

~~DESCRIPTION OF THE INVENTION:~~

~~Method for producing activated carbon~~

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METHOD FOR PRODUCING ACTIVATED CARBON

The invention relates to a method for producing activated carbon, said method comprising the steps of: mixing a carbonaceous precursor with chemically activating agents to obtain a feedstock mixture; producing activated carbon by heating the feedstock mixture under the atmosphere of a physically activating gas; and performing suitable post-activation treatment of the produced activated carbon. The invention also relates to an activated carbon species obtainable by such a method.

Activated carbon, also called active carbon, refers to a group of amorphous carbonaceous materials with a high degree of porosity and well-developed specific surface area (*i.e.* surface area per unit mass). It is normally manufactured by pyrolysis of different carbon-containing substances followed by activation through physical or chemical processes, and it can exist in many different forms, *e.g.* granules, powder, fibrous materials, cloth or monoliths. Activated carbon has been widely utilized in industrial fields, *e.g.* as an electrode material for supercapacitors, as a sorbent for water and gas purification, and as a metal-free catalyst or catalyst support due to its well-developed porosity, high specific surface area, and good thermal and chemical stability. The main criteria for selecting an activated carbon for a given application are its surface chemical composition, purity, electrical conductivity, and porous texture properties such as pore volume, specific surface area, and pore size distribution. The increasing attentions on electrical energy storage, pollution clean-up, and environmentally-friendly products are stimulating significant increase in demand for activated carbon.

Activated carbon can be produced from various carbonaceous source materials, including fossil-fuel sources such as petroleum coke, coal, and coal tar, biomass sources such as nutshells, coconut husk, and wood, and synthetic polymers such as polyacrylonitrile, polyvinylidene chloride, and phenolic resins, through physical or chemical activation. The choice of raw materials for activated carbon can affect the structure, purity, surface chemical composition, electrical conductivity, particle size, and texture properties of the final product. In selection of the raw materials, its price is often the deciding factor. Therefore, a large part of the activated carbon is nowadays manufactured from biomass due to its affordability, wide availability, and high sustainability. However, synthetic polymers have the advantage of high purity, so they are normally selected for the production of high purity activated carbon.

Most carbonaceous materials can be converted into activated carbon through pyrolysis and activation. The properties of the final product to a large degree depend on the nature of the raw carbonaceous precursor material, the nature of the activating agent, and the conditions of the activation process. The preparation of activated carbon with different textural properties can be achieved through physical or

chemical activation processes. Physical activation generally involves the carbonization of carbonaceous precursors in an inert atmosphere to remove the volatile components, followed by activation in the presence of a suitable gasification agent, such as steam, carbon dioxide, oxygen, air, ammonia, or a gas mixture containing any of these gases, to develop the porosity at a high temperature. The generation of porosity takes place via selective elimination of the more reactive carbon of the structure, and further gasification leads to the production of the activated carbon with the sought pore structure. In general, the activation with carbon dioxide leads to the creation and widening of small micropores, whereas activation with steam only promotes widening of the existing micropores. Additionally, activated carbon with low oxygen content can be produced when ammonia is selected as activating agent.

Chemical activation is generally conducted by mixing carbonaceous materials with a chemically activating agent, such as potassium hydroxide, zinc chloride, or phosphoric acid, followed by activation under inert gas at a high temperature. Chemical activation methods have been utilized to produce activated carbons for many years, and the activation mechanism has been investigated intensively. It is a generally accepted view on the specific activation mechanism of alkali metal compounds, such as potassium hydroxide, that it comprises redox reactions between the carbon structure and the metal compound, metal intercalation into the carbon lattice, and steam- and carbon dioxide-resulted gasification. Therefore, activated carbon with a wide range of pore size distributions can be produced in a very efficient way by utilizing alkali metal compounds as activating agents. In chemical activation with phosphoric acid and metal chlorides, such as zinc chloride, these chemicals act as dehydrating agents which alter the pyrolysis behaviour of carbonaceous materials, thereby causing less of the objectionable tarry products to be formed. Both phosphoric acid and metal chloride cause hydrogen and oxygen atoms in the source materials to be stripped away as water rather than as hydrocarbons or oxygenated organic compounds. As a result, the carbon yield is generally higher than that from physical activation. In addition, pore size distribution of activated carbon can be somewhat controlled by tuning the mass ratio of carbonaceous precursor and phosphoric acid or metal chloride. Compared to physical activation, chemical activation has superior advantages, such as lower activation temperatures, higher yields, better efficiency, higher specific surface area, and larger pore volume. However, physical activation has the advantages of mild activation rate, which is favourable for micropore size regulation. Therefore, the combination of physical activation with chemical activation makes the activation process more efficient, controllable, and flexible.

