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(54) Title: METHOD FOR PRODUCING A CARBON ENRICHED MATERIAL FROM HEAT TREATED LIGNIN

(57) Abstract: The present invention relates to a method for producing completely thermally stabilized agglomerated lignin, the method comprising the steps of a) providing agglomerated lignin having an average particle size in the range of from 50 to 500 μm; and b) heating the agglomerated lignin to a temperature in the range of from 140 to 300°C for a time period of at least 30 minutes, so as to obtain completely thermally stabilized agglomerated lignin. The present invention also relates to completely thermally stabilized agglomerated lignin and a method for producing a carbon enriched material obtained by subjecting the completely thermally stabilized agglomerated lignin to heat treatment.

METHOD FOR PRODUCING A CARBON ENRICHED MATERIAL FROM HEAT TREATED LIGNIN

Field of the invention

The present application relates to a method for producing completely thermally stabilized agglomerated lignin and a completely thermally stabilized agglomerated lignin. The present application further relates to a method for producing a carbon enriched material from said completely thermally stabilized agglomerated lignin, a negative electrode for a non-aqueous secondary battery comprising said carbon enriched material as active material, and use of said carbon enriched material as active material in a negative electrode of a non-aqueous secondary battery.

Background

Secondary batteries, such as lithium-ion batteries, are electrical batteries which can be charged and discharged many times, i.e. they are rechargeable batteries. In lithium-ion batteries, lithium ions flow from the negative electrode through the electrolyte to the positive electrode during discharge, and back when charging. Today, typically a lithium compound, in particular a lithium metal oxide such as lithium nickel manganese cobalt oxide (NMC) or alternatively a lithium iron phosphate (LFP) is utilized as material of the positive electrode and a carbon enriched material is utilized as material of the negative electrode.

Graphite (natural or synthetic graphite) is today utilized as material of the negative electrode in most lithium-ion batteries due to their high energy density and stable charge/discharge performance over time. An alternative to graphite is amorphous carbon materials, such as hard carbons (non-graphitizable amorphous carbons) and soft carbons (graphitizable amorphous carbons), which lack long-range graphitic order. Common to graphite and amorphous carbons is that the volume changes during charge and discharge are small. This results in a good mechanical stability of the electrode material and helps to maintain good cycling stability. Amorphous carbons can be used as sole active electrode materials or in mixtures with graphite. Hard carbons often have good charge/discharge rate performance which is desired for fast charging and high-power systems.

Amorphous carbons can be derived from lignin. Lignin is an aromatic polymer, which is a major constituent in e.g. wood and one of the most abundant carbon sources on earth. In recent years, with development and commercialization of technologies to extract lignin in a highly purified, solid and particularized form from the pulp-making process, it has attracted significant attention as a possible renewable substitute to primarily aromatic chemical precursors currently sourced from the petrochemical industry. Amorphous carbons derived from lignin are typically non-graphitizable, i.e. hard carbons.

Today, the most commercially relevant source of lignin is Kraft lignin, obtained from hardwood or softwood through the kraft process. The lignin can be separated from alkaline black liquor using for example membrane- or ultrafiltration. One common separation process is described in WO2006031175 A1. In this process lignin is precipitated from alkaline black liquor by addition of acid and then filtered off. The lignin filter cake is in the next step re-slurried under acidic conditions and washed prior to drying and pulverization.

One problem with using lignin as a precursor for a carbon enriched material is that direct use of lignin, in the form of a fine powder, is not suitable since it exhibits undesired thermoplastic behaviour. During thermal conversion of lignin powder into a carbon enriched material, lignin undergoes plastic deformation/melting, aggressive swelling and foaming. Combined with the strong tendency for dust formation during handling, this severely limits processability of lignin in an industrially relevant scale, in terms of equipment dimensioning and process throughput as well as need of intermediate processing.

WO2021250604 A1 describes a method of producing carbon from lignin, involving compacting lignin powder and subsequently crushing the compacted lignin to obtain agglomerated lignin having a particle size distribution such that at least 80 wt% of the agglomerates have a diameter within the range of from 0.2 to 5.0 mm. The agglomerated lignin is subsequently heat treated to obtain thermally stabilized agglomerated lignin, which can be converted to a carbon enriched material with retained shape and dimension, avoiding melting/swelling deformation.

However, there is still a need for an improved process of obtaining a carbon enriched material from lignin, where the lignin retains its shape and dimension during conversion to a carbon enriched material with no melting/swelling deformation, and where the obtained carbon enriched material has a high capacity when used as the active material in an anode in a secondary battery.

Summary of the invention

It is an object of the present invention to provide an improved method for producing a carbon enriched material, which method allows use of a renewable carbon source, and which method eliminates or alleviates at least some of the disadvantages of the prior art methods.

It is a further object of the present invention to provide a method for producing an improved carbon enriched material suitable for use as active material in the negative electrode of a non-aqueous secondary battery, such as a lithium-ion battery, or a sodium-ion battery, in particular where the capacity of the non-aqueous secondary battery is improved by use of the carbon enriched material as active material in the negative electrode.

It is a further object of the present invention to provide a method for producing a carbon enriched material from lignin, which method allows use of lignin in powder form while avoiding problems with dust formation and maintaining the shape and dimension of lignin during heat treatment to obtain a carbon enriched material.

It is a further object of the present invention to provide a method for producing a carbon enriched material, which method is scalable and thus suitable for large-scale manufacturing.

The above mentioned objects, as well as other objects as will be realized by the skilled person in light of the present disclosure, are achieved by the various aspects of the present disclosure.

According to a first aspect, the present invention relates to a method for producing completely thermally stabilized agglomerated lignin, said method comprising the steps of:

a) providing agglomerated lignin having an average particle size in the range of from 50 to 500 µm; and

b) heating the agglomerated lignin to a temperature in the range of from 140 to 300°C for a time period of at least 30 minutes, so as to obtain completely thermally stabilized agglomerated lignin.

By heating the agglomerated lignin it is ensured that no melting/swelling deformation occurs during any subsequent heat treatments. It has surprisingly been found that by heating agglomerated lignin having an average particle size in the range of from 50 to 500 µm, a completely thermally stabilized agglomerated lignin is obtained. During thermal stabilization, the agglomerated lignin is cross-linked. The degree of cross-linking within the obtained completely thermally stabilized agglomerated lignin is uniform, or substantially uniform, throughout the completely thermally stabilized agglomerated lignin. A uniform degree of cross-linking ensures that a carbon enriched material with uniform properties may be obtained from the thermally stabilized agglomerated lignin. Due to the relatively small size of the provided agglomerated lignin, penetration of oxidative species is facilitated during the step of thermal stabilization, ensuring that the obtained thermally stabilized agglomerated lignin is completely cross-linked, also in the core of the agglomerates. In other words, a uniform degree of cross-linking within the completely thermally stabilized agglomerated lignin means that the material is homogenous. A carbon enriched material obtained from a homogenous thermally stabilized agglomerated lignin will also be homogenous in terms of structure.

