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(54) Title: ELECTRODE ASSEMBLY FOR A LITHIUM ION BATTERY, PROCESS FOR THE PRODUCTION OF SUCH ELECTRODE ASSEMBLY, AND LITHIUM ION BATTERY COMPRISING SUCH ELECTRODE ASSEMBLY

(57) Abstract: The invention provides an electrode assembly for a lithium ion battery, the electrode assembly comprising a lithium storage electrode layer on a current collector, wherein the lithium storage electrode layer is a porous layer having a porosity in the range of 35%, with pores having pore widths in the range of 1-100 µm, and having a porous layer thickness in the range of 5-500 µm. The invention also provides a lithium ion battery comprising such electrode assemblies as anode and cathode. Further, a process for the production is provided.

FIG. 1b
Electrode assembly for a lithium ion battery, process for the production of such electrode assembly, and lithium ion battery comprising such electrode assemblies

FIELD OF THE INVENTION

The invention relates to an electrode assembly for a lithium ion battery, to a process for the production of such electrode assembly, and to a lithium ion battery comprising such electrode assemblies as anode and cathode, respectively.

BACKGROUND OF THE INVENTION

Lithium ion batteries and high capacity lithium ion batteries are known in the art. WO2011056847, for instance, describes a high capacity silicon based anode active materials for lithium ion batteries. These materials are suggested to be effective in combination with high capacity lithium rich cathode active materials. Supplemental lithium is suggested to improve the cycling performance and reduce irreversible capacity loss for at least certain silicon based active materials. In particular silicon based active materials can be formed in composites with electrically conductive coatings, such as pyrolytic carbon coatings or metal coatings, and composites can also be formed with other electrically conductive carbon components, such as carbon nanofibers and carbon nanoparticles. Additional alloys with silicon are explored in this document.

Further, WO2009131700 describes combinations of materials in which high energy density active materials for negative electrodes of lithium ion batteries. In general, metal alloy/intermetallic compositions can provide the high energy density. These materials can have moderate volume changes upon cycling in a lithium ion battery. The volume changes can be accommodated with less degradation upon cycling through the combination with highly porous electrically conductive materials, such as highly porous carbon and/or foamed current collectors. Whether or not combined with a highly porous electrically conductive material, metal alloy/intermetallic compositions with an average particle size of no more than a micron can be advantageously used in the negative electrodes to improve cycling properties.

Hence, especially WO2009131700 describes a lithium ion battery comprising a positive electrode, a negative electrode, a separator between the positive electrode and the negative electrode and an electrolyte comprising lithium ions, wherein the negative electrode comprises a foamed current collector impregnated with an active material comprising a metal alloy/intermetallic material and wherein the negative electrode lacks a foil current collector.
or a grid current collector separate from the foamed current collector. Further, this document describes a powder comprising amorphous metal alloy/intermetallic particles wherein the particles have an average particle size of no more than about 1 micron. In addition, WO2009131700 describes a method for forming a metal alloy/intermetallic composition having a reduced degree of crystallinity, the method comprising milling amorphous elemental powders to form the alloy/intermetallic composition.

JP2005158401 describes a manufacturing method of manufacturing effectively a positive electrode active material having a porous structure, a positive electrode active material manufactured by this method, and a secondary battery using the active material. The manufacturing method comprises a process of obtaining a mixture containing a primary particle of lithium-containing complex oxide and a pore forming particle, a process of producing a compound particle of the primary particle and the pore forming particle from the mixture, and a process of forming a porous particle made mainly of lithium-containing complex oxide by removing and/or melting the pore-forming particle constituting material contained in the compound particle. This positive electrode active material, according to JP2005158401, is suitable as a positive electrode active material of lithium-ion secondary battery using a normal temperature molten salt electrolyte.

US2011129732 describes forming an electrochemical device and device components, such as a battery cell or super capacitor, using thin-film or layer deposition processes and other related methods for forming the same. In one embodiment, a battery bi-layer cell is provided. The battery bi-layer cell comprises an anode structure comprising a conductive collector substrate, a plurality of pockets formed on the conductive collector substrate by conductive microstructures comprising a plurality of columnar projections, and an anodically active powder deposited in and over the plurality of pockets, an insulative separator layer formed over the plurality of pockets, and a cathode structure joined over the insulative separator.

US2011052997 describes a negative electrode for a lithium battery including an active material layer and a current collector. The active material layer has a plurality of crystal grains and the plurality of crystal grains include a plurality of pores. A first pore of the plurality of pores has a first length and a second length, the first length being the maximum length orthogonal to the current collector and the second length being the maximum length orthogonal to the first length, and the first length is greater than the second length.

WO2010050347 describes a sintered lithium complex oxide having excellent high-rate discharge characteristics; a positive electrode composition for batteries, which uses
the sintered lithium complex oxide; a positive electrode for batteries; and a lithium ion battery. The sintered lithium complex oxide is obtained by sintering fine particles of lithium complex oxide together, and is characterized in that the peak pore size giving the maximum differential pore volume is 0.80-5.00 µm, that the total pore volume is 0.10-2.00 mL/g, that the average particle size is not less than the above-specified peak pore size but not more than 20 µm, that there is a sub-peak giving a differential pore volume not less than 10% of the maximum differential pore volume on the smaller pore size side with respect to the above-specified peak pore size, that the pore size corresponding to the sub-peak is more than 0.50 µm but not more than 2.00 µm, that the BET specific surface area of the sintered lithium complex oxide is 1.0-10.0 m²/g, and that the half width of the maximum peak among X-ray diffraction peaks in an X-ray diffraction measurement is 0.12-0.30°.

US2010159346 describes an electrode comprising a carbon material obtained from an azulmic acid and a current collector and/or a binder.

15 SUMMARY OF THE INVENTION

Lithium ion batteries consist of an anode, cathode and in between an electrolyte. The electrodes contain the active materials in which Li can be stored in order to store energy. In practice the design of the battery is such that a large amount of inactive materials is necessary, reducing the weight percentage of the amount of active electrode materials, and with it the energy density of the battery. The physically limited diffusion of lithium ions and electrons through the electrodes are the reason why currently only small amounts of active material can be used on the metal current collector foils. The basic problem is how to increase the amount of active material on the current collector foils, leading to a high energy density battery by the reduction of inactive materials.

It is recognized as a problem and much effort has been devoted to increase the intrinsic conductivity in the materials by e.g. nanostructuring and carbon coating. This has led to the present state of the art. Using the nanostructured and carbon coated materials we now address the conductivity on larger length scales because the rechargeability of the electrodes appears to be limited to a few microns of active material.

Hence, it is an aspect of the invention to provide an alternative electrode (or electrode assembly), which preferably further at least partly obviate one or more of above-described drawbacks, and which preferably allows quicker charging and/or higher capacities. It is yet a further aspect of the invention to provide a lithium ion battery comprising such alternative electrode (or electrode assembly).
Surprisingly, it has been found that a major step can be made when providing micro porosity. By making the electrodes porous on a scale of microns, with a pore volume fraction of for instance 10 - 20%, or even more, it is possible to have fast conduction and rechargeability up to layer thicknesses of hundreds of microns. For the same energy storage capacity then a largely reduced amount of copper and/or aluminum foils as well as electrolyte and separator layers may be required, which reduces the weight. In all it can be estimated that in this way a 2 times higher energy density of the battery can be realized than present state of the art batteries. Alternatively, the same methods can be applied to obtain electrodes that (dis-)charge faster than the current state of the art. In that case the invention makes the prior art choice of more active material on the current collector superfluous but rather provides the porous electrode for faster (dis-)charging.

Hence, to this end, the invention provides an electrode assembly for a lithium ion battery, the electrode assembly comprising a lithium storage electrode layer on a current collector, wherein the lithium storage electrode layer comprises an active lithium storage material, carbon and binder, and wherein the lithium storage electrode layer is a porous layer, especially having a porosity in the range of 5-45 %, such as 10-40%, like 30-40%. In an embodiment, the pores may have pore widths in the range of 0.5-50 μm, and having a porous layer thickness in the range of 5-500 μm. In a specific embodiment, the porosity is in the range of 10-40%, wherein the pores have widths in the range of 1-30 μm, and having a porous layer thickness in the range of 10-200 μm. Even more especially, the porosity is in the range of 30-40%, wherein the pores have widths in the range of 1-30 μm, and having a porous layer thickness in the range of 10-200 μm.