Generally, activated carbon with a predominant pore size can be produced by carefully controlling the activation conditions when a single activating agent is utilized. For example, micropores are preferentially introduced into activated carbon when carbon dioxide or ammonia is selected as activating agent, while mesopores are preferentially introduced into activated carbon when phosphoric acid or zinc chloride with high agent loading is selected as activating agent. Therefore, the combination of two different activating agents in the activation process is used to produce activated carbon with better control over the resulting pore size distribution. Additional benefits of using two activating agents include higher activation efficiency, higher activated carbon yield, and better process flexibility.

Due to the many applications for activated carbon, substantial research is put into methods of its

production. For example, a two-stage activation process has been disclosed in U.S. Pat. No. 5,416,056, which comprises a first stage activation with phosphoric acid to introduce wide pores, followed by a second stage activation with potassium hydroxide to introduce micropores. Activated carbon produced by this two-stage activation process is characterized by a high amount of micropores (>85% of total pore volume), and large micropore volume (> 0.7 cm³/g). However, this two-stage activation increases the cost of the activation process due to the two consecutive activation steps at high temperature required.

In patent application WO2014/077714A1, a self-activation process has been disclosed. Activated carbon is manufactured from tobacco leaves by simultaneous carbonization and self-activation in an inert gas atmosphere. The activated carbon produced by this method has a specific surface area of 600 to 2000 m²/g, preferably 1700 m²/g, and has an extensive amount of small micropores and mesopores. In the self-activation method, the carbonization and activation processes of the raw material take place simultaneously and autogenously, so the second phase of chemical or physical activation is needless. The ability to carry out the self-activation process depends, however, on the chemical composition of the carbonaceous precursor and the type of substances generated during the carbonization. This is an efficient activation process, but the limitations on the carbonaceous precursor selection is a barrier for a wider application.

Caturla *et al.* (Carbon, 1991. 29: 999-1007) reported chemical activation of peach stones with zinc chloride followed by physical activation with carbon dioxide to produce activated carbon with high surface area of about 3000 m²/g, and a yield of about 20%. However, it is essentially microporous, which is not favourable as electrode material for supercapacitors.

Virote *et al.* (Separation and Purification Technology, 2005. 42:159-168) studied the preparation of activated carbon from coffee residues by a concurrently chemical activation with zinc chloride and physical activation with carbon dioxide or steam. A high yield of 80.3% has been achieved when zinc chloride and steam are selected as activating agents. However, the specific surface areas of the obtained activated carbon are lower than 1000 m²/g.

Budinova *et al.* (Fuel Processing Technology, 2006. 87(10): 899-905) performed activation of woody biomass birch through a combination of chemical activation with phosphoric acid and physical activation with steam in a single activation step. The results show the advantage of combining physical and chemical activation in terms of high specific surface area (1360 m²/g), though it is still not sufficient as electrode material for supercapacitors.

US 2013089738 A1 describes preparation of activated nanocarbon from food waste material, comprising impregnation of waste material powder with an activating agent, and activating the impregnated material in the presence of an activating gas.

US 2012174936 A1 discloses a method for incorporating mesopores into microporous carbon comprising impregnation of microporous carbon granules with at least one of an alkaline earth metal salt and an alkali metal salt, followed by steam activation.

BRPI 0501030 A describes production of activated carbon from coconut shell fibers in which ZnCl_2 or NaAc activating agent is impregnated to the raw material, followed by heating under nitrogen and carbon dioxide.

FR 818175 A describes manufacture of activated carbon where carbonization and activation take place in the same rotary kiln in the presence of a continuous stream of water vapor and seeds which may first be impregnated with bi-ammonium orthophosphate.

