

METHOD FOR MANUFACTURING OF SLURRY FOR PRODUCTION OF BATTERY FILM

Technical field

5 The available invention regarding a process for manufacturing of a slurry for production of a battery film, more specific deal with the available invention process for generating a slurry for application of anode and cathode materials in batteries, a process for manufacturing of cathodes and anodes for lithium batteries and a process for manufacturing of a lithium battery cell.

Background technique

10 A lithium battery is made from three main components: anode, cathode and electrolyte.

Anode and cathode normally consist of metal foils which are covered by a thin layer of a powder mixture, active materials, which are bound together by a binder. The binders function is to glue the powder particles together and glue these firmly to the metal foil. The binder must be flexible and chemically stable towards the electrolyte.

15 A typical anode consist of a copper foil which is covered by a thin layer (40 – 100 microns) with graffiti powder, carbon, which is tied together by means of the plastic material PVDF (polyvinylidene fluoride).

A typical cathode consist of an aluminum foil which is coated by a thin layer (40-100 microns) of lithium metal oxide which is bound together by the plastic material PVDF.

20 A typical electrolyte is a mixture of a lithium salt such as lithium hexafluorophosphate (LiPF_6), lithium tetrafluorophosphate (LiPF_4), lithium hexafluoroarsenate (LiAsF_6), lithium perchlorate (LiClO_4), Lithium tetrafluoroborate (LiBF_4), and lithium triflate (LiCF_3SO_3) and organic carbonates, for instance EC (ethylene carbonate), DEC (diethyl carbonate) and DMC(dimethyl carbonate).

25 The most common manufacturing process for making a battery film for lithium ion batteries is to blend active materials and PVDF, and mix this into a solvent dissolving the PVDF. The purpose to dissolve the binder is to disperse the material evenly between the particles in the powder mixture in order to secure a good binding between these. This mixture is then applied to the metal foil by means of extrusion, rolling or tape-casting depending on selected process

and amount of solvents used. After application the foil will be dried by evaporation of solvents.

The most common solvent in order to dissolve PVDF is NMP (N- Methyl-Pyrrolidone), which is both a toxic and environmentally harmful chemical. There are a variety of alternative solvents, but most of them have in common that they are either toxic, liable to catch fire or unfavorable relating to the chemical structure of the finished battery. Consequently, it is important that the solvent is fully removed from the battery film during production and that the evaporation of NMP is controlled with regards to the environmental requirements. The process of removing the last remnants of the solvent (down to ppm level) from the battery film is a demanding process which is both energy- and space demanding and make substantial demands from the technical equipment.

There are waterborne manufacturing processes in which the powder is mixed with water to form a paste or thin slurry. The disadvantage of using water is the relatively energy demanding process to evaporate the water so that the dried battery film must be completely free from water so that the battery shall operate.

From US 2005/0271797 A1 it is known that a production process for a lithium battery consisting of the steps of a) prepare an EC (ethylene carbonate) solution by loosening EC-crystals in a suitable solvent, (b) then dissolve a binder in a suitable solvent in order to make a binder solution and then add and mix sufficiently an active electrode material and an electric conductive material of a wanted composition into the binder solution, (c) add a defined amount of the EC mixture prepared in step (a) into the binder solution from step (b), blend the mixture of EC solution and the binder solution sufficiently so that the slurry in form of an electrode binder can be coated onto an electrode, (e) coat a collector with the slurry, (f) dry the paste layer at a given temperature, and complete the electrode production by pressing a dried electrode structure at a given pressure after the slurry has dried. The process described in US 2005/0271797 A1 also comprises mixing a solvent together with an ethylene carbonate plus insert a second solvent to a binder solution together with an active material for then subsequently to add a given amount of the solvent mixed with ethylene carbonate to the mixture of the binder solution with the other solvent. Thus the process comprises the application of at least one solvent for generating the slurry.

There is a need for providing a manufacturing process of slurry for electrode materials for lithium batteries which is not burdened with the problems associated with use of solvents indicated above.

Summary of the invention

- 5 There is a purpose with the present invention to provide a method for manufacturing of slurry for application onto cathode and anode materials in batteries, a method for manufacturing of cathodes and anodes for lithium batteries plus a method for manufacturing of a lithium ion battery cell, where the above mentioned problems are solved.