In a specific embodiment, the invention further provides an electrode assembly for a lithium ion battery, the assembly comprising a lithium storage electrode layer on a current collector, wherein the lithium storage electrode layer is a porous layer having a porosity in the range of 5-35 %, with pores having pore widths in the range of 0.5-100 μm, especially 1-10 μm, and having a porous layer thickness in the range of 5-500 μm, especially 10-200 μm.

Using such electrode assembly in a lithium ion battery, the above indicated advantages of the invention, i.e. faster charging and/or higher energy density (capacity) may be obtained.

Herein, the term “electrode assembly” is used to indicate that the electrode or electrode assembly comprises the active layer, herein indicated as lithium storage electrode layer (which is a porous layer)(and which may comprise the active lithium storage material),
and a current collector, on which the active layer is arranged (see also below). Often the term “electrode” is used for the active layer only, although the electrode also comprises a current collector. Therefore, for the sake of understanding, herein the term “electrode assembly” is further applied. Herein, the term “lithium storage electrode layer” may also refer to a plurality of layers (i.e. a multi-layer structure). Such multi-layer structure may in an embodiment comprise layers with different compositions, such as different types of active material.

A specific feature of the electrode assembly is its porous layer. Porosity or void fraction is a measure of the void spaces in the layer and is a fraction of the volume of voids over the total volume as a percentage between 0–100%. As indicated above, especially, the porosity is in the range of 5-45%, such as 5-40%, like 5-35 %, such as in the range of 10-30 %. For instance with SEM measurements and/or gas measurements, the porosity may be determined. Alternatively or additionally, the chemical composition, the density, the thickness and the weight can be used to evaluate the porosity.

The pore widths are preferably in the range of 0.5-100 μm, such as 0.5-80 μm, especially 0.5-50 μm, more especially at least 1 μm, even more especially in the range of 1-50 μm, such as at least 30 μm, like in the range of 1-30 μm, such as 1-10 μm. Preferably, at least 50%, more especially at least 80%, yet even more especially at least 90% of the pores have such pore dimensions. Due to the presence of those pores, the lithium storage electrode layer has its above indicated porosity. Width may for instance also refer to diameter of substantially circular cross-sections of pores. Not all pores may substantially have circular cross-sections, hence the pore width is chosen. Preferably, the pores show interconnectivity, which may be beneficial for good access of the liquid electrolyte in the battery.

Instead of pore width, the effective diameter may be chosen, which is preferably also in the range of 0.5-100 μm, such as 0.5-80 μm, especially 0.5-50 μm, more especially at least 1 μm, even more especially in the range of 1-50 μm, such as at least 30 μm, like in the range of 1-30 μm, such as 1-10 μm. The effective diameter can be evaluated by calculating the circumferential length of the cross-section of the pore, using the length as circumferential length of a (virtual) circle, and based thereon calculating the diameter of that circle. In this way, the effective diameter can be estimated of the pore.

For effective batteries, the porous layer thickness will be at least 5 μm, such as 5-500 μm, preferably at least 10 μm, such as 10-200 μm. The term “porous layer thickness” is used to indicate the thickness of the porous layer (on the current collector).
Hence, in a specific embodiment, the invention provides an electrode assembly as indicated above, wherein the porosity is in the range of 10-30\%, wherein the pores have widths in the range of 1-100 μm, especially 1-30 μm, even more especially 1-10 μm, and having a porous layer thickness in the range of 10-200 μm.

In general, the lithium storage electrode layer further comprises carbon (especially carbon black)(herein also indicated as conductive carbon), for electronic conductivity reasons, and optionally some remaining binder (see below), and optionally some remaining pore former material (see below). Carbon will in general be present in the lithium storage electrode layer in the range of at least 1.5 wt.\%, such as especially about 1.5-20 wt.\%, such as 5-20 wt.\%, like 5-15 wt.\%.

The active material will in general be present in the lithium storage electrode layer in the range of 60-95 wt.\%, such as 75-95 wt.\%, like at least 85 wt.\%.

Remaining binder may be present in an amount of about 0-20 wt.\%, such as 0.5-20 wt.\%, like e.g. 5-20 wt.\%, such as 10-15 wt.\%.

Remaining pore former material will in general be in the amount of 1 wt.\% or less, such as 0.5 wt.\% or less, like 0.1 wt.\% or less. In an embodiment, the remaining amount of pore former material is in the range of 100 ppm – 0.05 wt.\%. These amounts are relative to the total weight of the lithium storage electrode layer. The presence (or absence) of the pore former material and traces thereof may be detected with X-ray scattering (assuming crystalline pore former material) and/or elemental analysis (EDX, as is often possible with SEM apparatus) and/or NMR spectroscopy. When carbon is the active material, as in an anode embodiment, this material may then be present in the lithium storage electrode layer in the range 85-95 wt.\%. When the electrode is assembled in the battery configuration the liquid electrolyte will penetrate into the porous electrode.

Especially, the lithium storage electrode layer may especially comprise particulate active lithium storage material, particulate carbon, and binder. Hence, the porosity may be due to channels within the lithium storage electrode layer between the particles of the particulate active lithium storage material and the particulate carbon.

In a specific embodiment, the number average particle size of the particulate active lithium storage material is in the range of 50 nm – 1 μm, and wherein the number average particle size of the particulate carbon is in the range of 1 nm – 0.1 μm. For instance, based on one or more of XRD, SEM and TEM, the particle size may be determined.

Further, the lithium storage electrode layer may have a density in the range of 50 – 90 \% of the theoretical density of packed active lithium storage material, carbon, and
binder. The theoretical density is about 60-65% of the density of the materials due to the packing of the particles. From this theoretical density, the lithium storage electrode layer has a density of at least 50%, such as 50-90%, especially at least 80%, such as 80-90%.

The lithium storage electrode layer comprises as active material an active lithium storage material. In uncharged state, substantially all mobile or free lithium will be present in the cathode, whereas in the charged state, a substantial part may (also) be present in the anode. However, in uncharged state, the anode (or more especially the lithium storage electrode layer of the anode) may comprise substantially no free lithium. In addition mobile Li ions are always present in the electrolyte present between the electrodes and inside the porous electrodes. In a specific embodiment 1 molar LiPF₆ dissolved in 50%-50% EC (ethylene carbonate) – DMC (dimethyl carbonate) is applied as electrolyte. The electrolyte penetrates in the pores and thus provides rapid Li ion access throughout the electrode.

The electrode assembly can be used as cathode or as anode, based on the active materials used. Especially, the lithium storage electrode layer may comprise a material selected from the group consisting of LiFePO₄, LiMn₂O₄, LiNi₀.₅Mn₁.₅O₄, LiCoO₂, and Li[NiMnCo]O₂, Li[Li,Ni,Mn,Co]O₂, LiCo₁/₃Ni₁/₃Mn₁/₃O₂, LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂, LiNiO₂, Li₃V₂(PO₄)₃, Li₂FePO₄F, LiC₆, Li₄Ti₅O₁₂, Si (for Li₄.₄Si), and Ge (for Li₄.₄Ge). These materials can have a carbon coating and/or can be doped with transition metals when required for electrical conductivity. Carbon itself can also be used as active lithium storage material for the anode (see also below).

In an embodiment, for use as cathode, the lithium storage electrode layer may comprise ≥ 75 wt.% of a material selected from the group consisting of LiFePO₄, LiMn₂O₄, LiNi₀.₅Mn₁.₅O₄, LiCoO₂, and Li[NiMnCo]O₂, Li[Li,Ni,Mn,Co]O₂, LiCo₁/₃Ni₁/₃Mn₁/₃O₂, LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂, LiNiO₂, Li₃V₂(PO₄)₃, and Li₂FePO₄F. In another embodiment, which may be combined with the former, for use as anode, the lithium storage electrode layer may comprise ≥ 75 wt.% of a material selected from the group consisting of Li₄Ti₅O₁₂, TiO₂, Si, Ge, and C. Again, these materials can have a carbon coating, though the pure carbon material may not need such coating. For instance, silicon may also refer to carbon coated silicon (core shell particles). When carbon is applied as active lithium storage material in an anode, this may be one or more of hard, soft, or graphitic carbon.