According to a second aspect, the present invention relates to a completely thermally stabilized agglomerated lignin with an average particle size in the range of from 50 to 500 µm. Since the agglomerated lignin is completely thermally stabilized, the degree of cross-linking of the completely thermally stabilized agglomerated lignin is uniform throughout the completely thermally stabilized agglomerated lignin.

According to a third aspect, the present invention relates to a method for producing a carbon enriched material, said method comprising the steps of:

1) providing a completely thermally stabilized agglomerated lignin obtainable by the method according to the first aspect;
2) subjecting the thermally stabilized agglomerated lignin to heat treatment at one or more temperatures in the range of from 300 to 1500°C, wherein the heat treatment is carried out for a total time in the range of from 30 minutes to 10 hours, so as to obtain a carbon enriched material; and

3) optionally pulverizing the obtained carbon enriched material.

It has surprisingly been found that when heat treating a completely thermally stabilized agglomerated lignin, the obtained carbon enriched material has a reduced amount of volatiles compared to a carbon enriched material obtained from agglomerated lignin that has only been partially thermally stabilized. This is important in terms of yield and process efficiency. The carbon enriched material obtained according to the inventive method also has a pore size distribution that is beneficial in terms of providing a carbon enriched material with a high capacity when used as the active anode material in non-aqueous secondary battery.

According to a fourth aspect, the present invention relates to a negative electrode for a non-aqueous secondary battery comprising the carbon enriched material obtainable by the method according to the third aspect as active material.

According to a fifth aspect, the present invention relates to use of the carbon enriched material obtainable by the method according to the third aspect as active material in a negative electrode of a non-aqueous secondary battery.

Detailed description

Step a) of the method according to the first aspect of the present invention involves providing agglomerated lignin having an average particle size (D_{v50}) in the range of from 50 to 500 µm, or from 100 to 400 µm, or from 200 to 500 µm.

In some embodiments, the agglomerated lignin has an average particle size in the range of from 50 to 500 µm, or from 50 to 400 µm, or from 50 to 300 µm, or from 100 to 500 µm, or from 100 to 400 µm, or from 100 to 300 µm, or from 200 to 500 µm, or from 200 to 400 µm, or from 300 to 500 µm.

In the present application, the average particle size is defined as the volume average particle size (D_{v50}). This value refers to the maximum particle size below which 50% of the volume of the sample exists. The particle size is in the context of the present invention taken to be the diameter of the particle. The average particle size may be determined using for example laser diffraction. In the context of the present invention, the diameter of a particle is the equivalent spherical diameter of the particle, if the particle is not spherical. The equivalent spherical diameter is the diameter of a sphere of equivalent volume.

It is intended throughout the present disclosure that the term "lignin" refers to any kind of lignin which may be used as the carbon source for making a carbon enriched material. Examples of said lignin are, but are not limited to, lignin obtained from vegetable raw material such as wood, e.g. softwood lignin, hardwood lignin, and lignin from annular plants. Also, the lignin can be chemically modified.

Preferably, the lignin has been purified or isolated before being used in the method according to the present invention. The lignin may be isolated from black liquor and optionally be further purified before being used in the method according to the present invention. The purification is typically such that the purity of the lignin is at least 90%, preferably at least 95%, more preferably at least 98%, based on the dry weight of the lignin material. Thus, the lignin material used according to the method of the present invention preferably contains less than 10%, preferably less than 5%, more preferably less than 2% impurities, such as cellulose, carbohydrates and inorganic compounds, based on the dry weight of the lignin material.

The lignin used in method according to the present invention may be obtained through different extraction methods such as an organosolv process or a kraft process. The lignin may also be obtained from processes such as steam explosion or acidic pre-treatment followed by enzymatic hydrolysis. Preferably, the lignin used in the method according to the present invention is kraft lignin, i.e. lignin obtained through the kraft process. The kraft lignin may be obtained from hardwood or softwood. The lignin may be obtained by the process disclosed in WO2006031175 A1 commonly referred to as the LignoBoost process. Typically, this process involves the steps of precipitation of lignin from alkaline black liquor by acidification; separation of the precipitated lignin; and re-slurrying the lignin under acidic conditions at least once. The obtained lignin may be dried and pulverized and thus provided as solid particles.

The term “agglomerated lignin” as used herein refers to macroscopic particles in turn comprising clustered smaller particles of lignin. By providing the lignin in agglomerated form, a more compact and hard material is achieved. Hard agglomerates are advantageous during subsequent processing as they can resist physical impact during processing. In addition, the tendency for dusting is reduced when lignin is provided in agglomerated form. The agglomerated lignin of the present invention is prepared by a method comprising a step of compacting lignin. This means that the agglomerated lignin is not in the form of spontaneously aggregated secondary lignin particles formed during e.g. precipitation of lignin.

The agglomerated lignin provided in step a) may have a bulk density in the range of from 0.4 to 0.8 g/cm^3, such as from 0.5 to 0.7 g/cm^3.

The agglomerated lignin provided in step a) may comprise at least one additive, or no additives. In the context of the present invention, an additive is a substance that is added to improve either the process or the functionality of the obtained materials. Thus, additives are substances that are added, but that are not present in the lignin starting material. Thus, neither moisture, such as water, nor other components already present in the lignin starting material are considered additives in the context of the present invention.

The total amount of additive(s) is preferably less than 5 wt%, such as from 0 to 5 wt%, or from 0.1 to 5 wt%, or less than 2 wt%, such as from 0 to 2 wt%, or from 0.1 to 2 wt%, as based on the total dry weight of the agglomerated lignin. The agglomerated lignin thus comprises at least 95 wt%, such as at least 98%, lignin, as based on the total dry weight of the agglomerated lignin.

Step b) of the method according to the first aspect involves heating the agglomerated lignin to a temperature in the range of from 140 to 300°C for a time period of at least 30 minutes, so as to obtain completely thermally stabilized agglomerated lignin.

The term “thermal stabilization” as used herein, refers to a process of heating the agglomerated lignin at a temperature lower than the temperature required for carbonization. By performing a thermal stabilization, the obtained thermally stabilized agglomerated lignin can be heat treated with retained shape and dimension, avoiding melting/swelling and deformation during any subsequent heat treatment. Thermal stabilization is preferably performed in an oxidative atmosphere. Cross-linking of lignin will occur during thermal stabilization due to both oxidative and thermal effects. The cross-linking is facilitated by the combined oxidative and thermal effects. Due to the cross-linking, lignin within the agglomerates will become hard and not melt/swell during any subsequent heat treatment. Prior to thermal stabilization, the lignin agglomerates behave as a thermoplastic material, whereas after thermal stabilization, the lignin agglomerates instead behave as a thermoset material. The terms “thermal stabilization” and “heating” are both used throughout the disclosure to define processes for obtaining thermally stabilized agglomerated lignin.

