100 comprises an anode 110 with a silicon-carbon composite material 10. In contrast to the embodiment shown in FIG. 1, the surface coating 11 of the silicon-carbon composite material 10 is applied partially on the surface area of the silicon-carbon composite material 10 remain without the surface coating 11.

[0164] In the following an exemplary electrochemical energy storage device 100 is provided and the cycling behavior was examined.

[0165] The electrochemical energy storage device 100 was arranged as follows.

[0166] The anode 110 was formed by the following components (defined in wt.-% relating to the anode):

[0167] 73% Si carbon composite material (Group 14);

[0168] 20% Graphite (Imerys, KS6);

[0169] 1,95% Carbon black (Imerys, Super C65);

[0170] 0.05% CNT (Tuball, 0.2 to 0.4% SW-CNT in CMC based water solution);

[0171] 5% CMC/SBR (BASF SE) in water

[0172] The cathode 120 was formed by the following components (defined in wt.-% relating to the anode):

[0173] 96% cathode material as a mixture of $\geq 70\%$ NCM-83-12-05 and polycrystalline 30% NCM-83-12-05 and single crystal;

[0174] 2% Super C65 (carbon black);

[0175] 2% Polyvinylidene fluoride (PVDF) in N-Methyl-2-pyrrolidone (NMP)

[0176] The used separator 130 comprises of a trilayer polymer separator with a thickness of approximately 12 μm and an inorganic coating layer like Al_2O_3 on both sides of the separator 130 to improve the safety of cells. The electrolyte 140 contains 1 molar mixture of Li salts (60% LiPF_6 and 40% LiFSi) in a solvent mixture of $\geq 5\%$ FEC, 5% PC, 20% EC and 68% EMC, 2% VC

[0177] FIG. 3 shows the electrochemical behavior of an electrochemical energy storage device 100 arranged as described above. In particular, the behavior over a plurality of charging cycles at different C-rates, i.e. more than 250 cycles, is shown.

[0178] It was proven that the capacity decreased only in an acceptable manner over a long lifetime, i.e. over more than 250 charging cycles at elevated temperature or 45°C . and fast charging. Further, the coulombic efficiency, which describes the charge efficiency by which electrons are transferred in batteries, remained in a very good range. Thus, FIG. 1 shows that an electrochemical energy storage device 100 according to the invention remains its good electrical performance even over a large amount of charging cycles.

[0179] FIG. 4 shows the temperature which arises in the battery cell and the charge capacity for different charging parameters. In detail, FIG. 4 shows the charging and discharging behavior at different charging and discharging rates or in other words at different so-called C-ratings. With this regard, the C-rating of 1 C/1 C describes fully charging/discharging the cell each in 1 hour. Correspondingly, the C-rating of 3 C/1 C describes fully charging the cell in 20 minutes and fully discharging the cell in 1 hour, the C-rating of 4 C describes fully charging the cell in 15 minutes and fully discharging the cell in 1 hour, and the C-rating of 5 C describes fully charging the cell in 12 minutes and fully discharging the cell in 1 hour.

[0180] Before the fast charging experiment, the cells were transferred to the same starting conditions of $\geq 5\%$ SOC with a constant current and a C-rate of $\geq 0.1\text{ C}$. Afterwards, fast charging with the 3 C, 4 C and 5 C rate was started at a state of charge (SOC) of $\geq 5\%$ and approximately until 80% SOC are reached. With this regard, it is firstly charged with constant current (CC) and afterwards with constant voltage (CV) when the respective parameter of $\geq 4.2\text{V}$ as threshold value was reached. Such CC-CV charging method is a known hybrid approach that combines the two previously mentioned charging methods. It uses CC charging in the first charging stage, and when the voltage reaches the maximum safe threshold value, the charging process shifts to the CV charging method.

[0181] FIG. 4 shows that when starting charging from a comparable starting temperature, the end temperature clearly stays at very well acceptable values even in case the fastest C-rating (5 C) was used. Therefore, it was shown that the electrochemical energy storage device 100 may perform charging cycles without providing any temperature problem, which is an important factor for using such electrochemical energy storage devices 100 in vehicles, for example.

[0182] In the following table 1, respective charging times are given.

TABLE 1

Charging times at different C-rates					
	Time to reach SOC 5%	Time for CC step/min	Time for CV step/min.	Time for CC + CV step/min.	Total time/min.
3C/1C	00:08:28	00:15:08	00:11:56	00:27:03	00:35:31
4C/1C	00:08:11	00:10:31	00:11:45	00:22:16	00:30:27
5C/1C	00:08:02	00:07:48	00:11:46	00:19:34	00:27:36
3C/1C	00:07:50	00:13:43	00:10:59	00:24:42	00:32:32
4C/1C	00:07:37	00:09:26	00:11:18	00:20:44	00:28:21
5C/1C	00:07:24	00:06:55	00:11:26	00:18:22	00:25:46

[0183] According to table 1, it could be shown that outstanding charging times could be reached. The most important value for electrically driven vehicles is especially the CC-charging sequence, as charging from 5 to 80% SOC is a preferred charging scenario. When using a C-rating of 5 C the charging time from 5 to 80% SOC lasts only less than 7 minutes which value is only very hard to achieve when using secondary batteries according to the prior art. Additionally, even when using smaller C-ratings, outstanding charging times may be achieved.