Hence, in an embodiment, the active lithium storage material, not being carbon, is carbon coated.

The invention is not limited to the herein mention active (lithium storage) material.
For use as cathode, the lithium storage electrode layer may comprise for instance LiFePO₄, Li[Ni,Mn,Co]₂O₄, such as LiMn₂O₄ or LiNi₀.₅Mn₁.₅O₄, or Li[Ni,Mn,Co]₁O₂, such as LiCoO₂, or other high potential materials. Especially, the lithium storage electrode layer may comprise at least 75 wt.% of one of those materials. In another embodiment, the lithium storage electrode layer may comprise at least 75 wt.% of one of those materials. In a specific embodiment, the invention provides the electrode assembly as indicated above, especially for use as cathode, wherein the lithium storage electrode layer comprises ≥ 75 wt.% of a material selected from the group consisting of LiFePO₄, LiMn₂O₄, LiNi₀.₅Mn₁.₅O₄, LiCoO₂, and Li[Ni,Mn,Co]₁O₂. In an embodiment, the lithium storage electrode layer may also refer to a layer comprising different types of active materials. These materials are herein also indicated as active lithium storage material.

For use as anode, the lithium storage electrode layer may comprise for instance Li₄Ti₅O₁₂, TiO₂, Si (including carbon coated Si) and C, or other high potential materials, may be applied. Hence, the lithium storage electrode layer may in an embodiment comprise at least 75 wt.% of one of those materials. In another embodiment, the lithium storage electrode layer may comprise at least 75 wt.% of one or more of those materials. Therefore, in a specific embodiment, the invention provides the electrode assembly as described above, (however) for use as anode, wherein the lithium storage electrode layer comprises ≥ 75 wt.% of one of those material selected from the group consisting of Li₄Ti₅O₁₂, TiO₂, Si and C. Hence, whereas the cathode in general starts as lithium based lithium storage electrode layer, the anode may originally be provided as lithium based and as non-lithium based lithium storage electrode layer (for instance based on Si or on C).

In an embodiment, the lithium storage electrode layer has a porous layer thickness in the range of 5-500 μm. In a variant, the lithium storage electrode layer has a porous layer thickness of at least 5 μm. Especially, the lithium storage electrode layer has a porous layer thickness of at least 100 μm. In a specific embodiment, the porous layer thickness is at least 80 μm, more especially at least 100 μm, such as 100-500 μm, like 100-200 μm, such as especially 120-200 μm. Hence, in an embodiment, lithium storage electrode layer has a porous layer thickness of at least 100 μm. These relative thick layers (≥100 μm) may especially be of interest for use in high capacity batteries. When using the electrode assemblies of the invention in a battery (see also below), the amounts of active material (and Li capacity that can be contained in that) which is related to the layer thicknesses, as well as the porosities and (mean) pore widths will in general be similar for both the cathode and anode, such as values for those respective features differing not more than 20%, preferably
not more than 10%, of each other. In this way the Li contained in one electrode can be charged completely and most rapidly into the other and vice versa. Hence, the capacities of a couple of a cathode and anode (which are separated by the electrolyte) preferably do not differ more than 20%.

For instance the pore widths, for instance when averaged over the number of pore widths measured (for instance with SEM), may be about 25 μm for the cathode and 30 μm for the anode (or vice versa). As reference the value for the layer with the larger value may be taken. In the above example, and assuming a 20% tolerance, the anode may have mean pore widths of 30 μm, and thus the cathode may have mean pore widths in the range of 24-36 μm. However, other values may also be possible, and were also obtained. This may e.g. depend upon the particle size of the pore former, the amount of pore former, the way the pore former is removed and the (amount of) liquid used. For instance when averaged over the number of pore widths measured (for instance with SEM), may be about 2.5 μm for the cathode and 3 μm for the anode (or vice versa). As reference the value for the layer with the larger value may be taken. In the above example, and assuming a 20% tolerance, the anode may have mean pore widths of 3 μm, and thus the cathode may have mean pore widths in the range of 2.5-3.6 μm.

The current collector in general comprises a foil. This foil may be used as support for the lithium storage electrode layer. The current collector may for instance comprise a Cu (copper) foil or an Al (aluminum) foil. In an embodiment, the current collector comprises a multi-layer foil. In a specific embodiment, the current collector comprises a foil selected from the group consisting of a Cu foil and an Al foil, and preferably, the foil has a foil thickness in the range of 1-40 μm, such as in the range of 5-30 μm, such as in the range of 5-25 μm. Optionally, the current collector is a non massive layer, for instance comprising holes. In an embodiment, the current collector has a gauze shape. In an embodiment, the lithium storage electrode layer will substantially adopt such shape. This may depend upon the dimensions of the holes in the gauze. Optionally, such foil may be coated with carbon, for instance with a layer of a few micron (this may add to the total thickness as indicated above. Such carbon layer may facilitate layer formation of the lithium storage electrode layer and better contact with and adhesion to the current collector.

In an embodiment, the current collector comprises a foil selected from the group consisting of a Cu foil and an Al foil, and the foil has a foil thickness in the range of 1-30 μm. Especially, Cu foil may have a thickness of at least 6 μm; Al foil may have a thickness in the range of e.g. 10-20 μm. In an embodiment, the current collector comprises a
carbon coated Al foil. As indicated above, this may further be beneficial in view of adhesion of the lithium active storage material to the foil.

In an embodiment, the lithium storage electrode layer comprises at least 85 wt.% of the active lithium storage material and at least 1.5 wt.% carbon, related to the total weight of the lithium storage electrode layer. In a specific embodiment, the lithium storage electrode layer comprises at least 85 wt.% of the active lithium storage material and at least 5 wt.% carbon, related to the total weight of the lithium storage electrode layer, and especially the active lithium storage material is selected from the group consisting of LiFePO₄, LiMn₂O₄, LiNi₀.₅Mn₁.₅O₄, LiCoO₂, Li[Ni,Mn,Co]O₂, Li[Li,Ni,Mn,Co]O₂, LiCo₀.₇Ni₁/₃Mn₁/₃O, LiNi₀.₅Co₀.₁₅Al₀.₀₅O₂, LiNiO₂, Li₂FePO₄F, LiC₆, Li₄Ti₅O₁₂, Si (including C coated Si, such as for Li₄.₄Si), Ge (such as for Li₄.₄Ge), and (hard, soft or graphitic) carbon. Such lithium storage electrode layer may especially give good results.

In a specific embodiment, the lithium storage electrode layer comprises at least 85 wt.% of the active lithium storage material and at least 5 wt.% carbon, related to the total weight of the lithium storage electrode layer, and wherein the active lithium storage material is selected from the group consisting of LiFePO₄, LiMn₂O₄, LiNi₀.₅Mn₁.₅O₄, LiCoO₂, Li[Ni,Mn,Co]O₂, Li[Li,Ni,Mn,Co]O₂, LiCo₀.₇Ni₁/₃Mn₁/₃O, LiNi₀.₅Co₀.₁₅Al₀.₀₅O₂, LiNiO₂, Li₂FePO₄F, LiC₆, and Li₄Ti₅O₁₂. In yet a further specific embodiment, the lithium storage electrode layer comprises at least 85 wt.% of the active lithium storage material and at least 5 wt.% carbon, related to the total weight of the lithium storage electrode layer, and wherein the lithium storage electrode layer has a porous layer thickness of at least 100 µm.