The term “completely thermally stabilized” as used herein in expressions such as “completely thermally stabilized agglomerated lignin”, refers to agglomerated lignin that has been thermally stabilized to an extent that the same degree, or substantially the same degree, of cross-linking is achieved all through the material. Thus, the degree of cross-linking is uniform, or substantially uniform, throughout the completely thermally stabilized agglomerated lignin. This means that the material properties, such as structure and hardness, will be the same throughout the entire completely thermally stabilized agglomerated lignin. For example, the core of the completely thermally stabilized agglomerated lignin will have the same hardness and the same degree of cross-linking as the shell. The completely thermally stabilized agglomerated lignin is homogenous in structure. The completely thermally stabilized agglomerated lignin may also be referred to as completely cross-linked agglomerated lignin.

The glass transition temperature (Tg) of lignin typically increases after the heating step, so that the Tg of the thermally stabilized agglomerated lignin is higher than the agglomerated lignin prior to heating. The Tg of the completely stabilized agglomerated lignin is typically higher than the Tg of the agglomerated lignin prior to heating, and typically also higher than the Tg of the partially thermally stabilized agglomerated lignin.

A carbon enriched material obtained from completely thermally stabilized agglomerated lignin will have improved properties in terms of e.g. the pore size distribution.

The heating in step b) to produce completely thermally stabilized agglomerated lignin is preferably carried out in an oxidative atmosphere. Oxidative species that can react so as to cross-link lignin are present in such oxidative atmosphere. The heating may be carried out for example in the presence of oxygen, iodine, ozone, nitrogen dioxide, nitrobenzene, hydrogen peroxide and peracetic acid. Preferably, the heating is carried out in air. Alternatively, any suitable oxidative species may be supplied in a nitrogen atmosphere.

By providing agglomerated lignin having an average particle size in the range of from 50 to 500 µm, penetration of the oxidative species is facilitated and after heating the agglomerated lignin will be completely thermally stabilized.

If instead providing agglomerated lignin having a relatively large particle size, for example such that at least 80 wt% of the agglomerated lignin has a diameter within the range of from 0.2 to 5.0 mm (corresponding to an average particle size in the range of from 0.8 to 2.0 mm), the agglomerated lignin will only be partially thermally stabilized after the heat treatment. Thus, the degree of cross-linking will not be uniform throughout the thermally stabilized agglomerated lignin. The outer shell of the thermally stabilized agglomerated lignin will be completely cross-linked and hard, whereas the core remains largely non-cross-linked and soft. Thus, the obtained thermally stabilized agglomerated lignin is only partially cross-linked, or partially thermally stabilized. The non-cross-linked core may be subjected to foaming/swelling during subsequent heat treatments, which will have an impact on the structure of the carbon enriched material obtained from such lignin. The obtained carbon enriched material will have different structures on the surface compared to in the core, which is undesirable in terms of performance.

The term “partially thermally stabilized” as used herein in expressions such as “partially thermally stabilized agglomerated lignin”, refers to agglomerated lignin that has been partially cross-linked during thermal stabilization. The degree of cross-linking is non-uniform, with some parts (e.g. the shell) being completely cross-linked, and other parts (e.g. the core) being non-cross-linked. In other words, the shell may be completely thermally stabilized, whereas the core has not been thermally stabilized and retains a thermoplastic behaviour. The partially cross-linked thermally stabilized agglomerated lignin is heterogenous in structure. The partially thermally stabilized agglomerated lignin may also be referred to as partially cross-linked agglomerated lignin.

The agglomerated lignin provided in step a) may be non-cross-linked (i.e. not subjected to any heat treatments), or partially cross-linked (i.e. partially thermally stabilized), depending on the method used for preparing the agglomerated lignin.

The heating in step b) to produce the completely thermally stabilized agglomerated lignin can be carried out continuously or in batch mode. The heating can be carried out using methods known in the art and may preferably be carried out in a rotary kiln, moving bed furnace or rotary hearth furnace.

The heating to produce the completely thermally stabilized agglomerated lignin is carried out such that the agglomerated lignin is heated to a temperature in the range of from 140 to 300°C, preferably from 180 to 260°C. The heating is carried out for at least 30 minutes, i.e. the residence time of the agglomerated lignin inside the equipment used for the heating is at least 30 minutes. In one embodiment, the heating is carried out for at least 1 hour, or at least 1.5 hours. Preferably, the heating is carried out for less than 12 hours. The heating may be carried out at the same temperature throughout the entire heating stage or may be carried out at varying temperature, such as a stepwise increase of the temperature or using a temperature gradient. More preferably, the heating is carried out such that the agglomerated lignin is first heated to a temperature in the range of from 140 to 175°C for a period of at least 15 minutes and subsequently heated to a temperature in the range of from 175 to 300°C for at least 15 minutes.

Compared to the agglomerated lignin prior to heating to obtain the completely thermally stabilized material, there may be a small weight loss during the heating. The weight loss typically amounts to less than 15 wt% and is mainly due to evaporation of moisture and loss of volatiles due to decomposition of lignin during heating.

By controlling and optimizing parameters such as temperature and time during the heating step, a completely thermally stabilized agglomerated lignin that retains its shape and dimensions with no fusing or swelling during subsequent processing can be obtained. The described process has an excellent compatibility with the typical process requirements for continuous production, using a rotary kiln for example, due to the mechanical stability of the agglomerated lignin and a relatively short residence time. This is of particular importance for achieving an economical large industry-scale process for producing carbon enriched materials. Due to the agglomerated lignin having an average particle size in the range of from 50 to 500 µm, the time required for complete thermal stabilization is typically short, which is beneficial from a process efficiency perspective.

The completely thermally stabilized agglomerated lignin may have a bulk density in the range of from 0.4 to 0.8 g/cm^3, or from 0.5 to 0.7 g/cm^3. The heating might lead to a slight increase or decrease in bulk density compared to the agglomerated lignin prior to heating. The bulk density of the completely thermally stabilized agglomerated lignin will however preferably remain within the same range as prior to the heating step.

During heating, the structure of lignin will change due to cross-linking. It has surprisingly been realized that the degree of thermal stabilization of the lignin will influence the pore size distribution in a carbon enriched material obtained from the thermally stabilized lignin. In a carbon enriched material obtained from completely thermally stabilized agglomerated lignin the pore size distribution is such that a high capacity is obtained when the carbon enriched material is used as active anode material in a secondary battery. The pore size distribution of carbon enriched material obtained from completely thermally stabilized agglomerated lignin typically features a broad range of pore sizes, including a large number of pores of a relatively small size. In a carbon enriched material instead obtained from partially thermally stabilized agglomerated lignin, the pore size distribution is less favourable in terms of capacity. The pore size distribution of a carbon enriched material obtained from a partially thermally stabilized agglomerated lignin typically features a narrow range of pore sizes, with most pores having a relatively large size.