More exactly, the present invention is stating a method for manufacturing of slurry for coating
10 of electrodes for use in lithium ion batteries. The method comprises as a minimum the steps of

- a) Mix active materials with a binder into a binder solution, and
- b) Add an organic carbonate to a binder solution so that a slurry is generated

According to one aspect of the invention, the mixing process is executed according to the
15 steps a and b at a temperature above the melting temperature of the binder.

According to another aspect of the invention the active materials are adapted to one anode and one cathode respectively.

In accordance with yet another aspect of the invention is the active cathode material collected from the group of: LiCoO_2 , LiFePO_4 , LiMn_2O_4 , LiNiO_2 ,
20 $\text{Li}_2\text{FePO}_4\text{F}$, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, $\text{Li}(\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_z)$ and the active anode material is collected from the group of: LiC_6 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Si ($\text{Li}_{4,4}\text{Si}$) or Ge ($\text{Li}_{4,4}\text{Ge}$).

In accordance with an additional aspect of the invention the binder is a polyvinyl fluoride and the organic carbonate is collected from the group: ethylene carbonate, dimethyl carbonate or diethyl carbonate.

25 An additional aspect of the invention comprises the method's further process at least in the steps of:

- a) Mix active materials with a binder into a binder solution,
- b) Add an organic carbonate to the binder solution such that a slurry is generated
- c) Coat an electrode material with the slurry

- d) Evaporate/ dry the coating on the electrode material by drying/evaporation of the organic carbonate, and
- e) Surface treatment of the slurry so that the electrode is prepared for use in a lithium battery cell. The process is also characterized by the fact that step d
- 5 further may comprise a parallel step of recovery 4 where gases from the organic carbonate is collected for re-use. The collected organic carbonate can be condensed, filtered and cleaned before being used again.

In another implementation step e comprises one or more sub-steps of :

- i) Roll the electrode material
- 10 ii) Bake the electrode material, and
- iii) Finalize the electrode material for use in a lithium battery cell

In accordance with another aspect of the available invention, the active materials are adjusted for one anode and one cathode respectively, and the active cathode material may be collected from the group of: LiCoO_2 , LiFePO_4 , LiMn_2O_4 , LiNiO_2 , $\text{Li}_2\text{FePO}_4\text{F}$, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$,

15 $\text{Li}(\text{Li}_a\text{Ni}_x\text{Mn}_y\text{Co}_z)$ and the active anode material collected from the group of : LiC_6 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Si}(\text{Li}_{4,4}\text{Si})$ or $\text{Ge}(\text{Li}_{4,4}\text{Ge})$.

In accordance with an aspect from the available invention, then the binder is a polyvinylidene fluoride.

The organic carbonate can be collected from the group: ethylene carbonate, diethyl carbonate

20 or dimethyl carbonate.

In another aspect according to the available invention then a method for generating a lithium battery cell is provided, where the method at least comprises of the steps of :

Make a slurry for coating of electrodes for use in lithium ion batteries, where the slurry comprises active materials, binder and an additional diluting agent (thinner), where the

25 diluting agent consists of a component in an electrolyte material for a manufactured lithium battery cell,

- a) Coating of an anode material and a cathode material with the slurry,
- b) Evaporate/ dry the coating on the anode- and cathode material by steaming/ drying of the organic carbonate, and

- c) Surface treatment of the slurry so that the electrode is made ready for use in a lithium ion battery cell.
- d) Arrange one or several cathodes and anodes in layers with lithium permeable membranes lying between
- 5 e) Arrange cathodes, anodes and the permeable membranes in a house with one or more openings, and
- f) Fill the house with an electrolyte , where the electrolyte includes salts and diluents with lithium content

Further aspects and characteristics of the available invention are brought forward by the
10 belonging independent patent claims.

Short description of the drawings

The available invention will be more easy to understand with support of the belonging figures, where

Fig.1. shows a principle drawing for manufacturing of slurry for battery electrodes according
15 to the available invention.