Further, especially the mass loading of the active lithium storage material in the lithium storage electrode layer on the current collector is at least 10 mg/cm², and especially 80% of said active lithium storage material can be charged within 1 hour. This may provide an assembly (and a battery), with a high energy density. State of the art cathodes or anodes may have a higher loading, but then have relatively bad charging characteristics. Especially, the mass loading of the active lithium storage material in the lithium storage electrode layer on the current collector is at least 15 mg/cm², and 70% of said active lithium storage material can be charged within 1 hour. In yet a further aspect (see also above), the invention provides a lithium ion battery comprising a cathode and an anode, wherein one or more of the cathode and the anode comprise an electrode assembly as defined herein. Especially, the invention provides a lithium ion battery comprising a cathode and an anode, wherein the cathode and anode comprise electrode assemblies as described herein. Such battery may be charged quickly and/or may have a high capacity.
In a specific embodiment, the invention provides such lithium ion battery, wherein the lithium storage electrode layers of the electrode assembly have porous layer thicknesses of at least 80 μm, especially at least 100 μm, and wherein the lithium ion battery has a capacity of at least 2.5 mAh/cm², especially at least 3 mAh/cm². Prior art high performance lithium ion batteries may not have capacities over about 1 mAh/cm², especially not larger than about 2.5 mAh/cm².

Hence, in an embodiment the invention provides a lithium ion battery, such as defined above, wherein the lithium storage electrode layers of the electrode assemblies have porous layer thicknesses of at least 100 μm. In a further embodiment the lithium storage electrode layers of the electrode assemblies have porous layer thicknesses of at least 100 μm, and wherein the lithium ion battery has a capacity of at least 3 mAh/cm². In yet a further embodiment, the lithium ion comprises a first electrode assembly and a second electrode assembly according to any one of the preceding claims, with liquid electrolyte configured between the first and the second electrode assembly, wherein the pores of the porous layers are at least partly filled with said electrolyte.

The invention provides in a further aspect a process for the production of an electrode assembly.

For producing the cathodes the process may for instance involve the mixing of (10–40 wt.%) (micron sized) NaHCO₃ crystals (or an equally suitable other material) into the slurry that is used to produce a cathode. Such slurry may for instance include in the order of about 80 wt.% LiFePO₄ active material, 10 wt.% PVDF (polyvinylidene fluoride) binder, and 10 wt.% conducting carbon altogether dissolved in a suitable organic solvent such as NMP (N-methylpyrrrolidone). The NaHCO₃ (or equivalent) should not (substantially) dissolve in the NMP (or other solvent) because these crystallites are present to produce after removing them the porous structure. The NaHCO₃ that does dissolve in NMP can recrystallize when the NMP is removed by evaporation. After casting the electrode, evaporation of the solvent, pressing for a compacted and well contacted layer, and drying in an oven, the NaHCO₃ is washed away in water upon which CO₂ gas evolves and NaOH is dissolved and washed away through the pores. The gas evolution is expected to especially contribute to the formation of connected pores. After thorough drying in a vacuum oven the electrode is ready for use in a battery with a liquid electrolyte. For producing the anodes a similar method may be applied with TiO₂, or other materials, such as carbon or carbon coated silicon.
An alternative material for NaHCO₃ and water may for instance be other carbonate salts, like (NH₄)₂CO₃ or NH₄HCO₃ that can be removed by thermal treatment, NaCl (and/or LiCl) that can be dissolved in water. (NH₄)₂CO₃ is suitable in combination with Li₄Ti₅O₁₂ anode material. In general salts that do not dissolve in NMP, and that show no H (or other ion exchange) for Li exchange with the electrode materials. The advantage of NaHCO₃, and/or similar systems, is that it forms CO₂ gas at room temperature, while the other materials do not. The emerging gas may help to form the pores and connect them. For instance the complete removal of NaHCO₃ indicates that the pores when they are being made are connected and accessible by water. In an embodiment, the binder is selected from the group consisting of PVDF (polyvinylidene fluoride) and PTFE (polytetrafluoroethylene).

Therefore, the mixture may in an embodiment comprise 5-40 parts pore former material, 6-90 parts active material, 1-15 parts binder, and 1-20 parts (conductive) carbon.

Therefore, the mixture may in an embodiment comprise 5-40 wt.% pore former material, 6-90 wt.% active material, 1-15 wt.% binder, and 1-20 wt.% (conductive) carbon. This mixture is then used and dissolved in a sufficient amount of solvent to dissolve the binder but not the pore former material (and applied to the (optionally carbon coated) current conductor).

In a further aspect, the invention also provides a process for the production of an electrode assembly, for instance as described herein, comprising:

- providing a current collector (such as a foil as indicated above);
- applying a layer of a mixture of an active lithium storage material, a binder, (conducting) carbon, a pore former material, especially having dimensions in the range of 0.5-100 μm, such as 1-100 μm, like especially 1-50 μm, to at least part of the current collector, and optionally one or more of a liquid and a plasticizer;
- removing the pore former material.

As indicated above (and below), after applying the layer with mixture to the current collector and prior to removing the pore former material, the process may comprise applying pressure to the thus formed layer.

With such process, the electrode assemblies as described above may be produced. The mixture may for instance be a slurry or a suspension. As active lithium storage material, a material selected from the group comprising LiFePO₄, Li[Ni,Mn,Co]₂O₄, such as LiMn₂O₄ or LiNi₀.₅Mn₁.₅O₄, or Li[Ni,Mn,Co]₁O₂, such as LiCoO₂ for the cathode may be applied, and for the anode a material selected from the group comprising Li₄Ti₃O₁₂, TiO₂, Si,
C coated Si, and C may be applied (see also above, especially for further possible active materials).

The binder may comprise one or more of PVDF (polyvinylidene fluoride), CMC (carboxymethyl cellulose), and PTFE (polytetrafluoroethylene), although other materials may be applied as well. The binder may be a solid material, but may also be a liquid material. When using a slurry or suspension, the binder may be a liquid material during processing and/or a liquid is part of the mixture (and may be used to provide the liquid properties of the slurry or suspension). The liquid is especially chosen that the pore former material does not (substantially) solve therein. In an embodiment, the liquid comprises one or more of NMP (N-methylpyrrolidone), acetone, and (dissolved)THF (tetrahydrofuran), but also other liquids may be applied. The binder may especially be solved in a solvent. In this way a liquid is obtained which may be used to form for instance the liquid material, such as a slurry or suspension, with the other herein indicated ingredients.

As pore former material (or pore forming material) any suitable material may be applied, but preferably a pore former material that may easily be solvable in water or ethanol, especially in water. Further, preferably materials are used that may also form, upon salvation or reaction with a solvent a gas, as gas formation may contribute to pore formation. In an embodiment, the pore former material comprises one or more of NaHCO₃, NaCl, MgCl₂, and (NH₄)₂CO₃, though other systems may also be applied (see above). Preferably, the pore former material is a solid, crystalline material. Hence, in an embodiment the pore former material may be removed by dissolving the pore former material in a solvent for the pore former material. The pore former material is preferably not (well) solvable in the liquid (such as one of the indicated solvents).

Hence, in an embodiment, the pore former comprises a crystalline material.

In a specific embodiment, the pore former is soluble in water. However, in another specific embodiment the pore former is non-soluble in water. In such embodiment, the binder may be soluble in water (may be on a water basis). Especially, the solvent for the pore former material is not a solvent for the binder (an in an embodiment vice versa). For instance, PVDF or PTFE solvable in organic solvents, whereas CMC or SBD are solvable in water.

In an embodiment, the pore former material is removed by thermal treatment of the layer obtained as described herein. Especially, the pore former comprises (NH₄)₂CO₃, and/or (NH₄)HCO₃. These materials may thermally be removed (due to decomposition upon heating). Thermal treatment may especially beneficial in view of processing considerations.
The pore former is applied to provide a porous structure. Interconnection of the pores with the present process may especially be created. The pore former is used as a kind of templating agent, and is therefore also indicated as template, templating material, etc.

In a further embodiment, the liquid is a solvent for the binder, and the pore former material does not or only partly dissolve in the solvent for the binder. In a specific embodiment, the pore former material is removed by dissolving the pore former material in a solvent for the pore former material.

Carbon may be provided per se, and may be present as coating on the active material. For instance, carbon coated Li$_4$Ti$_5$O$_{12}$ is commercially available. However, even when using carbon coated Li$_4$Ti$_5$O$_{12}$, or other carbon coated materials, the addition of carbon may be desired, in order to further improve electrical conductivity.

The mixture may be applied by casting the mixture to the current collector. In an embodiment, the mixture is melted to the current collector.