The colour of the thermally stabilized agglomerated lignin is different from the colour of the agglomerated lignin prior to thermal stabilization. The colour can be determined for example by using a spectrophotometer and reported in accordance with the CIELAB colour space. In the CIELAB colour space, colour can be reported as lightness (L*), green-red (a*) and blue-yellow (b*) components. Preferably, the lightness (L*) of the surface of the completely thermally stabilized agglomerated lignin is in the range of from 34 to 39. The lightness of the surface of the agglomerated lignin prior to thermal stabilization is above 44, such as in the range of from 44 to 52. Thus, the lightness of the agglomerated lignin decreases during thermal stabilization.

Preferably, the sum of the absolute values of the CIELAB green-red component (a*) and the CIELAB blue-yellow component (b*) of the surface of the completely thermally stabilized agglomerated lignin is less than 5.0, i.e. $|a^*| + |b^*| < 5.0$. More preferably, the sum of the absolute values of the CIELAB green-red component (a*) and the CIELAB blue-yellow component (b*) of the surface of the completely thermally stabilized agglomerated lignin is less than 3.0. The sum of the absolute values of the CIELAB green-red component (a*) and the CIELAB blue-yellow component (b*) of the surface of the completely thermally stabilized agglomerated lignin may be in the range of from 0.5 to 5.0, or from 0.5 to 3.0. The absolute value of the CIELAB green-red component (a*) of the surface of the completely thermally stabilized agglomerated lignin is preferably less than 3.0, or less than 2.0. The absolute value of the CIELAB blue-yellow component (b*) of the surface of the completely thermally stabilized agglomerated lignin is preferably less than 3.0, or less than 2.0.

The colour of the core of the thermally stabilized agglomerated lignin may be measured by first crushing the agglomerates to obtain lignin particles of a smaller size. The lignin particles of smaller size will represent all parts of the agglomerates, i.e. both core and surface parts, and may thus be used to give an average colour value for the thermally stabilized agglomerated lignin.

For completely thermally stabilized agglomerated lignin, the surface of lignin particles obtained by crushing the agglomerated lignin has the same, or very similar, values of L*, a* and b* as those measured on the surface of the agglomerated lignin.

For partially thermally stabilized agglomerated lignin the values for L*, a* and b* will differ between the surface and the core of the agglomerates. The surface of the partially thermally stabilized agglomerated lignin will be completely thermally stabilized and have values for L*, a* and b* in the same ranges as discussed above for the completely thermally stabilized agglomerated lignin. After crushing, the surface of the obtained lignin particles may have a lightness of 40-44, and the sum of the absolute values of the CIELAB green-red component (a*) and the CIELAB blue-yellow component (b*) of the surface of the obtained lignin particles is less than

10, i.e. |a*| + |b*| <10. The absolute value of the CIELAB green-red component (a*) of the surface of the lignin particles may be less than 5.0. The absolute value of the CIELAB blue-yellow component (b*) of the surface of the lignin particles may be less than 5.0.

Thus, the values of L*, a* and b* measured on the surface of crushed agglomerated lignin can be used to evaluate and monitor the degree of thermal stabilization, and thus also crosslinking, obtained during heating of the agglomerated lignin.

The agglomerated lignin provided in step a) may be obtained by compacting a lignin powder and crushing the obtained lignin powder to obtain agglomerated lignin having an average particle in the range of from 50 to 500 µm. Two embodiments of a method for obtaining the agglomerated lignin will now be described in detail.

In a first embodiment, the agglomerated lignin provided in step a) is obtained by a method comprising the steps of:

- providing lignin in the form of a powder;
- compacting the lignin powder to obtain compacted lignin;
- crushing the compacted lignin so as to obtain agglomerated lignin having an average particle size in the range of from 50 to 500 µm.

The lignin powder is preferably dried before compacting. The drying of the lignin powder is carried out by methods and equipment known in the art. The lignin in powder form may have a moisture content of less than 45 wt%. Preferably, the moisture content of the lignin before compacting is less than 25 wt%, preferably less than 10 wt%, more preferably less than 8 wt%. The moisture content of the lignin before compacting may be at least 1 wt%, such as at least 5 wt%. The temperature during the drying is preferably in the range of from 80 to 160°C, more preferably in the range of from 100 to 120°C.

The size distribution of the lignin powder is preferably such that 80 wt% of the particles have a diameter less than 0.2 mm.

The lignin powder obtained after drying has a wide particle size distribution ranging from 1 µm to 2 mm which is significantly skewed towards the micrometer range, meaning that a significant proportion of the particles has a diameter in the range of 1 to 200 µm. The lignin powder preferably has a bulk density in the range of from 0.3 to 0.4 g/cm^3.

The compaction of the lignin is preferably carried out by roll compaction. The roll compaction of lignin can be achieved by a roller compactor to agglomerate the lignin particles.

In the compaction step, an intermediate product is generated. Here, the fine lignin powder is usually fed through a hopper and conveyed by means of a horizontal or vertical feeding screw into the compaction zone where the material is compacted into flakes by compaction rollers with a defined gap. By controlling the feeding screw speed, the pressure development in the compaction zone, flakes with uniform density can be obtained. The pressure development in the compaction zone can preferably be monitored and controlled by the rotational speed of the compaction rolls. As the powder is dragged between the rollers, it enters what is termed as the nip area where the density of the material is increased and the powder is converted into a flake or ribbon. The rolls used have cavities. The depth of each cavity used in the roll compaction is from 0.1 to 10 mm, preferably from 1 to 8 mm, more preferably from 1 to 5 mm or from 1 to 3 mm. The specific press force exerted during the compaction may vary depending on the equipment used for compaction, but may be in the range of from 1 to 100 kN/cm. Equipment suitable for carrying out the compaction are known in the art.

After compaction, crushing is preferably carried out. In the crushing step, the intermediate product from the compaction step is subjected to crushing or grinding, such as by means of rotary granulator, cage mill, beater mill, hammer mill or crusher mill and/or combinations thereof.

After crushing, the crushed material may be subjected to a sieving step, to remove additional fine material. In addition, large material may be removed and/or recirculated back to the crushing step.

In the sieving step, the intermediate product from the crushing step is screened by means of physical fractionation such as sieving, also referred to as screening, to obtain a product which is agglomerated lignin with a defined particle size distribution set by the pore size of the sieves or screens in this step. The sieve or screen is selected such that particles of small size, such as fines, pass through the screen and are rejected and preferably returned to the compaction step. In other embodiments, the sieve may be selected such that most particles having a diameter below 50 µm, or below 100 µm, pass through the screen and are rejected and preferably returned to the compaction step. Particles having a diameter large enough not to pass through the sieve are retained and subjected to the subsequent process steps according to the present invention. The sieve may be selected such that most particles having a diameter above 50 µm, or above 100 µm, will be retained. The sieving may be carried out in more than one step, i.e. the sieving can be carried out such that the crushed material from the crushing step passes sequentially through more than one screen or sieve.