GB 484197 A describes production of active carbon where a carbonaceous material in granular form is impregnated with an activating chemical and admixed with a mixture of materials which on heating to the activating temperature, react together to give a nonoxidizing gas which flows through the granules of impregnated carbonaceous material.

One particularly advantageous implementation of activated carbon is incorporation into a carbon-based electrode of a supercapacitor. A supercapacitor, also known as a double-layer capacitor or ultracapacitor, stores electrical energy by physical charge separation at electrode/electrolyte interfaces. The mechanism is highly reversible, which allows the supercapacitor to be charged and discharged up to a million times. Additionally, this fast charge separation mechanism also allows the supercapacitor to have high power density. A supercapacitor typically comprises two porous electrodes that are isolated from electrical contact with each other by a porous dielectric separator. The separator and the electrodes are impregnated with an electrolytic solution that allows ionic current to flow between the electrodes while preventing electronic current from discharging the cell. Each electrode is typically in electrical contact with a current collector. The current collector, which can comprise a sheet or plate of electrically conductive material (e.g., aluminium) can reduce internal resistance while providing physical support for the porous electrode material.

As electrode materials for supercapacitors, the performance of activated carbon depends strongly on the porous texture properties, specifically the specific surface area and pore size distribution. The pore size is generally divided into three types: micropores with diameter less than 2 nm, mesopores with a diameter between 2 nm and 50 nm, and macropores with a diameter greater than 50 nm. The micropores strengthen the specific capacitance (*i.e.* capacitance per unit mass) due mainly to distortion of the solvation shells and shorter distance between the ions and the pore walls, whereby a high energy density is achieved. The mesoporous channels provide low-resistant pathways for the ions through the porous particles, and the macropores serve as ion-buffering reservoirs to minimize the diffusion distances to the interior surfaces. Accordingly, mesopores and macropores improve the rate capability and thus the power density of supercapacitors. Therefore, the pore size distribution of activated carbon for use in energy storage devices requires careful control to achieve a high specific capacitance, good rate capability, and high energy density. However, the efficient production of activated carbon with a predefined ratio of micropores, mesopores, and macropores is still a challenge by utilizing known methods.

Accordingly, it would be advantageous to provide an activation process for producing activated carbon materials by using a more efficient and flexible route with high yield and control over the resulting

porosity and pore size distribution. Such a method will be able to produce activated carbon for a multitude of applications. For example, for the fabrication of carbon-based electrodes that enable efficient, durable, and energy-dense storage devices, the activated carbon should possess a large specific surface area and predetermined pore size distribution.

The present invention has for its object to remedy or to reduce at least one of the drawbacks of the prior art, or at least provide a useful alternative to prior art. The object is achieved through features, which are specified in the description below and in the claims that follow. The invention is defined by the independent patent claims. The dependent claims define advantageous embodiments of the invention.

In a first aspect, the invention relates more particularly to a method for producing activated carbon, said method comprising the steps of:

- a) mixing a carbonaceous precursor with chemically activating agents to obtain a feedstock mixture;
- b) producing activated carbon by heating the feedstock mixture under the atmosphere of a physically activating gas; and
- c) performing suitable post-activation treatment of the produced activated carbon,

wherein step a) comprises in sequence the sub-steps of

- i. addition of a first chemically activating agent to obtain an impregnated precursor; and
- ii. addition of a second chemically activating agent to obtain the feedstock mixture.

The carbonaceous precursor may come from any source material with sufficient carbon content and purity. In one embodiment, the carbonaceous precursor may be from a source of biomass and derivatives, such as wood, coconut shell, food processing remainders, food waste, newspapers, books, wheat, walnut, corn, rice, potato, beets, millet, soybean, barley, and cotton. In another embodiment, the carbonaceous precursor may be from fossil-fuel sources such as petroleum coke, coals, and coal tar pitches. In another embodiment, the carbonaceous precursor may be from synthetic polymeric materials such as rubber, polyacrylonitrile, polyvinylidene chloride, polyvinyl alcohol, polyaniline, polypyrrole, and phenolic resins. The embodiments are not limited thereto, but may comprise any chemically suitable precursor capable of being carbonized and activated.