In an embodiment, wherein after applying the layer with mixture to the current collector (and removal of solvent, for instance by evaporation) and prior to removing the pore former material, the process comprises applying pressure to the thus formed layer. In an embodiment, pressure may be applied after drying, and in another embodiment, pressure may be applied during drying.

In yet another embodiment, which may be combined with the previous one, wherein after removing the pore former from the layer and prior to drying the layer, the process comprises applying pressure to the thus formed layer. In an embodiment, pressure may be applied after drying, and in another embodiment, pressure may be applied during drying.

Hence, in a further embodiment, the invention further provides a process comprising:

- providing a current collector;
- applying a layer of a mixture of a lithium storage material, a binder, conducting carbon, a liquid, and a pore former material having dimensions in the range of 1-100 μm to at least part of the current collector;
- optionally drying the layer (in this way, solvent – if any – may be removed), or alternatively removing the liquid (especially solvent);
- applying pressure to the layer, (in this way good conducting contact in the layer and high tap density are insured)
- removing the pore former material; and
drying the layer (again).

In a preferred embodiment, the lithium storage material comprises LiFePO$_4$ or Li$_4$Ti$_5$O$_{12}$, the binder comprises one or more of PVDF, CMC, and PTFE, the liquid comprises one or more of NMP, acetone, and THF, and the pore former material comprises one or more of NaHCO$_3$, NaCl, MgCl$_2$, (NH$_4$)$_2$CO$_3$ and NH$_3$HCO$_3$. However, also other combinations of materials may be applied.

Hence, in an embodiment of the process of the invention the lithium ion storage material comprises particulate active lithium storage material, wherein the carbon comprises particulate carbon, and binder. Especially, the number average particle size of the particulate active lithium storage material may be in the range of 100 nm – 1 μm, and the number average particle size of the particulate carbon is in the range of 1 nm – 0.1 μm.

In a specific embodiment, the amount of lithium ion storage material is at least 85 wt.%, wherein the amount of carbon is at least 2 wt.%, and the amount of binder is at least 2 wt.% relative to the total amount of active lithium storage material, carbon and binder. In a further embodiment, the active lithium ion storage material comprises LiFePO$_4$ or Li$_4$Ti$_5$O$_{12}$, the binder comprises one or more of PVDF, CMC, and PTFE, the liquid comprising one or more of NMP, acetone, and THF, and the pore former material comprises one or more of NaHCO$_3$, NaCl, LiCl, MgCl$_2$, and (NH$_4$)$_2$CO$_3$, NH$_3$HCO$_3$. In yet a further embodiment, the binder comprises one or more of PVDF and PTFE. Especially such embodiment may give good Li storage properties.

Hence, the invention provides also a lithium storage electrode layer on a current collector, obtainable by the process as defined herein. Further, the invention also provides an electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer is obtainable by the process as defined herein.

In an embodiment, a combination of two or more different pore formers is applied. Alternatively or additionally, in an embodiment, a combination of two or more different liquids (especially solvents) is applied. Alternatively or additionally, in an embodiment, a combination of two or more different binders is applied.

Hence, to enhance the power density of Li-ion battery electrodes without compromising the tap density a simple and cost effective templating technique was developed using hydrogen carbonate salts. The solid templating material makes compaction for good electronic contact possible while upon subsequent removal these salts and the gas released create an interconnected network with only slight increase of electrode porosity. Application to commercially available carbon coated LiFePO$_4$ (crystallite size ~140nm)
results in 35% charge capacity retention at 60 C with tap densities close to 2 g/cm³. Up to date similar rate performances are only achieved by nanostructured electrodes generally having much lower tap densities (higher porosities) and electrode thickness, which results in effectively much lower energy densities. The improved performance is explained by improved Li⁺ ion electrolyte accessibility through the interconnected network in the electrode matrix, effectively lifting constraints of through solid ionic diffusion. This enables high energy density LiFePO₄ electrodes to retain good capacity during (dis)charging at relatively high current i.e., up to 60C. Such facile templating methods will be more generally applicable for other types of Li-ion insertion electrode materials.

The term “substantially” herein will be understood by the person skilled in the art. The term “substantially” may also include embodiments with “entirely”, “completely”, “all”, etc. Hence, in embodiments the adjective substantially may also be removed. Where applicable, the term “substantially” may also relate to 90% or higher, such as 95% or higher, especially 99% or higher, even more especially 99.5% or higher, including 100%. The term “comprise” includes also embodiments wherein the term “comprises” means “consists of”.

Furthermore, the terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. Use of the verb "to comprise" and its conjugations does not exclude the presence of elements or steps other than those stated in a claim. The article "a" or "an" preceding an element does not exclude the presence of a plurality of such elements. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.
BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying schematic drawings in which corresponding reference symbols indicate corresponding parts, and in which:

Figs. 1a-1d schematically depicts some aspects of the invention. These drawings are not necessarily on scale;

Fig. 2a schematically depicts a SEM figure of the macro porous lithium storage electrode layer (here a LiFePO₄-based layer);

Figs. 2b-2c schematically depict some aspects of the invention;

Figs 3a-3b schematically depict some embodiments of a battery; These drawings are not necessarily on scale; and

Figs. 4a-4d (a) show the charging voltage profiles with respect to a Li/Li⁺ reference electrode for different rates for a non-templated electrode with 2.6 mg/cm² active material loading; (b) Charging voltage profile for different rates for a templated electrode with 2.7 mg/cm² active material loading; (c) Charging voltage profile for different rates for a templated electrode with 7.5 mg/cm² active material loading; (d) Charge rate comparison between templated and non-templated electrodes.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Fig. 1a schematically depicts an electrode assembly 100 ("assembly 100") for a lithium ion battery, the assembly 100 comprising a lithium storage electrode layer 110 on a current collector 120, such as a Cu foil, wherein the lithium storage electrode layer 110 is a porous layer 10 having a porosity in the range of 5-35%, comprising pores 11 having pore widths d (see below) in the range of 1-100 μm, and having a porous layer thickness h1 in the range of 5-500 μm. The current collector 120 has a height h2; the total height of the electrode assembly 100 is indicated with h. Reference 7 indicates carbon, such as present as particulate carbon. Reference 17 indicates lithium active storage material, such as present as particulate lithium active storage material, and reference 27 indicates a binder.

Fig. 1b very schematically depicts a lithium ion battery 200, with anode 101 and cathode 102. Both the anode 101 and the cathode 102 are electrode assemblies 100 as described herein, but with different properties, such as for instance the lithium storage electrode layer 110 of the cathode 102 being based on LiFePO₄ as Li storage material, and the lithium storage electrode layer 110 of the anode 101 being based on C. During charging of the lithium ion battery 200, Li ions will enter the anode (for instance via the electrolyte in
the pores of the lithium storage electrode layer 110 of the anode 101). Reference 201 indicates a separator (which is soaked in the liquid electrolyte). Note that only the most relevant elements for the invention have been depicted. Reference 103 indicates electrolyte, that is in between the electrode assemblies 100, and which also penetrates the pores. Examples of electrolytes are 1 molar LiPF₆ dissolved in a mixture of EC/DMC (ethylene carbonate / dimethylcarbonate), or 1 molar LiPF₆ dissolved in a mixture of EC/DEC (diethylene carbonate) or LiClO₄ dissolved in 1M LiClO₄ in propylene carbonate.

Figs. 1c-1d schematically depict in more detail the lithium storage electrode layer 110. As can be seen, pores 11 can also be interconnected. Especially when the pore former material has a volume fraction of at least 7 wt.%, and expands when removed interconnection may be achieved. Interconnection of the pores 11 is preferred.

Fig. 2a is a SEM picture of the lithium storage electrode layer 110 based on LiFePO₄. In this example, the presence of pore former after removal was below the detection limit of the elemental analysis unit of the SEM.

Fig. 2b is another schematic drawing of the lithium storage electrode layer, with a phase of particles, carbon 7 and active lithium storage material 17, and in between binder 27. Large pores 11, substantially not in the particulate material, but as pores in the entire layer are the basis of the porosity. The figure shows interconnectivity of the pores.