In one embodiment of the roll compaction, the roll configuration is such that the first roll has an annual rim in such configuration so that the powder in the nip region is sealed in the axial direction along the roller surface.

In one embodiment, the roll configuration is such that the nip region is sealed in the axial direction along the roller surface with a static plate. By ensuring that the nip region is sealed, loss of powder at the axial ends of the rollers is minimized as compared to entirely cylindrical nip rollers.

Due to the compaction of the lignin powder during preparation of agglomerated lignin, the bulk density of lignin will increase as pressure is applied to the lignin powder. This means that the agglomerated lignin will have a higher bulk density than the lignin powder. More compact lignin particles may be beneficial during subsequent processing to carbon enriched materials, as compact lignin particles have been found to retain its shape and dimensions with no melting or swelling. The agglomerated compacted lignin particles will also have a relatively higher hardness after compaction. Hard agglomerates are advantageous during subsequent processing as they can resist physical impact during processing. Further, when using hard, compacted particles processing problems that might arise due to the presence of lignin dust on the surface of the particles are avoided. This is of particular importance in a large-scale process since dust can form explosive mixtures with air and also cause blockings inside processing equipment.

In a second embodiment, the agglomerated lignin provided in step a) is obtained by a method comprising the steps of:

- providing lignin in the form of a powder;
- compacting the lignin powder to obtain compacted lignin;
- crushing the compacted lignin so as to obtain agglomerated lignin having an average particle size in the range of from 0.8 to 2.0 mm.
- heating the obtained agglomerated lignin to a temperature in the range of from 140 to 250°C for a time period of at least 1.5 hours, so as to obtain partially thermally stabilized agglomerated lignin;
- crushing the obtained partially thermally stabilized agglomerated lignin, so as to obtain agglomerated lignin having an average particle size in the range of from 50 to 500 µm.

Compared to the method of the first embodiment, the method of the second embodiment involves first preparing agglomerated lignin having an average particle size in the range of from 0.8 to 2.0 mm, which in a first heating step is heated such that partially thermally stabilized agglomerated lignin is obtained. The obtained partially thermally stabilized agglomerated lignin is crushed to agglomerated lignin having an average particle size in the range of from 50 to 500 µm.

The steps of providing lignin powder and compacting the lignin powder are defined such as detailed above for the first embodiment. The first crushing step is carried out such as detailed above for the first embodiment except that lignin agglomerates having an average particle size in the range of from 0.8 to 2.0 mm is obtained. In the optional sieving step, the sieve or screen is selected such that most particles having a diameter below 100 µm (or 500 µm) pass through the screen, and most particles having a diameter above 100 µm (or 500 µm) are retained. In addition, large particles are preferably removed.

The equipment used in the compaction and crushing steps are the same regardless of the particle size of the obtained agglomerates. Instead, suitable sieves or screens are selected depending on the desired agglomerate size.

After the first crushing step the obtained agglomerated lignin having an average particle size in the range of from 0.8 to 2.0 mm is subjected to heating. The heating is carried out such as described above for the thermal stabilization step. Due to the relatively larger particle size, a partially thermally stabilized agglomerated lignin is obtained. In a second crushing step, the partially thermally stabilized agglomerated lignin is crushed to obtain lignin agglomerates of a size in the range of from 50 to 500 µm. The second crushing step is carried out such as described above for the first embodiment. After heating of the agglomerated lignin with an average particle size in the range of from 0.8 to 2.0 mm a partially thermally stabilized material will be obtained. Thus, the agglomerated lignin having a particle size in the range of from 50 to 500 µm obtained after the second crushing step will be thermally stabilized to a varying degree depending on its location within the agglomerates prior to the second crushing step. Such agglomerated lignin will collectively be referred to as "partially thermally stabilized" also after the second crushing step.

An advantage with the first embodiment is the reduced number of process steps compared to the second embodiment. A low number of process steps is beneficial from a cost perspective. However, the first embodiment involves handling of lignin agglomerates of a small size. The small size may lead to problems with clogging in the process equipment and also increases the risk for dust explosions during handling. In addition, lignin agglomerates of a smaller size have a tendency to melt during thermal stabilization, prior to cross-linking.

The problems may however be overcome by careful selection of process equipment. If melting during stabilization is severe, it may also be possible to perform an additional crushing step on the completely thermally stabilized agglomerated lignin to obtain the desired particle size.

In the method according to the second embodiment the drawbacks of the first embodiment are avoided. Since agglomerates of a relatively larger size are handled, clogging and dust explosions are avoided. Once the agglomerated lignin has been partially thermally stabilized, subsequent handling is facilitated, also after crushing to further reduce the particle size, so that agglomerated lignin having an average particle size in the range of from 50 to 500 µm is obtained. Melting during thermal stabilization of the agglomerated lignin of small size is not a problem when the agglomerated lignin has already been partially thermally stabilized prior to crushing to a smaller size.

Both the first and second embodiments can comprise the additional steps of:

- providing at least one additive; and
- mixing the lignin powder with the at least one additive.

Any suitable additive can be provided. For example, the at least one additive may be selected from any suitable type of binder or lubricant, which may facilitate the subsequent compaction process and improve the density and mechanical properties of the obtained agglomerated lignin. The at least one additive may be a functionality-enhancing additive, that has an influence on the carbon enriched material obtained from the agglomerated lignin. Examples of such functionality-enhancing additives include carbon additives and silicon-containing additives. Carbon additives may be selected from at least one of graphite, graphene, carbon nanotubes, charcoal, biochar, hard carbon, soft carbon, carbon black and electrically conductive carbon. Silicon-containing additives may be selected from at least one of: elemental silicon, a silicon suboxide, a silicon-metal alloy or a silicon-metal carbon alloy. The silicon suboxide may be SiOx with $0 \leq x \leq 2$. The silicon-metal alloy may be any suitable silicon-metal alloy, such as e.g. SiFex or SiFexAly. The silicon-metal carbon alloy may be e.g. SiFexCy.

The total amount of additive(s) is preferably less than 5 wt%, such as from 0 to 5 wt%, or from 0.1 to 5 wt%, or less than 2 wt%, such as from 0 to 2 wt%, or from 0.1 to 2 wt%, as based on the total dry weight of the lignin-additive powder mixture.

The mixing of the lignin powder and the at least one additive is performed by methods and equipment as known in the art. One example of a suitable method is a vertical mixer, such as paddle, screw or ribbon-screw mixer in a batch or continuous mode. The mixing process may be carried out in a low-, medium- or high-shear impact mode.