The carbonaceous precursor may be a single carbonaceous precursor material or a combination of precursor materials, which can be used to optimize the properties of the activated carbon product. The carbonaceous precursor may be in the form of powder, sheets, fibers, solution, suspension, gel, and any mixture of these forms. The carbonaceous precursor materials may require different pretreatments, such as washing, drying, grinding, or carbonisation, before mixing with chemically activating agents.

As a first step, the carbonaceous precursor is mixed with a first chemically activating agent to obtain an

impregnated precursor. The first chemically activating agent serves as a dehydrating agent to improve the yield and introduce mesopores into the activated carbon. According to various non-limiting embodiments, the first chemically activating agent may be chosen from e.g. H_3PO_4 , P_2O_5 , H_2SO_4 , MgCl_2 , AlCl_3 , CaCl_2 , FeCl_3 , ZnCl_2 , or any combination of these agents in any ratio. The embodiments are not limited thereto, but may comprise any chemical capable of dehydrating the carbonaceous precursor.

In embodiments, the carbonaceous precursor may be impregnated with a solution of the first chemically activating agent. If a solution is used, it may preferably be an aqueous solution, but it may also be an organic solvent, such as ethanol, acetone, or isopropyl alcohol. The concentration of the chemically activating agent in the solution may range from about 1-90 wt.%, e.g. 1, 2, 3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, or 90 wt.%. Using a solution of the first chemically activating agent for the impregnation may promote a more homogenous mixing with the carbonaceous precursor. This mixing may facilitate formation of a more homogeneously activated carbon that comprises a uniform distribution of physical characteristics, including pore size, pore size distribution, pore structure, etc. In other embodiments, the carbonaceous precursor may be combined with the first chemically activating agent to form a dry impregnated precursor material, i.e. without the use of any liquid or solvent, by physical mixing such as grinding or ball milling.

The carbonaceous precursor and the first chemically activating agent may be combined in any suitable ratio to form the impregnated precursor. The specific value of a suitable ratio may depend, for example, on the physical form of the carbonaceous precursor and the first chemically activating agent, and on the concentration if one or both are in the form of a mixture or solution. The ratio of carbonaceous precursor to first chemically activating agent on the basis of dry material weight may range from about 1:10 to 1000:1. For example, the ratio may be about 1:1, 1:2, 1:3, 1:4, 1:5, 1:10, 500:1, 100:1, 25:1, 10:1, or 2:1. The carbonaceous precursor and the first chemically activating agent may be dried for 0.5-72 hours, e.g. for 0.5, 1, 2, 3, 5, 8, 10, 12, 15, 18, 24, 36, 48, or 72 hours, to form the impregnated precursor. The drying may take place at 50-200 °C, e.g. 50, 75, 90, 100, 120, 140, 170, or 200 °C.

After drying of the impregnated precursor, the feedstock mixture is produced by introducing a second chemically activating agent into the impregnated precursor to improve the activation efficiency and help porosity development during the activation process. The second chemically activating agent may preferably be an alkali metal compound, e.g. KOH , NaOH , LiOH , K_2CO_3 , Na_2CO_3 , Li_2CO_3 , KHCO_3 , NaHCO_3 , LiHCO_3 , $\text{C}_7\text{H}_7\text{K}$ (benzyl potassium), or any combination of these agents in any ratio. The alkali metal may intercalate into the carbon material, and during a later washing step said alkali metal may react with water and generate a large amount of gas, which will exfoliate the carbon material and thus increase the porous surface area. The second chemically activating agent may be mixed with the impregnated precursor by physical mixing such as grinding and ball milling. The ratio of impregnated precursor to second chemically activating agent may range from about 1:10 to 1000:1, e.g. 1:1, 1:2, 1:3, 1:4, 1:5, 1:10, 500:1, 100:1, 25:1, 10:1, or 2:1.

The feedstock mixture may thereafter be heated at a suitable temperature under the atmosphere of a physically activating gas to form activated carbon via simultaneous chemical and physical activation in

a single step. In embodiments, the heating means may for example be a conventional furnace, a microwave oven, or laser-induced heating. During heating, the physically activating agent reacts with carbonaceous precursor mainly from the gas phase to generate micropores, while the chemically activating agents react with the carbonaceous precursor primarily from the liquid or solid phase to generate mesopores. This presence of more than one phase makes the activation process more efficient and flexible than single phase activation because physical and chemical activations take place simultaneously in a single step. Additionally, the intensity of these two activations can be easily controlled by tuning the composition of the physically activating gas and the weight ratio of first and second chemically activating agents to carbonaceous precursor, whereby the pore size distribution of the activated carbon ~~can~~ may be adjusted.