Due to the fact that substantially the entire amount of pore former is released during removal of the pore former, it seems apparent, that the pores are interconnected. Substantially no pore former is left in the lithium storage layer 110 (which is the porous layer 10). In some instances, gas formation in the solvent of the pore former is perceived, which is also an indication of the fact that the pores are interconnected.

Fig. 2c shows schematically the impact of templating. The spheres represent the active lithium storage material. Left (I): Non-templated electrode with high tortuosity and resulting long Li-ion diffusion pathway (47) towards the active material deep in the electrode near the current collector 120. Middle (II): NaHCO₃ template, with NaHCO₃ (or other template (i.e. pore former) being indicated with reference 37. After removal of the pore former or template 37, Right (III): Short Li-ion diffusion pathway 47 towards the active material due to removal of the (NaHCO₃) template ribbons. Due to the larger pores and/or better interconnectivity, in the situation III, the pathway 47 of Li⁺ is much shorter and for a large part through a liquid electrolyte, leading to better properties. In the situation I, without template or pore former 37, the liquid pathway may sometimes be blocked. Though Li⁺ may
finally reach the current collector through the solid electrode material, this may be slow or very slow, which is indicated with the dashed line 57.

Figs. 3a and 3b schematically depict two different embodiments of a lithium ion battery 200. References 120a and 120c indicate current collector anode and current collector cathode respectively. In between anode and cathode there is a separator 103 soaked in a liquid electrolyte. In the embodiment depicted in fig. 3a, the lithium storage electrode layers 110, which sandwich the respective current collector anodes and current collector cathodes are relatively thin, leading to a battery that may be charged and discharged fast (e.g. for high power applications). In the embodiment schematically depicted in fig. 3a, the lithium storage electrode layers 110 are much thicker. This may be a high energy density application where there is realized a relatively large amount of active material in the battery compared to the other materials such as current collectors, separator and electrolyte.

Figs. 4a-4d (a) show the charging voltage profiles relative to a Li/Li⁺ counter electrode for different rates for a non-templated electrode with 2.6 mg/cm² active material loading; (b) Charging voltage profile for different rates for a templated electrode with 2.7 mg/cm² active material loading; (c) Charging voltage profile for different rates for a templated electrode with 7.5 mg/cm² active material loading; (d) Charge rate comparison between templated and non-templated electrodes. These figures are also further elucidated below.

EXAMPLES

Example 1: Production of electrodes

For producing the cathodes: The method involves the mixing of 10 - 40% micron sized NaHCO₃ crystals (or an equally suitable other material) into the normal slurry that is used to produce a cathode. Such slurry involves of the order of 80 wt.% LiFePO₄ active material, 10 wt.% PVDF binder, and 10wt.% conducting carbon altogether dissolved in a suitable organic solvent such as NMP. The NaHCO₃ (or equivalent) should not dissolve in the NMP (or other solvent) because these crystallites are present to produce after removing them the porous structure. After casting, evaporation of the solvent, pressing for a compacted layer, and drying in an oven, the NaHCO₃ is washed away in water upon which CO₂ gas evolves and the NaOH is dissolved and washed away through the pores. The gas evolution is expected to contribute to the formation of good porosity. After thorough drying in a vacuum oven the electrode is ready for use in a battery with a liquid electrolyte.
For producing the anodes: a similar method based on pore former \((\text{NH}_3)_2\text{CO}_3\) has been used with \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) (LTO) where the pore former is removed by thermal treatment. No water is used here because that will exchange Li for H in this material.

5 Example 2: Measurements

Lithium ion batteries with electrode assemblies as described herein were made and compared to similar systems, but without porosity of the lithium storage electrode layer of the anode and cathode.

<table>
<thead>
<tr>
<th>Charge rate</th>
<th>Capacity untreated electrode</th>
<th>Capacity NaHCO₃ treated electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/20 (20h)</td>
<td>98%</td>
<td>98%</td>
</tr>
<tr>
<td>C/10 (10h)</td>
<td>91%</td>
<td>97%</td>
</tr>
<tr>
<td>C/5 (5h)</td>
<td>85%</td>
<td>95%</td>
</tr>
<tr>
<td>C/2 (2h)</td>
<td>65%</td>
<td>95%</td>
</tr>
<tr>
<td>1C (1h)</td>
<td>35%</td>
<td>94%</td>
</tr>
<tr>
<td>2C (30min)</td>
<td>0%</td>
<td>92%</td>
</tr>
<tr>
<td>5C (12min)</td>
<td>0%</td>
<td>82%</td>
</tr>
<tr>
<td>10C (6min)</td>
<td>0%</td>
<td>70%</td>
</tr>
<tr>
<td>20C (3min)</td>
<td>0%</td>
<td>55%</td>
</tr>
</tbody>
</table>

Table 1: Capacity measurements

Comparison of the capacity (C) of an untreated and treated electrode for increasing charge rate. 100% capacity means 170 mAh/g, the theoretical capacity of LiFePO₄. The thickness and weight of both films is approximately 100 micron and 20 mg/cm² carbon coated LiFePO₄. C/20 indicates the capacity when charging 20 h. The percentages are relative to an ideal material. As can be seen, the micro porous lithium storage electrode layers provide a superior capacity, especially at the preferred shorter charging times.

Example 3: Production of electrodes

LiFePO₄ cathodes were prepared by thoroughly mixing carbon coated LiFePO₄ (140nm, Phostech) powder with PVDF (Aldrich), and Super P carbon black (TAMCIL) in a 90:5:5 weight ratio using NMP as solvent. For preparing templated electrodes 20% to 50
wt% NaHCO₃ (Aldrich) is added to the electrode slurry. First the NaHCO₃ is stirred in NMP forming a sodium hydrogen carbonate suspension followed by the addition of PVDF and again stirring until the binder is dissolved. Part of the NaHCO₃ dissolves as is evident from the formation of long, thin, ribbon like crystals, while the remainder forms micron sized crystals in a slightly turbid suspension. Once the suspension becomes almost transparent by PVDF dissolution, the carbon coated LiFePO₄ and the carbon black are added and stirred for approximately 12 hours. The resulting slurry was casted using different doctor blade thicknesses onto carbon coated Al foils (Exopad) and the resultant electrode thickness is measured by using a Timos Vectra-Touch precession instrument. The electrodes are dried at 40°C for 48 hours in a vacuum oven to evaporate the NMP. To enhance good electronic contact between active materials and carbon black, it is essential to mechanically compress the dried electrodes using a roller hand press. This also makes the electrode density high. After mechanical compaction the NaHCO₃ templated electrodes are washed with demineralized water which reacts with the NaHCO₃ towards water soluble NaOH and gaseous CO₂, resulting in a compacted but porous electrode. The gas formation is visible as tiny gas bubbles evolving at the electrode surface (see Supporting Information). From the fact that all NaHCO₃ can be removed (elemental analysis) it is clear that the crystals are providing connected pathways that the water is capable of opening connected pores completely. The washing step is followed by drying the electrodes for a few hours at 100°C to 140°C.