In embodiments where at least one additive is present, the compaction step is carried out such as described above also when at least one additive is present. The at least one additive is compacted along with the lignin powder. The at least one additive will be dispersed within the obtained agglomerated lignin.

The second aspect of the present invention relates to a completely thermally stabilized agglomerated lignin with an average particle size in the range of from 50 to 500 µm. The degree of cross-linking is uniform throughout the thermally stabilized agglomerated lignin. The completely thermally stabilized agglomerated lignin according to the second aspect can be prepared by the method according to the first aspect. The completely thermally stabilized agglomerated lignin may be further defined as set out above with reference to the first aspect.

In particular, the completely thermally stabilized agglomerated lignin is cross-linked throughout the material. The thermally stabilized agglomerated lignin is hard, dark in colour, and retains its shape and dimensions with no melting/swelling deformation during any subsequent heat treatments. The structure of the completely thermally stabilized agglomerated lignin is suitable for its use as a starting material for obtaining a carbon enriched material with a pore size distribution suitable for use as an anode material with high capacity.

The third aspect of the present invention relates to a method for producing a carbon enriched material by heat treatment of the completely thermally stabilized agglomerated lignin according to the first aspect. The method according to the third aspect may thus comprise performing the method according to the first aspect.

The term “heat treatment” as used herein, refers to a process of heating the completely thermally stabilized agglomerated lignin at one or more temperatures and for a sufficient time so that the lignin is converted to a carbon enriched material. The process may also be referred to as “carbonization” or “calcination”. After heat treatment, the carbon content is higher than 80 wt%, or higher than 90 wt%, or higher than 95 wt%, or higher than 98 wt%. Depending on the temperature during the heat treatment, different types of carbon, such as charcoal or hard carbon, can be obtained from the thermally stabilized agglomerated lignin.

The term “carbon enriched material” as used herein, refers to a carbon material obtained by heat treatment of completely thermally stabilized agglomerated lignin. The carbon content of the carbon enriched material is higher than 80 wt%, or higher than 90 wt%, or higher than 95 wt%, or higher than 98 wt%. The carbon enriched material may also comprise for example heteroatoms, such as oxygen, hydrogen, nitrogen or sulphur atoms, inorganic impurities, and functional additives. The carbon enriched material of the present invention is an amorphous (i.e. non-crystalline) carbon, preferably hard carbon.

Step 1) of the method according to the third aspect involves providing a completely thermally stabilized agglomerated lignin obtainable by the method according to the first aspect. As outlined above, the completely thermally stabilized agglomerated lignin is completely cross-linked. Due to the cross-linking, the lignin will retain its shape and dimension with no melting/swelling deformation during the heat treatment to convert it to a carbon enriched material. The obtained carbon enriched material will therefore have the same shape as the completely thermally stabilized agglomerated lignin.

Step 2) of the method according to the third aspect involves subjecting the completely thermally stabilized agglomerated lignin to heat treatment at one or more temperatures in the range of from 300 to 1500°C, wherein the heat treatment is carried out for a total time in the range of from 30 minutes to 10 hours, so as to obtain a carbon enriched material.

The heat treatment may be carried out at the same temperature throughout the entire heat treatment or may be carried out at varying temperature, such as a stepwise increase of the temperature or using a temperature gradient. The heat treatment may comprise a temperature ramp from a starting temperature to a target temperature. The heating rate may be 1-100°C/min. For example, the heat treatment may involve several intermediate temperatures, with temperature ramps in between them, before reaching the target temperature needed for carbonization of the completely thermally stabilized agglomerated lignin. The heat treatment may be carried out as a batch process or a continuous process. Any suitable reactor can be used, such as rotary kiln, moving bed furnace, pusher furnace or rotary hearth furnace. The heat treatment is preferably carried out under inert atmosphere, preferably nitrogen atmosphere.

Preferably, the heat treatment comprises a preliminary heating step, preferably followed by a final heating step. The preliminary heating step is preferably carried out at one or more temperatures in the range of from 300 to 800°C, such as from 500 to 700°C. The preliminary heating step is preferably carried out under inert atmosphere, preferably nitrogen atmosphere. The duration of the preliminary heating step is at least 30 minutes and preferably less than 10 hours. The surface area of the carbon enriched material obtained after the preliminary heating step is typically in the range of from 300 to 700 m^2/g, measured as BET using nitrogen gas.

The final heating step is preferably carried out at one or more temperatures in the range of from 800 to 3000°C. The final heating step is preferably carried out under inert atmosphere, preferably nitrogen atmosphere. The duration of the final heating step is at least 30 minutes and preferably less than 10 hours. After the final heating step carried out at 1000°C or higher, the surface area of the carbon enriched material obtained is typically 50 m^2/g or less.

The preliminary and final heating steps may be carried out as discrete steps or as one single step in direct sequence. The preliminary and final heating steps may involve heating at one or more temperatures, as discussed above for the heat treatment. For example, the preliminary heating starts at about 300°C and the temperature is subsequently increased to about 500°C. The final heating step is preferably carried out between 900 and 1300°C, such as at about 1000°C.

The preliminary and final heating steps may be carried out as batch processes or as continuous processes. Any suitable reactors can be used. The preliminary heating step and the final heating step can be carried out in the same reactor or in separate reactors.

The colour of the carbon enriched material may be slightly different from the colour of the completely thermally stabilized agglomerated lignin, or may be slightly different. The colour can be determined for example by using a spectrophotometer and reported in accordance with the CIELAB colour space. In the CIELAB colour space, colour can be reported as lightness (L*), green-red (a*) and blue-yellow (b*) components. Preferably, the lightness (L*) of the surface of the carbon enriched material is in the range of from 34 to 39.

Preferably, the sum of the absolute values of the CIELAB green-red component (a*) and the CIELAB blue-yellow component (b*) of the surface of the carbon enriched material is less than 2.0, or less than 1.0, i.e. $|a^*| + |b^*| < 2.0$, or $|a^*| + |b^*| < 1.0$. The absolute value of the CIELAB green-red component (a*) of the surface of the carbon enriched material is preferably less than 1.5, or less than 1.0. The absolute value of the CIELAB blue-yellow component (b*) of the surface of the carbon enriched material is preferably less than 1.5, or less than 1.0. In some embodiments, the sum of the absolute values of the CIELAB green-red component (a*) and the CIELAB blue-yellow component (b*) of the surface of the carbon enriched material is zero. In some embodiments, the sum of the absolute values of the CIELAB green-red component (a*) and the CIELAB blue-yellow component (b*) of the surface of the carbon enriched material is in the range of from 0 to 2.0, or from 0 to 1.0.