In one embodiment, the activation may be performed in a batch process, which may include feeding the feedstock mixture into a crucible and loading the crucible into a temperature-controlled reactor capable of reaching high temperatures, e.g. a conventional furnace or a microwave oven. Suitable crucibles and reactors are stable at high temperature, compatible with microwave processing, and resistant to chemical corrosion from the chemically activating agent. Examples of crucibles can include metallic (nickel or stainless steel) crucibles, quartz crucibles, porcelain crucibles, silicon carbide crucibles or silicon carbide-coated crucibles such as silicon carbide coated mullite. In another embodiment, the feedstock mixture may be introduced into the reactor using a continuous feed process, for example using screw-fed or rotary-fed operation. In yet another embodiment, the carbon material in the feedstock mixture may be activated in a semi-continuous process, where crucibles with the feedstock mixture are conveyed through a high-temperature reactor during the acts of heating and thus activating. The feedstock material may be dry-fed or wet-fed into a reactor. A wet feedstock mixture, for example, can comprise a slurry that may be atomized or sprayed into a reactor. Similarly, a dry feedstock mixture may be atomized or sprayed into the reactor.

The physically activating gases, which may for example be H_2O , O_2 , CO_2 , H_2 , NH_3 , or any gas mixture containing these gases, may be introduced into the reactor via at least one gas inlet in order to activate the feedstock mixture from the gas phase to generate micropores. Additionally, depending on the specific physically activating gas, conditions may be chosen such that said activating gas may also serve as protective gas to avoid the carbonaceous precursor from oxidizing by oxygen in the air and fluidize the feedstock mixture within the reactor. For example, O_2 may be diluted by N_2 , while NH_3 may be used as pure gas. The physically activating gas may be introduced into the activation reactor at any stage, either before heating or after the reactor is heated to a specific temperature. The physically activating gases may be introduced into the activation reactor continually or intermittently. The physically activating gases may be diluted with inert gases to any concentration before being introduced into the activation reactor in order to tune the physical activation intensity.

The feedstock mixture may be heated under the atmosphere of a physically activating gas at a heating rate of 2 to 1000 °C/min, e.g. 2, 5, 10, 20, 50, 100, 250, 500, 750, or 1000 °C/min, to a temperature that may be between 400 °C and 1500 °C, e.g. 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950,

1000, 1100, 1200, 1300, 1400, or 1500 °C, for a predetermined time, e.g. 0.1, 0.2, 0.5, 1, 2, 4, 8, 12, 24, 48, or 72 hours or longer to perform the activation. After activation, the activated product may be cooled down at a cooling rate between 2 and 200 °C/min, e.g. 2, 3, 5, 10, 20, 50, 100, 150, or 200 °C/min.

5 In embodiments, the activated carbon may be subjected to suitable post-activation treatment, which, depending on applications, may include washing, drying, and grinding to a desired particle size. The washing may be optimised to remove residual amounts of carbon, retained chemically activating agents, or any chemical by-product derived from reactions involving the chemically activating agent. In one embodiment, the activation step may be quenched by rinsing the activated carbon with water, and thus the
10 acts of quenching and washing may also be combined. Waste water used for quenching and/or washing may be filtered and recycled in order to reduce waste water discharging and process cost.

Activated carbon produced *via* the present invention may be characterized by a high specific surface area, preferably >2000 m²/g, and predefined pore size distribution, which may be tuned according to applications. For activated carbon to be used in supercapacitors, the desired pore size distribution comprises
15 predominately small micropores and small mesopores. Thus, activated carbon produced according to the invention may be a very attractive electrode material for supercapacitor.

In a second aspect, the invention relates to an activated carbon species obtainable by the method according to the first aspect of the invention. The activated carbon species may thus be tuned to have a pore size distribution optimised for use in a carbon electrode, e.g. similar to the pore size distributions
20 shown in figure 1-7. The carbon species with pore size distribution optimized for a carbon electrode comprises small micropores, which are beneficial for a high specific capacitance, and small mesopores, which are beneficial for fast ion transfer. Said carbon electrode with optimised pore size distribution may be used in e.g. supercapacitors or lithium ion capacitors.