[0184] FIGS. 5 to 7 further show the temperature profile over a plurality of hours and thus over a plurality of charging cycles with different C-ratings. With this regard, FIG. 5 shows the temperature profile of an electrochemical energy storage device 100 obtained at a C-rate charging/discharging of 3 C/1 C, FIG. 6 shows the temperature profile of an electrochemical energy storage device obtained at a C-rate charging/discharging of 4 C/1 C, and FIG. 7 shows the temperature profile of an electrochemical energy storage device obtained at a C-rate charging/discharging of 5 C/1 C.

[0185] Using a C-rate of 3 C/1 C, the mean temperature lies at 48,22° C. and the maximum temperature lies at 51,4° C. Further, using a C-rate of 4 C/1 C, the mean temperature lies at 48,48° C. and the maximum temperature lies at 52,8° C. and using a C-rate of 5 C/1 C, the mean temperature lies at 48,65° C. and the maximum temperature lies at 54,5° C.

[0186] It could be shown that the temperature remains in a well manageable range. The occurrence of temperature-related problems can therefore be reduced and safe operation can be ensured. Moreover, the temperature increase was very limited even with increasing C-rate.

1. Anode for an electrochemical energy storage device, at least comprising

- a silicon-carbon composite material in the amount of ≥ 45 wt.-% to ≤ 90 wt.-%, relating to the anode,
- graphite in the amount of ≥ 5 wt.-% to ≤ 47 wt.-%, relating to the anode;
- carbon nanotubes in the amount of > 0 wt.-% to < 1 wt.-%, relating to the anode; and
- a binder, in particular a polymer binder, in particular in the amount of ≥ 2.5 wt.-% to 8 wt.-%, relating to the anode.

2. Anode according to claim 1, wherein the silicon-carbon composite material has a silicon content in the amount of ≥ 18 wt.-% to ≤ 55 wt.-%, relating to the silicon-carbon composite material.

3. Anode according to claim 1, wherein the silicon-carbon composite material has a carbon scaffold with pores, wherein the pores of the carbon scaffold have a total pore volume of ≥ 0.5 cm³/g.

4. Anode according to claim 1, wherein the silicon-carbon composite material is present in a bimodal particle size distribution, wherein a first particle size d₅₀ is in the range of ≥ 1 μ m to < 6 μ m and wherein a second particle size d₅₀ is in the range of ≥ 6 μ m to ≤ 20 μ m.

5. Anode according to claim 1, wherein the silicon-carbon composite material is present in a monomodal particle size distribution, wherein the particle size d₅₀ is in the range of ≥ 7 μ m to < 12 μ m.

6. Anode according to claim 1, wherein the surface area of the silicon-carbon composite material is less than 30 m²/g.

7. Anode according to claim 1, wherein the carbon nanotubes are single wall carbon nanotubes.

8. Anode according to claim 1, wherein the binder is a styrene-butadiene rubber/carboxymethylcellulose (CMC/SBR) mixture, a polyacrylic acid (PAA) and/or a lithium polyacrylic (LiPAA) or a sodium polyacrylic. (NaPAA).

9. Anode according to claim 1, wherein the anode further comprises carbon black in an amount of ≥ 0.5 wt.-% to ≤ 2 wt.-%, relating to the anode.

10. Anode according to claim 1, wherein the anode comprises

- a silicon-carbon composite material in the amount of ≥ 65 wt.-% to ≤ 80 wt.-%, relating to the anode, and a silicon content in the amount of ≥ 26 wt.-% to ≤ 32 wt.-%, relating to the silicon carbide composite material;
- graphite in the amount of ≥ 9 wt.-% to ≤ 29 wt.-%, relating to the anode;
- carbon nanotubes in the amount of > 0.01 wt.-% to < 0.1 wt.-%, relating to the anode;
- carbon black in the amount of > 0.5 wt.-% to < 3 wt.-%, relating to the anode; and
- a binder in the amount of > 2.5 wt.-% to < 8 wt.-%, relating to the anode.

11. Electrochemical energy storage device, comprising an anode according to claim 1;

a cathode;

a separator disposed between the cathode and the anode; and

an electrolyte comprising lithium ions.

12. Electrochemical energy storage device according to claim 11, wherein the cathode comprises lithium nickel manganese cobalt oxide, wherein the lithium nickel manganese cobalt oxide is present in a mixture of a polycrystalline form and a single crystal form.

13. Electrochemical energy storage device according to claim 11, wherein the separator is laminated to the anode.

14. Electrochemical energy storage device according to claim 11, wherein the electrolyte comprises at least one compound selected from the group consisting of fluoroethylene carbonate, propylene carbonate, ethylene carbonate, lithium hexafluorophosphate, and lithium bisimide.

15. Electrically driven vehicle, comprising an electric engine and an electrochemical energy storage device for supplying electrical energy to the electric engine, wherein the electrochemical energy storage device is formed according to claim 11.

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