**Example 4: Battery preparation**

Battery cells were assembled in Swagelok type cells under argon atmosphere (<0.1 ppm O₂/H₂O). Lithium metal was used as anode and glass fiber disks (Whatman) as separators. The electrolyte used was 1.0 molar LiPF₆ in EC/DMC (ethylene carbonate and dimethyl carbonate in a 1:1 ratio) (Novolyte, battery grade). To characterize the obtained batteries the cells were tested at variable charge rate between C/20 up to 60C and always discharged with a C/5 rate within a voltage window of 4.2 and 2.5 V vs Li/Li⁺ using a Maccor 4300 battery cycler. The electrode thickness and microstructure were studied by a scanning electron microscope JEOL 7500F. An inbuilt EDX detector was applied for elemental analysis and mapping. The crystal structure of active material and template material before removal from the electrodes was characterized by the PANalytical’s X’Pert PRO X-ray diffractometer applying Cu Ka x-rays and using a monochromator to suppress fluorescence.
Example 5: Electrode characterization

The characteristic Sodium energy levels observed in the Energy Dispersive X-Ray spectra in Figure 1 confirm the presence of NaHCO$_3$ in the dried electrodes before washing. Element mapping suggested and confirmed a distribution of NaHCO$_3$ in the LiFePO$_4$ electrode composite where the largest distances between NaHCO$_3$ concentrations are a few μm and apparent concentration area’s are ranging from 0.5 to 1.5 μm. The presence of NaHCO$_3$ in the LiFePO$_4$ electrodes before washing is also confirmed by the characteristic XRD (X-Ray Diffraction) reflections of NaHCO$_3$. Electron micrographs showed that the NaHCO$_3$ also forms ribbons with a thickness of less than 50nm and a length of more than 10 μm on top of the LiFePO$_4$ electrodes. Apparently, the NaHCO$_3$ partly dissolves in the NMP and recrystallizes forming ribbons upon drying, a surprising and interesting process that we are currently studying in further detail. During the densification, required for providing good electronic contact through the electrode, the solid NaHCO$_3$ acts as temporary rigid support preventing the collapse of the interconnected porous structure. The result after washing and subsequent drying is a highly porous network with micrometer dimensions. The EDX spectrum and the XRD pattern after washing showed the complete removal of the Na, suggesting that the NaHCO$_3$ was completely decomposed through the following reaction: NaHCO$_3$ + H$_2$O → NaOH + CO$_2$ + H$_2$O.

The formation of CO$_2$ is clearly observed during the washing step which most likely also attributes to the interconnectivity of the porous network. The electrodes without the NaHCO$_3$ template, also have a high degree of porosity; however, the pores appear much less well connected.

<table>
<thead>
<tr>
<th>Electrode type</th>
<th>Thickness [cm]</th>
<th>Active material [mg/cm$^2$]</th>
<th>Electrode density [g/cm$^3$]</th>
<th>Porosity [%]</th>
<th>Tap density [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non Templated</td>
<td>0.0013</td>
<td>2.6</td>
<td>2.25</td>
<td>33.7</td>
<td>2.02</td>
</tr>
<tr>
<td>Non Templated</td>
<td>0.0021</td>
<td>4.1</td>
<td>2.17</td>
<td>35.9</td>
<td>1.94</td>
</tr>
<tr>
<td>Non Templated</td>
<td>0.0032</td>
<td>6.1</td>
<td>2.15</td>
<td>36.6</td>
<td>1.93</td>
</tr>
<tr>
<td>Templated</td>
<td>0.0013</td>
<td>2.7</td>
<td>2.23</td>
<td>34.2</td>
<td>2.01</td>
</tr>
<tr>
<td>Templated</td>
<td>0.0028</td>
<td>5.3</td>
<td>2.12</td>
<td>37.5</td>
<td>1.91</td>
</tr>
<tr>
<td>Templated</td>
<td>0.0039</td>
<td>7.5</td>
<td>2.11</td>
<td>37.9</td>
<td>1.90</td>
</tr>
</tbody>
</table>

25 Table 2 Prepared electrodes listing the thickness, active material loading, electrode density, porosity and tap density. The porosity is calculated from the apparent weights and thickness.
Measurement of the electrode thickness and weight per cm² electrode is used to determine the porosity and tap density as shown for all electrodes in Table 2. The increase in porosity for both, templated and non templated electrodes with increasing loading density is due to application of the same calendaring pressure during electrode fabrication. Table 2 also illustrates that the templated electrodes have typically only 2 to 3% higher porosity due removal of the NaHCO₃ template.

Results and Discussion

The electrochemical charge curves of the non-templated LiFePO₄ electrode with loading density 2.6 mg/cm² (porosity ~34%) were determined (see fig. 4a). As expected, the charging capacity strongly depends on the charge rate, decreasing from ~144mAh/g at C/5 to 40 mAh/g at 60C (see summary in fig. 4d).

Increasing the LiFePO₄ loading density (active material per cm² electrode) results in smaller capacities at the same charge rate as shown for the 6.1 mg/cm² (porosity 37%) non-templated electrode in fig. 4d. Faster charging allows a decreasing fraction of the electrode to participate.

Fig. 4b shows the charge voltage profiles for the NaHCO₃ templated LiFePO₄ electrode with comparable loading density and porosity compared to one of the non-templated electrodes, 2.7 mg/cm² (porosity ~34%). The higher charge capacities at all rates decreasing from ~163mAh/g at C/5, to ~60 mAh/g at 60C illustrate the superior performance of the templated electrode (see also fig. 4d). Such rate performances should be compared in the context of the active material loading density, which strongly affects the rate dependent capacity and the tap density of the electrode which determines the volumetric energy density. Where the nano-sizing is very effective for improving the rate performance, it negatively affects the tap density (inversely related to the porosity) generally towards values below 1 g/cm³ leading to low volumetric energy densities.

The templated materials with tap density close to 2 g/cm³ result in almost 120 mAh/g at 20C charge (albeit with C/5 discharge) illustrating the excellent performance in combination with high volumetric energy density of the templated electrodes. For comparison, recently high performance monodisperse porous microspheres were reported to reach less than half at 20C with a lower tap density around 1.2 g/cm³. Higher charge rates are reported in literature, 90 mAh/g at 60C for core-shell nanostructured LiFePO₄/carbon composites and 80 mAh/g at 60C for 50 nm LiFePO₄ coated with a fast ionic conducting
phases\textsuperscript{7}, however, these electrodes have only a very limited active material loading of less than 1 \text{ mg/cm}^2.

In Figure 4(c) the charge curves of a templated electrode with a larger loading density of 7.5 \text{ mg/cm}^2 (porosity~38\%) is also shown. Hence, as expected, the larger loading density decreases the charge capacity for each rate (see also Fig. 4d). However, the charge capacity for the C/5 to 2C rate of the templated 7.5 \text{ mg/cm}^2 is comparable to the non-templated electrode with loading density 2.6 \text{ mg/cm}^2. This illustrates how the better rate performance of the templated electrodes can enable thicker electrodes with a rate performance comparable to that of the three times thinner non-templated electrode. The larger loading density of the templated electrodes will increase the amount of active material per \text{ cm}^2 battery, thereby increasing the overall effective energy density of the battery.
CLAIMS:

1. An electrode assembly for a lithium ion battery, the electrode assembly comprising a lithium storage electrode layer on a current collector, wherein the lithium storage electrode layer comprises an active lithium storage material, carbon and binder, and wherein the lithium storage electrode layer is a porous layer having a porosity in the range of 5-45%.

2. The electrode assembly according to claim 1, with pores having pore widths in the range of 0.5-50 μm, and having a porous layer thickness in the range of 5-500 μm.

3. The electrode assembly according to any one of the preceding claims, wherein the porosity is in the range of 10-40%, wherein the pores have widths in the range of 1-30 μm, and having a porous layer thickness in the range of 10-200 μm.

4. The electrode assembly according to any one of the preceding claims, wherein the porosity is in the range of 30-40%, wherein the pores have widths in the range of 1-30 μm, and having a porous layer thickness in the range of 10-200 μm.

5. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer comprises particulate active lithium storage material, particulate carbon, and a binder.

6. The electrode assembly according to claim 5, wherein the porosity is due to channels within the lithium storage electrode layer between the particles of the particulate active lithium storage material and the particulate carbon.

7. The electrode assembly according to any one of claims 5-6, wherein the number average particle size of the particulate active lithium storage material is in the range of 50 nm – 1 μm, and wherein the number average particle size of the particulate carbon is in the range of 1 nm – 0.1 μm.
8. The electrode assembly according to any one of the preceding claims, wherein the binder is selected from the group consisting of PVDF (polyvinylidene fluoride) and PTFE (polytetrafluoroethylene).

9. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer has a density in the range of 50 – 90% of the theoretical density of packed active lithium storage material, carbon, and binder.

10. The electrode assembly according to any one of the preceding claims, wherein the mass loading of the active lithium storage material in the lithium storage electrode layer on the current collector is at least 10 mg/cm², and wherein 80% of said active lithium storage material can be charged within 1 hour.

11. The electrode assembly according to any one of the preceding claims, wherein the mass loading of the active lithium storage material in the lithium storage electrode layer on the current collector is at least 15 mg/cm², and wherein 70% of said active lithium storage material can be charged within 1 hour.

12. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer comprises a material selected from the group consisting of LiFePO₄, LiMn₂O₄, LiNi₀.₅Mn₁.₅O₄, LiCoO₂, and Li[NiₓMn₁₋ₓ]O₂, Li[LiₓNiₓMn₁₋ₓ]O₂, Li[NiₓMn₁₋ₓ]O₂, LiCoO₁₋ₓMn₁₋ₓO₂, and LiNi₀.₅Al₀.₅O₂.

13. The electrode assembly according to any one of the preceding claims, for use as cathode, wherein the lithium storage electrode layer comprises ≥ 75 wt.% of a material selected from the group consisting of LiFePO₄, LiMn₂O₄, LiNi₀.₅Mn₁.₅O₄, LiCoO₂, and Li[NiₓMn₁₋ₓ]O₂, Li[LiₓNiₓMn₁₋ₓ]O₂, LiCo₁₋ₓNi₁₋ₓMn₁₋ₓO₂, LiNi₀.₅Al₀.₅O₂, and LiNi₀.₅Al₀.₅O₂.

14. The electrode assembly according to any one of the preceding claims, for use as anode, wherein the lithium storage electrode layer comprises ≥ 75 wt.% of a material selected from the group consisting of Li₄Ti₅O₁₂, TiO₂, Si, Ge, and C.
15. The electrode assembly according to any one of the preceding claims, wherein the active lithium storage material, not being carbon, is carbon coated.

16. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer comprises at least 85 wt.% of the active lithium storage material and at least 1.5 wt.% carbon, related to the total weight of the lithium storage electrode layer.

17. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer comprises at least 85 wt.% of the active lithium storage material and at least 5 wt.% carbon, related to the total weight of the lithium storage electrode layer, and wherein the active lithium storage material is selected from the group consisting of LiFePO₄, LiMn₂O₄, LiNi₀.₅Mn₁.₅O₄, LiCoO₂, Li[Ni,Mn,Co]₁O₂, Li[Li,Ni,Mn,Co]₁O₂, LiCo₁/₃Ni₁/₃Mn₁/₃O, LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂, LiNiO₂, Li₂FePO₄F, LiC₆, Li₄Ti₅O₁₂, Si, Ge, and carbon.

18. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer comprises at least 85 wt.% of the active lithium storage material and at least 5 wt.% carbon, related to the total weight of the lithium storage electrode layer, and wherein the active lithium storage material is selected from the group consisting of LiFePO₄, LiMn₂O₄, LiNi₀.₅Mn₁.₅O₄, LiCoO₂, Li[Ni,Mn,Co]₁O₂, Li[Li,Ni,Mn,Co]₁O₂, LiCo₁/₃Ni₁/₃Mn₁/₃O, LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂, LiNiO₂, Li₂FePO₄F, LiC₆, and Li₄Ti₅O₁₂.

19. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer comprises at least 85 wt.% of the active lithium storage material and at least 5 wt.% carbon, related to the total weight of the lithium storage electrode layer, and wherein the lithium storage electrode layer has a porous layer thickness of at least 100 μm.

20. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer has a porous layer thickness in the range of 5-500 μm.

21. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer has a porous layer thickness of at least 5 μm.
22. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer has a porous layer thickness of at least 100 μm.

23. The electrode assembly according to any one of the preceding claims, wherein the current collector comprises a foil selected from the group consisting of a Cu foil and an Al foil, and wherein the foil has a foil thickness in the range of 1-30 μm.

24. The electrode assembly according to claim 23, wherein the current collector comprises a carbon coated Al foil.

25. The electrode assembly according to any one of the preceding claims, wherein the lithium storage electrode layer is obtainable by the process according to any one of claims 25-34.

26. A lithium ion battery comprising a cathode and an anode, wherein one or more of the cathode and the anode comprise an electrode assembly according to any one of claims 1-25.

27. The lithium ion battery according to claim 27, wherein the lithium storage electrode layers of the electrode assemblies have porous layer thicknesses of at least 100 μm.

28. The lithium ion battery according to any one of claims 26-27, wherein the lithium storage electrode layers of the electrode assemblies have porous layer thicknesses of at least 100 μm, and wherein the lithium ion battery has a capacity of at least 3 mAh/cm².

29. The lithium ion battery according to any one of claims 26-28, comprising a first electrode assembly and a second electrode assembly according to any one of the preceding claims, with liquid electrolyte configured between the first and the second electrode assembly, wherein the pores of the porous layers are at least partly filled with said electrolyte.

30. A process for the production of an electrode assembly, comprising:
   - providing a current collector;
applying a layer of a mixture of an active lithium storage material, binder, carbon, a pore former material having dimensions in the range of 0.5-50 µm, especially 1-50 µm to at least part of the current collector, and optionally one or more of a liquid and a plasticizer;

removing the pore former material.

31. The process according to claim 30, wherein after applying the layer with mixture to the current collector and prior to removing the pore former material, the process comprises applying pressure to the thus formed layer.

32. The process according to any one of claims 30-31 comprising:

- providing a current collector;
- applying a layer of a mixture of a lithium ion storage material, a binder, carbon, a liquid, and a pore former material having dimensions in the range of 0.5-50 µm to at least part of the current collector;
- drying the layer;
- applying pressure to the layer;
- removing the pore former material; and
- drying the layer.

33. The process according to claim 32 wherein the liquid is a solvent for the binder, and wherein the pore former material does not or only partly dissolve in the solvent for the binder.

34. The process according to any one of claims 30-33, wherein the pore former material is removed by dissolving the pore former material in a solvent for the pore former material.

35. The process according to claim 34, wherein the solvent for the pore former material is not a solvent for the binder.

36. The process according to any one of claims 30-35, wherein the pore former comprises a crystalline material.
37. The process according to any one of claims 30-36, wherein the pore former is soluble in water.

38. The process according to any one of claims 30-36, wherein the pore former is non-soluble in water.

39. The process according to any one of claims 30-38, wherein the pore former material is removed by thermal treatment of the layer obtained by any one of claims 30-38.

40. The process according to claim 39, wherein the pore former comprises one or more of \((\text{NH}_4)_2\text{CO}_3\) and \((\text{NH}_4)\text{HCO}_3\).

41. The process according to any one of claims 30-40, wherein the lithium ion storage material comprises particulate active lithium storage material, wherein the carbon comprises particulate carbon, and binder.

42. The process according to any one of claims 30-41, wherein the number average particle size of the particulate active lithium storage material is in the range of 100 nm – 1 \(\mu\)m, and wherein the number average particle size of the particulate carbon is in the range of 1 nm – 0.1 \(\mu\)m.

43. The process according to any one of claims 30-42, wherein the amount of lithium ion storage material is at least 85 wt.%, wherein the amount of carbon is at least 2 wt.%, and wherein the amount of binder is at least 2 wt.% relative to the total amount of active lithium storage material, carbon and binder.

44. The process according to any one of claims 30-43, wherein the active lithium ion storage material comprises \(\text{LiFePO}_4\) or \(\text{Li}_{x}\text{Ti}_y\text{O}_2\), wherein the binder comprises one or more of PVDF, CMC, and PTFE, wherein the liquid comprises one or more of NMP, acetone, and THF, and wherein the pore former material comprises one or more of \(\text{NaHCO}_3\), \(\text{NaCl}\), \(\text{LiCl}\), \(\text{MgCl}_2\), \((\text{NH}_4)_2\text{CO}_3\), and \(\text{NH}_4\text{HCO}_3\).

45. The process according to claim 44, wherein the binder comprises one or more of PVDF and PTFE.
46. A lithium storage electrode layer on a current collector, obtainable by the process according to any one of claims 30-45.
### A. CLASSIFICATION OF SUBJECT MATTER

- INV. H01M/4/62, H01M/4/66, H01M/4/134, H01M/10/0525, H01M/4/1395
- ADD. H01M/4/485, H01M/4/505, H01M/4/525, H01M/4/131, H01M/4/1391

According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

EPO-Internal

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of mailing of the international search report: 04/10/2012

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Authorized officer: Barenbrug-van Druten

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