In the following is described examples of preferred embodiments illustrated in the accompanying drawings, wherein:
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Fig. 1 Shows a diagram of the pore size distribution (presented as dV/dD , *i.e.* the total volume per unit mass of pores having a characteristic pore size) of the produced activated carbon of example 1 with H₃PO₄ and C₇H₇K as chemically activating agents and ammonia as physically activating agent according to the invention;

30 Fig. 2 Shows a diagram of the pore size distribution of the produced activated carbon from the method described in example 2;

Fig. 3 Shows a diagram of the pore size distribution of the produced activated carbon from the method described in example 3;

35 Fig. 4 Shows a diagram of the pore size distribution of the produced activated carbon from the method described in example 4;

Fig. 5 Shows a diagram of the pore size distribution of the produced activated carbon from the method described in example 5;

Fig. 6 Shows a diagram of the pore size distribution of the produced activated carbon from the method described in example 6;

5 Fig. 7 Shows a diagram of the pore size distribution of the produced activated carbon from the method described in example 7; and

Fig. 8 Shows a charge/discharge curve of a supercapacitor fabricated using activated carbon produced according to the invention as electrode and ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate as electrolyte.

10 Examples

In example 1, 10 g pine wood sawdust as carbonaceous precursor is impregnated with 30 ml 1 M H_3PO_4 aqueous solution as a first chemically activating agent, followed by drying at 120 °C for 12 hours in an oven to form an impregnated precursor. Afterwards, 2 g $\text{C}_7\text{H}_7\text{K}$ as a second chemically activating agent is grinded physically and homogeneously with the impregnated precursor to form a feedstock mixture.

15 The feedstock mixture is thereafter introduced into a tube furnace, heated to 900 °C at a heating rate of 5 °C/min, and dwelled for 2 hours under an ammonia atmosphere as a physically activating agent, after which the tube furnace is cooled down to ambient temperature under N_2 atmosphere. The activation is operated under atmospheric pressure. As post-activating treatment, the activated carbon is washed with 1 M HCl and hot water, and then dried in an oven. The obtained activated carbon exhibits a high specific
20 surface area ($>2000 \text{ m}^2/\text{g}$) and favourable pore size distribution, dominated by small micropores and small mesopores as seen in figure 1. A symmetrical supercapacitor fabricated by using this activated carbon as electrode materials and ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF_4) as electrolyte shows a high specific capacitance of about 190 F/g (calculated from the charge-discharge curve shown in figure 8).

25 In example 2, 10 g pine wood sawdust as carbonaceous precursor is impregnated with 30 ml 1 M ZnCl_2 aqueous solution as a first chemically activating agent before drying at 120 °C for 12 hours in an oven to form an impregnated precursor. Afterwards, 10 g KOH as a second chemically activating agent is grinded physically and homogeneously with the impregnated precursor to form a feedstock mixture. The feedstock mixture is thereafter introduced into a tube furnace, heated to 900 °C at a heating rate of 10
30 °C/min, and dwelled for 1 hour under a CO_2 atmosphere as a physically activating agent, after which the tube furnace is cooled down to ambient temperature under N_2 atmosphere. The activation is operated under atmospheric pressure. As post-activating treatment, the obtained product is washed with 1 M HCl and hot water, and then dried in an oven. The obtained activated carbon exhibits a high specific surface area ($>2000 \text{ m}^2/\text{g}$) and favourable pore size distribution (dominated by small micropores and small mes-
35 opores as seen in figure 2).

In example 3, 10 g waste newspaper as carbonaceous precursor is impregnated with 30 ml 0.5 M ZnCl_2

aqueous solution as a first chemically activating agent before drying at 120 °C for 12 hours in an oven to form an impregnated precursor. Afterwards, 5 g NaOH as a second chemically activating agent is grinded physically and homogeneously with the impregnated precursor to form a feedstock mixture. The feedstock mixture is thereafter introduced into a tube furnace, heated to 800 °C at a heating rate of 10 °C/min, and dwelled for 1 hour under an ammonia atmosphere as a physically activating agent, after which the tube furnace is cooled down to ambient temperature under N₂ atmosphere. The activation is operated under atmospheric pressure. As post-activating treatment, the obtained product is washed with 1 M HCl and hot water, and then dried in an oven. The obtained activated carbon exhibits a high specific surface area (>2200 m²/g) and favourable pore size distribution (dominated by small micropores and small mesopores seen in figure 3).