Detailed description of the invention

In the following text, the available invention will be described with support from the belonging figure

It shall be understood that according to the invention, the foil that normally is used as
20 cathodes and anodes also may comprise materials similar to fabrics or more generally, any conductive conductor which is compatible with the methods according to the available invention.

First, there will be a description of a general implementation of the invention, followed by examples of the methods that will be shown.

25 As indicated introductorily there exists a desire to change the process of manufacturing the slurry for coating of battery electrodes for lithium batteries.

Lithium ion batteries normally consist of three active elements, namely anode, cathode plus an electrolyte. As indicated above, it is the purpose of the available invention to find an
30 alternative to the disadvantageous use of solvents for coating of the electrode foils.

The slurry that is applied to the electrode foils must have the correct body and viscosity so that the active layer that is applied to the electrodes will have a correct dry film thickness and homogeneity.

- 5 In order to be able to form a paste or thinly liquid slurry from binder, such as PVDF and powder in the form of active materials, the mixture has to be added a liquid. By using a liquid which is entered as a component in the finished battery it is not necessary that the liquid is removed completely. This component will still be added at a later stage in the process. According to the execution of the available invention, a method for manufacturing of the
10 slurry for coating of battery electrodes is provided, where the slurry, meaning active components and a binder will be diluted with a diluting agent, where the diluting agent is a component of the electrolyte which shall be used in the same lithium battery

In general the process for manufacturing of slurry according to the available patent can be
15 described with support from figure 1. Active materials A which will be constituent parts in the final slurry, will be mixed with a binder B in a first homogenization step 1. in order to obtain correct viscosity and consistency of the slurry a solvent C is added. It is in accordance with the available invention that the solvent C represents a component of the final lithium ion battery cell.

20 After the homogenization step the slurry has obtained the desired body/viscosity and the electrode material D can be coated 2 with the slurry. The coating process may be in the form of extruding, rolling or tape casting, or other suitable coating processes known from the industry.

25 Step 3 in the process comprises evaporation of the thinner which was added to the homogenization process 1. The applied slurry will consequently change from being viscous slurry to become a more solid material.

In parallel with step 3 there may be an active recycling step 4 which recycles the thinner that evaporates.

30 The following step 5 that is the step following step 3 and 4 is a step where the electrode material with the applied coating is rolled.

The following step 6 comprises baking of the rolled electrode, this baking will among other things secure that the binder adheres sufficiently to the active electrode materials and to the electrode foil.

5 The final step 7 comprises further finishing of the lithium ion batteries.

It shall be understood that manufacturing according to the steps 1 to 7 may be run consecutively and continuously, so that when step 1 is finished and a batch from step 1 moves onto step 2, then new materials can be added a homogenization of step 1, same is valid for the
10 following steps, so that a manufacturing process can run continuously.

Implementation according to the available invention

In the following the available invention will be described with an example.

In this example in accordance with the available invention, the materials that will be used in
15 the manufacturing of a lithium ion battery cell will comprise the following.

The anode, that is the positive electrode, consists of a copper foil; this copper foil shall be coated with an active material, generally in the form of a graffiti powder (LiC_6). Also other active materials such as titanat ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), $\text{Si}(\text{Li}_{4,4}\text{Si})$ or $\text{Ge}(\text{Li}_{4,4}\text{Ge})$ can be used as active anode material. The graffiti powder shall be applied to the copper foil, in order for such a
20 coating process to be successful and give a homogeneous surface then the graffiti powder must be mixed with 1 PVDF, PVDF and the graffiti powder must consequently be given a viscosity which is suitable for coating and thus the mixture will be added an organic carbonate, such as ethylene carbonate (EC) C. This blending step corresponds to the homogenization step 1 according to the general process description. The mixture may be
25 heated to a temperature above the melting point of the thinner, i.e. the ingredient that was blended in order to give the right viscosity. The temperature may well be above the melting point of the thinner and close to the transition temperature of the binder.

The cathode, i.e. the negative electrode consists of an aluminum foil this aluminum foil shall be coated by an active material in the form of a lithium metal oxide. The lithium metal oxide
30 shall be coated on the copper foil, so that such a coating process shall be successful and give a homogeneous surface then the lithium metal oxide A must be mixed with 1 PVDF, PVDF and lithium metal oxide must consequently be given a viscosity suitable for coating therefore the

mixture will be added ethylene carbonate (EC) C. This step of the mixing corresponds with the homogenization step 1 according to the general process description

The following steps for cathode and anode follow roughly the same process as described in figure 1.