The absolute values of a* and b* of the surface of the carbon enriched material may be lower than the absolute values of a* and b* of the surface of the completely thermally stabilized agglomerated lignin prior to carbonization. The values of a* and b* may also be roughly the same on the surface of the carbon enriched material and on the surface of the completely thermally stabilized agglomerated lignin.

The carbon enriched material preferably has a bulk density in the range of from 0.2 to 0.4 g/cm^3. This is lower than the bulk density of the agglomerated lignin and the completely thermally stabilized lignin, primarily due to mass loss during the heat treatments.

The carbon enriched material preferably has a helium true density in the range of from 1.4 to 2.1 g/cm^3, such as from 1.7 to 2.0 g/cm^3. The helium true density may be determined using a pycnometer, as known by a person skilled in the art. It is important to have a helium true density in the range of from 1.4 to 2.1 g/cm^3 as the doping and de-doping capacity of the carbon enriched material when used as the active material in the negative electrode of a non-aqueous secondary battery may otherwise be reduced, and the irreversible capacity of the battery may become large. If the density of the carbon enriched material is too low, the energy density of the electrode may also be decreased.

The carbon enriched material of the present invention is suitable for use as active material in an anode of a secondary battery since it has a high capacity, in turn obtained by a favourable pore size distribution. The pore size distribution is the result of the carbon enriched material being obtained from a completely thermally stabilized agglomerated lignin, since the pore size distribution correlates with the degree of cross-linking of the lignin. The cross-linking results in a structure of the lignin that is favourable for creation of a suitable pore size distribution during conversion to a carbon enriched material.

The obtained carbon that is a product of step 2) may be useful for example as biochar, or as a precursor to activated carbon.

Step 3) of the method according to the third aspect involves optionally pulverizing the obtained carbon enriched material. In many applications, the particle size of the carbon enriched material obtained in step 2) must be reduced prior to use so as to obtain a carbon powder. For example, when the carbon enriched material of the present invention is to be used as active material in an anode of a secondary battery, the particle size is preferably reduced.

The pulverization may be performed by any suitable process, using for example a cutting mill, blade mixer, ball-mill, impact mill, hammer mill and/or jet-mill. Optionally, fine/coarse particle selection by classification and/or sieving may be performed subsequent to the pulverization.

The pulverization of the carbon enriched material and optional fine/coarse particle selection may be performed so as to obtain a carbon powder comprising powder particles having an average particle size in the range of from 1 to 25 µm.

It is possible to carry out more than one step of pulverizing or crushing. In addition, the carbon powder may be subjected to treatments such as coating or further heat treatments.

The fourth aspect of the present invention relates to a negative electrode for a non-aqueous secondary battery comprising the carbon enriched material obtainable by the method according to the third aspect as active material.

The carbon enriched material, preferably in powder form, of the present invention is preferably used as an active material in a negative electrode of a non-aqueous secondary battery, such as a lithium-ion battery or sodium-ion battery. When used for producing such a negative electrode, any suitable method to form such a negative electrode may be utilized. In the formation of the negative electrode, the carbon enriched material may be processed together with further components. Such further components may include, for example, one or more binders to form the carbon enriched material into an electrode, conductive materials, such as carbon black, carbon nanotubes or metal powders, and/or further Li storage materials, such as graphite or lithium. For example, the binders may be selected from, but are not limited to, poly(vinylidene fluoride), poly(tetrafluoroethylene), carboxymethylcellulose, natural butadiene rubber, synthetic butadiene rubber, polyacrylate, poly(acrylic acid), alginate, etc., or from combinations thereof. Optionally, a solvent such as e.g. 1-methyl-2-pyrrolidone, 1-ethyl-2-pyrrolidone, water, or acetone is utilized during the processing.

The fifth aspect of the present invention relates to use of the carbon enriched material obtainable by the method according to the third aspect as active material in a negative electrode of a non-aqueous secondary battery.

Examples

Example 1 - comparative

Agglomerated lignin having an average particle size of 1.25 mm was subjected to thermal stabilization in air at 250°C for 2 hours. After thermal stabilization a partially thermally stabilized material was obtained. The obtained lignin agglomerates had a black, non-meltable shell. The Tg of the lignin increased from 148°C (on the non-thermally stabilized lignin) to 158°C after the thermal stabilization. The colour of the agglomerated lignin after thermal stabilization was measured with a spectrophotometer and gave values of $L^*=38$, $|a^*|=0.5$ and $|b^*|=0.1$. After crushing of the agglomerated lignin to reduce the particle size, the obtained material had a dark brown colour, indicative of non-complete thermal stabilization of the core of the lignin agglomerates. Instead, the core remains largely non-stabilized and soft. The colour of the crushed material was measured and gave values of $L^*=43$, $|a^*|=3.7$ and $|b^*|=6.2$.

Example 2 – complete thermal stabilization

The partially thermally stabilized lignin granules of example 1 were crushed so that a powder having an average particle size of less than 500 µm was obtained. The powder was subjected to a thermal stabilization in air at 250°C for 2 hours. After thermal stabilization, a completely thermally stabilized material was obtained. The obtained lignin agglomerates were black in colour, indicative of a complete thermal stabilization. The Tg increased from 158°C to 173°C after the second thermal stabilization step. The colour of the agglomerated lignin after thermal stabilization was measured using a spectrophotometer and gave values of $L^*=37.5$, $|a^*|=0.5$ and $|b^*|=0.2$. The lignin agglomerates were also hard and had a closed porosity.

Example 3 – carbonization

The completely thermally stabilized agglomerated lignin of example 2 and the partially thermally stabilized agglomerated lignin of example 1 was further carbonized at a temperature of 1050°C with a residence time of 2 hours in a nitrogen atmosphere. The obtained carbon enriched material was milled to an average particle size of 10 µm. The colour of the obtained carbon enriched material was very similar to that of the completely thermally stabilized agglomerated lignin obtained in example 2.

Example 4 – capacity measurements

Electrodes were prepared from the carbon enriched material of example 3 together with PVDF (6 wt%), with a loading density for carbon enriched material of approximate 6 mg/cm^2. The half-cells were assembled in PAT cells (EL-CELL) in a glovebox, with lithium metal as the counter electrode, glass fiber as the separator and 1 M $LiPF_6$ in ethylene carbonate:diethyl carbonate (1:1, vol:vol) as electrolyte. The galvanostatic charge discharge tests were executed on an Arbin cycler system. The discharge test was first performed at a constant current of C/5 between 0 and 1.5 V (vs. Li/Li^+), and then at a constant voltage of 0 V and a cut-off current of C/20. The charge step was carried out at a constant current of C/5 between 0 and 1.5 V (vs. Li/Li^+). The carbon enriched material obtained from a completely thermally stabilized agglomerated lignin had a reversible capacity of 30-50 mAh/g higher than that of carbon enriched material obtained from a partially stabilized agglomerated lignin.