In example 4, 10 g waste newspaper as carbonaceous precursor is mixed with 20 g P₂O₅ as a first chemically activating agent by physical grinding to form an impregnated precursor. Afterwards, 5 g KOH as a second chemically activating agent is grinded physically and homogeneously with the impregnated precursor to form a feedstock mixture. The feedstock mixture is thereafter introduced into a tube furnace, heated to 750 °C at a heating rate of 5 °C/min, and dwelled for 2 hours under a CO₂ atmosphere as a physically activating agent, after which the tube furnace is cooled down to ambient temperature under N₂ atmosphere. The activation is operated under atmospheric pressure. As post-activating treatment, the obtained product is washed with 1 M HCl and hot water, and then dried in an oven. The obtained activated carbon exhibits a high specific surface area (>2000 m²/g) and favourable pore size distribution (dominated by small micropores and small mesopores seen in figure 4).

In example 5, 10 g pine wood sawdust as carbonaceous precursor is impregnated with 30 ml 1 M ZnCl₂ aqueous solution as a first chemically activating agent before drying at 120 °C for 12 hours in an oven to form an impregnated precursor. Afterwards, 5 g K₂CO₃ as a second chemically activating agent is grinded physically and homogeneously with the impregnated precursor to form a feedstock mixture. The feedstock mixture is thereafter introduced into a tube furnace, heated to 900 °C at a heating rate of 10 °C/min, and dwelled for 2 hours under a CO₂ atmosphere as a physically activating agent, after which the tube furnace is cooled down to ambient temperature under N₂ atmosphere. The activation is operated under atmospheric pressure. As post-activating treatment, the obtained product is washed with 1 M HCl and hot water, and then dried in an oven. The obtained activated carbon exhibits a high specific surface area (>2000 m²/g) and favourable pore size distribution (dominated by small micropores and small mesopores seen in figure 5).

In example 6, 10 g polyaniline powder as carbonaceous precursor is mixed with 5 g P₂O₅ as a first chemically activating agent by physical grinding to form an impregnated precursor. After drying for 12 hours at 120 °C, 5 g K₂CO₃ as a second chemically activating agent is grinded physically and homogeneously with the impregnated precursor to form a feedstock mixture. The feedstock mixture is thereafter introduced into a tube furnace, heated to 900 °C at a heating rate of 10 °C/min, and dwelled for 2 hours under a steam atmosphere as a physically activating agent, after which the tube furnace is cooled down to ambient temperature under N₂ atmosphere. The activation is operated under atmospheric pressure.

As post-activating treatment, the obtained product is washed with 1 M HCl and hot water, and then dried in an oven. The obtained activated carbon exhibits a high specific surface area ($>2300 \text{ m}^2/\text{g}$) and favourable pore size distribution (dominated by small micropores and small mesopores seen in figure 6).

In example 7, 10 g graphene oxide as carbonaceous precursor is mixed with 20 g ZnCl_2 as a first chemically activating agent by physical grinding to form an impregnated precursor. After drying for 12 hours at 120°C , 10 g KOH as a second chemically activating agent is grinded physically and homogeneously with the impregnated precursor to form a feedstock mixture. The feedstock mixture is thereafter introduced into a microwave oven and heated at a power of 600 W for 20 min under an ammonia atmosphere as a physically activating agent, after which the material is cooled down to ambient temperature under N_2 atmosphere. The activation is operated under atmospheric pressure. As post-activating treatment, the obtained product is washed with 1 M HCl and hot water, and then dried in an oven. The obtained activated carbon exhibits a high specific surface area ($>2200 \text{ m}^2/\text{g}$) and favourable pore size distribution (dominated by small micropores and small mesopores seen in figure 7).