5 Another performance specification according to the available invention

In the following the available invention will be described with another example.

In this example in accordance with the performance specification of the available invention the material used during the manufacturing of a lithium ion battery cell comprises the following.

- 10 The anode, that is the positive electrode consists of a copper foil, this copper foil shall typically be coated by an active material in the form of a graffiti powder, thus the process for the anode is according to the description above.

- 15 The cathode that is the negative electrode consists of an aluminum foil this aluminum foil shall be coated by an active material in the form of a metal oxide such like one of Lithium cobalt oxide (LiCoO_2), a polyanion such like Lithium iron phosphate (LiFePO_4) or a lithium manganese oxide (LiMn_2O_4). Further cathode materials are found in the not supplementary group, LiNiO_2 , $\text{Li}_2\text{FePO}_4\text{F}$, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{O}_2$ Li ($\text{Li}_a\text{Ni}_x\text{Mn}_y\text{Co}_z$) O_2 . For simplicity the term metal oxide will be used in the following for these mentioned phosphates/ oxides.

- 20 The metal oxide shall be coated on the copper foil, in order for such a coating process shall be successful and give a homogeneous surface, the metal oxide A must be mixed 1 with a binder B, for instance PVDF and the metal oxide must in addition be given a viscosity suitable for coating therefore the mixture is added an organic carbonate such as ethylene carbonate (EC) C or diethyl carbonate. This mixing step corresponds to the homogenization step 1 according to the general process description.

- 25 The following steps for cathode and anode will roughly follow the same process as described in figure 1.

It shall be understood that a number of binders and active raw materials can be combined, where the central issue is that the thinner shall be a component in the final battery.

In the following is a description of the electrolyte and the properties associated with the materials composing the parts of the electrolyte. The electrolyte in a normal battery normally consists of organic carbonates such as EC (ethylene carbonate), diethyl carbonate. EC which is the most common is a waxy material which melts at approximately 40⁰C and is then a liquid with low viscosity. EC is not poisonous; it is without smell and is only flammable at higher temperatures (above 140⁰C).

According to an aspect of the invention the desired viscosity of this slurry may be generated by mixing the binder B (such as PVDF), the powder A (active, materials) and molten EC C. The amount of EC is adjusted according to the desired viscosity of the mixture.

This mixture is homogenized 1 vigorously at a temperature above the melting point of EC and below the melting point of the binder (for example at approx. 180⁰C for PVDF). The particles with the binder will then because of the vigorous mixture be dispersed between all the particles in the mixture. If the homogenization takes place at a temperature above the melting temperature of the binder B, the mixture will obtain a lower viscosity.

When the mixture is homogenized sufficiently 1, so that the binder particles B are dispersed evenly between all the particles in the mixture, the metal foil D can be coated with the mixture. This may be done by extrusion, rolling or tape-casting. The battery film will then have to be heated 3 in order to evaporate the EC till the EC concentration is equal to or less than the desired EC concentration of the finished battery cell.

The consequent rolling 5 of the battery film will press the particles together and will improve the binding between the particles.

The EC- vapor which is formed by drying of the battery film can be condensed, filtered and reused in the process. EC is a harmless liquid with few health and environmental impacts.

A: Active materials, such as graffiti and lithium oxide

B: Binder, for example PVDF

C: Thinner according to the available invention, an electrolyte component such as organic carbonates

D: Leading foil, such as aluminum foil, copper foil, aluminum canvas and copper canvas among others

1: Homogenization

- 2: Coating, for instance by extruding, tape-casting, rolling or similar
- 3: Evaporation of solvents
- 4: Recycling of solvents
- 5: Rolling
- 5 6: Baking, to melt the binder
- 7: Further processing to build up the battery