Example 5 – pore size distribution

The pore size distribution of the carbon enriched material of example 3 was evaluated by the CO_2 isotherm obtained from porosimetry using the DFT model. It was found that the carbon enriched material obtained from partially thermally stabilized agglomerated lignin had a narrow pore size distribution with relatively large pores, whereas the carbon enriched material obtained from completely thermally stabilized agglomerated lignin instead had a broad pore size distribution with a large number of small pores.

In view of the above detailed description of the present invention, other modifications and variations will become apparent to those skilled in the art. However, it should be apparent that such other modifications and variations may be effected without departing from the spirit and scope of the invention.

Claims

1. A method for producing completely thermally stabilized agglomerated lignin, said method comprising the steps of:
    a) providing agglomerated lignin having an average particle size in the range of from 50 to 500 µm; and
    b) heating the agglomerated lignin to a temperature in the range of from 140 to 300°C for a time period of at least 30 minutes, so as to obtain completely thermally stabilized agglomerated lignin.

2. The method according to claim 1, wherein the agglomerated lignin provided in step a) is produced by a method comprising the steps of:
    - providing lignin in the form of a powder;
    - compacting the lignin powder to obtain compacted lignin;
    - crushing the compacted lignin so as to obtain agglomerated lignin having an average particle size in the range of from 50 to 500 µm.

3. The method according to claim 1, wherein the agglomerated lignin provided in step a) is produced by a method comprising the steps of:
    - providing lignin in the form of a powder;
    - compacting the lignin powder to obtain compacted lignin;
    - crushing the compacted lignin so as to obtain agglomerated lignin having an average particle size in the range of from 0.8 to 2.0 mm.
    - heating the obtained agglomerated lignin to a temperature in the range of from 140 to 300°C for a time period of at least 30 minutes, so as to obtain partially thermally stabilized agglomerated lignin;
    - crushing the obtained partially thermally stabilized agglomerated lignin, so as to obtain agglomerated lignin having an average particle size in the range of from 50 to 500 µm.

4. The method according to anyone of claims 2 or 3, wherein the method for producing agglomerated lignin comprises the additional steps of:
    - providing at least one additive; and
    - mixing the lignin powder with the at least one additive.

5. The method according to any one of the preceding claims, wherein the agglomerated lignin provided in step a) has a bulk density in the range of from 0.5 to 0.7 g/cm^3.

6. The method according to any one of the preceding claims, wherein the lignin is kraft lignin.

7. The method according to any one of the preceding claims, wherein the heating of the agglomerated lignin in step b) is carried out by first heating the agglomerated lignin to a temperature in the range of from 140 to 175°C for a period of at least 15 minutes and subsequently heating the agglomerated lignin to a temperature in the range of from 175 to 300°C for at least 15 minutes.

8. The method according to any one of the preceding claims, wherein the heating of the agglomerated lignin in step b) is carried out in an oxidative atmosphere.

9. A completely thermally stabilized agglomerated lignin with an average particle size in the range of from 50 to 500 µm.

10. The completely thermally stabilized agglomerated lignin according to claim 9, wherein the lignin is kraft lignin.

11. A method for producing a carbon enriched material, said method comprising the steps of:
    1) providing a completely thermally stabilized agglomerated lignin obtainable by the method according to any one of claims 1-8;
    2) subjecting the completely thermally stabilized agglomerated lignin to heat treatment at one or more temperatures in the range of from 300 to 1500°C, wherein the heat treatment is carried out for a total time in the range of from 30 minutes to 10 hours, so as to obtain a carbon enriched material; and
    3) optionally pulverizing the obtained carbon enriched material.

12. The method according to claim 11, wherein step 2) comprises a preliminary heating step, followed by a final heating step.

13. The method according to claim 12, wherein the preliminary heating step is carried out at a temperature between 400 and 800°C for at least 30 minutes.

14. The method according to any one of claims 12 or 13, wherein the preliminary heating step is carried out in inert atmosphere.

15. The method according to any one of claims 12-14, wherein the final heating step is carried out at a temperature between 800 and 1500°C for at least 30 minutes.

16. The method according to any one of claims 12-15, wherein the final heating step is carried out in inert atmosphere.

17. The method according to any one of claims 11-16, wherein the carbon enriched material obtained in step 2) has a true density in the range of from 1.7 to 2.0 g/cm^3.

18. A negative electrode for a non-aqueous secondary battery comprising the carbon enriched material obtainable by the method according to any one of claims 11-17 as active material.

19. Use of the carbon enriched material obtainable by the method according to any one of claims 11-17 as active material in a negative electrode of a non-aqueous secondary battery.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2024/055251

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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)

IPC: B29B, C01B, C07G, C08H

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

SE, DK, FI, NO classes as above

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

EPO-Internal, PAJ, WPI data, BIOSIS, COMPENDEX, EMBASE, INSPEC, MEDLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KÖHNKE, J. et al. "Comparison of Four Technical Lignins as a Resource for Electrically Conductive Carbon Particles" In: BioResources, 2019, Vol. 14, No. 1, pp. 1091-1109, ISSN: 1930-2126; whole document	1, 4-19
A	--	2-3
D, A	WO 2021250604 A1 (STORA ENSO OYJ), 16 December 2021 (2021-12-16); page 4, line 13 - line 16; page 9, line 3 - line 5; page 11, line 11 - line 13; claims 1-9,13 --	1-19
A	US 9593221 B1 (KURPLE KARL VINCENT), 14 March 2017 (2017-03-14); column 23, line 44 - line 55 --	1-19

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“D” document cited by the applicant in the international application

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search 21-08-2024	Date of mailing of the international search report 21-08-2024
Name and mailing address of the ISA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Authorized officer Ingemar Wistrand Telephone No. + 46 8 782 28 00

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2788404 A2 (UPM KYMMENE CORP), 15 October 2014 (2014-10-15); paragraph [0186]; claim 1 --	1-19
A	LINDSTRÖM, T. "The colloidal behaviour of kraft lignin" In: Colloid and Polymer Science, 1979, Mar., Vol. 257, No. 3, pp. 277-285, ISSN: 0303-402X (print); whole document --	1-19
A	NORGREN, M. et al "Aggregation of kraft lignin derivatives under conditions relevant to the process, part I: Phase behaviour" In: Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2001, Vol. 194, No. 1-3, pp. 85-96, ISSN: 0927-7757 (print); whole document --	1-19
A	RAGAN, S., MEGONNELL, N. "Activated carbon from renewable resources - lignin" In: Cellulose Chem. Technol, 2011, Vol. 45, No. 7-8, pp. 527-531,; whole document -- --------	1-19

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2024/055251

Continuation of: second sheet

International Patent Classification (IPC)

C08H 7/00 (2011.01)
B29B 9/08 (2006.01)
B29B 13/02 (2006.01)
C01B 32/05 (2017.01)
C01B 32/312 (2017.01)
C07G 1/00 (2011.01)

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