In example 8, an optimised electrode, based on activated carbon produced by the activation method disclosed within this application, is fabricated by combining the activated carbon with conductive carbon black as a conductive additive and polytetrafluoroethylene (PTFE) as a binder. A powder mixture comprising 60-90 wt% activated carbon, 5-20 wt% carbon black, and 5-20 wt% PTFE is rolled and pressed to form a carbon-based electrode with a thickness in the range of about 40-400 micrometers. A supercapacitor is assembled by using the carbon-based electrode as electrode and ionic liquid as electrolyte. The charge-discharge performance of a supercapacitor produced by this method is shown in figure 8.

It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. Use of the verb "comprise" and its conjugations does not exclude the presence of elements or steps other than those stated in a claim. The article "a" or "an" preceding an element does not exclude the presence of a plurality of such elements.

The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.

C l a i m s

1. A method for producing activated carbon, said method comprising the steps of:

a) mixing a carbonaceous precursor with chemically activating agents to obtain a feedstock mixture;

b) producing activated carbon by heating the feedstock mixture under the atmosphere of a physically activating gas; and

c) performing suitable post-activation treatment of the produced activated carbon,

c h a r a c t e r i s e d i n that step a) comprises in sequence the sub-steps of:

i. addition of a first chemically activating agent to obtain an impregnated precursor; and

ii. addition of a second chemically activating agent to obtain the feedstock mixture.

2. The method according to claim 1, wherein the first chemically activating agent is chosen from a group which comprises chemicals MgCl_2 , AlCl_3 , CaCl_2 , FeCl_3 , ZnCl_2 , H_3PO_4 , P_2O_5 and H_2SO_4 .

3. The method according to any of the claims 1-2, wherein a mass ratio of carbonaceous precursor to the first chemically activating agent ranges from 1:10 to 1000:1.

4. The method according to any of the claims 1-3, wherein the carbonaceous precursor and the first chemically activating agent are mixed with assistance of a solvent.

5. The method according to any of the claims 1-4, wherein the second chemically activating agent is chosen from a group which comprises K_2CO_3 , Na_2CO_3 , Li_2CO_3 , KHCO_3 , NaHCO_3 , LiHCO_3 , KOH , NaOH , LiOH and benzyl potassium ($\text{C}_7\text{H}_7\text{K}$).

6. The method according to any of the claims 1-5, wherein the mass ratio of the impregnated precursor and the second chemically activating agent ranges from 1:10 to 1000:1.

7. The method according to any of the claims 1-6, wherein the feedstock mixture is introduced into ~~the~~a reactor through a batch feed process.

8. The method according to any of the claims 1-6, wherein the feedstock mixture is introduced into ~~the~~a reactor through a continuous feed process.

9. The method according to any of the claims 1-8, wherein the physically activating ~~agent~~gas is chosen from a group which includes H_2O , H_2 , O_2 , CO_2 , SO_2 , SO_3 , and NH_3 .

10. The method according to any of the claims 1-9, wherein the physically activating agent-gas is introduced into the activation reactor after heating of said activation reactor.
11. The method according to any of the claims 1-10, wherein heating is carried out at a temperature ranging from 400 to 1500 °C.
- 5 12. An activated carbon species obtainable by the method according to any of the claims 1-11.
13. A carbon electrode comprising an activated carbon species according to claim 12.
14. A supercapacitor comprising at least one carbon electrode according to claim 13.

~~A b s t r a c t~~

~~In a first aspect, the invention relates to a method for producing activated carbon, said method comprising the steps of:~~

- ~~a) mixing a carbonaceous precursor with chemically activating agents to obtain a feedstock mixture;~~
- ~~b) producing activated carbon by heating the feedstock mixture under the atmosphere of a physically activating gas; and~~
- ~~c) performing suitable post-activation treatment of the produced activated carbon;~~

~~wherein step a) comprises in sequence the sub-steps of:~~

- ~~i. addition of a first chemically activating agent to obtain an impregnated precursor; and~~
- ~~ii. addition of a second chemically activating agent to obtain the feedstock mixture.~~

~~In a second aspect, the invention relates to an activated carbon species obtainable by the method according to the first aspect of the invention. The activated carbon species may thus be tuned to have a pore-size distribution optimised for use in a carbon electrode, e.g. dominated by micropores and mesopores as indicated in figure 1.~~

~~(Figure 1)~~