CLAIMS

1. Method for manufacturing of slurry for coating of electrodes for use in lithium ion batteries, characterized by the method as a minimum comprises the steps of:
 - a) Mix (1) active materials (A) with a binder (B) into a binder solution, and
 - 5 b) Add (1) an organic carbonate (C) to the binder solution so that slurry is generated.
2. Method according to requirement 1, characterized by the mixing process according to the steps a and b are carried out at a temperature above the melting temperature of the organic carbonate (C) and below the melting point temperature of the binder (B).
3. Method according to the requirements 1 or 2, characterized by the active materials (A)
10 are adapted to an anode and a cathode respectively.
4. Method according to requirement 3, characterized by the active cathode material is fetched from the group of : LiCoO_2 , LiFePO_4 , LiMn_2O_4 , LiNiO_2 , $\text{Li}_2\text{FePO}_4\text{F}$, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, $\text{Li}(\text{Li}_a\text{Ni}_x\text{Mn}_y\text{Co}_z)$ and the active anode material is fetched from the group of LiC_6 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Si}(\text{Li}_{4,4}\text{Si})$ or $\text{Ge}(\text{Li}_{4,4}\text{Ge})$.
- 15 5. Method according to the requirements 1-4, characterized by the binder (B) being a polyvinyliden fluoride.
6. Method according to the requirements 1-5, characterized by the organic carbonate (C) is fetched from the group: ethylene carbonate, dimethyl carbonate, or diethyl carbonate.
- 20 7. Method for manufacturing of electrodes for a lithium battery cell, characterized by the method at least will comprise the steps of :
 - a) Mix (1) active materials (A) with a binder (B) into a binder solution,
 - b) Add (1) an organic carbonate (C) to the binder solution so that a slurry is generated,
 - 25 c) Coat (2) an electrode material (D) with the slurry,
 - d) Evaporate/dry (3) the coating on the electrode material by evaporating/drying of the carbonate, and
 - e) Surface treatment of the slurry (5,6,7) so that the electrode is prepared for use in a lithium battery cell.
- 30 8. Method according to requirement 7, characterized by step d in addition comprises a parallel recycling step (4) where deaerator from the organic carbonate is collected for re-use.
9. Method according to requirement 8, characterized by the collected carbonate is condensed, filtered and cleaned before re-use.

10. Method according to requirements 7-9, characterized by step e comprises one or several of the sub-steps of:
 - i) roll(5) the electrode material
 - ii) bake (6) the electrode material, and
 - 5 iii) finish (7) the electrode material for use in a lithium battery cell.
11. Method according to the requirements 7-10, characterized by the active materials (A) are adapted for an anode and cathode respectively.
12. Method according to requirement 11, characterized by the active cathode material is fetched from the group of: LiCoO_2 , LiFePO_4 , LiMn_2O_4 , LiNiO_2 , $\text{Li}_2\text{FePO}_4\text{F}$,
10 $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, $\text{Li}(\text{Li}_a\text{Ni}_x\text{Mn}_y\text{Co}_z)$ and the active anode material is fetched from the group of: LiC_6 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Si ($\text{Li}_{4,4}\text{Si}$) or Ge ($\text{Li}_{4,4}\text{Ge}$).
13. Method according to the requirements 7-12, characterized by the binder (B) is a polyvinyliden fluoride.
14. Method according to the requirements 6-12, characterized by the organic carbonate
15 (C) is fetched from the group: ethylene carbonate, diethyl carbonate, or dimethyl carbonate.
15. Method for manufacturing of a lithium ion battery cell, characterized by the method at least comprise the steps of:
 - a) Generate a slurry for coating of electrodes for use in lithium ion batteries, where
20 the slurry comprise active materials (A), binder (B) and a further thinner (C), where the thinner (C) constitutes a component part in an electrolyte material for a manufactured lithium ion battery cell,
 - b) Coat (2) an anode material and a cathode material with the slurry,
 - c) Evaporate/dry (3) the coating on the anode and cathode material by the organic
25 carbonate (C) being steamed/dried, and
 - d) Surface treatment (5,6,7) of the slurry so that the electrode is prepared for use in a lithium battery cell,
 - e) Arrange one or several cathodes and anodes in layers with lithium ion permeable membranes in between,
 - 30 f) Arrange cathodes, anodes and the permeable membranes in a house with one or several openings, and
 - g) Fill an electrolyte into the house, where the electrolyte comprises lithium containing salts and thinner (C).