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(54) **CARBON ACTIVATION METHOD AND ENERGY STORAGE DEVICE THEREOF**

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(57) **ABSTRACT**

A method of making activated carbon including:

compressing a mixture of an alkali metal hydroxide, a carbon source, and a solid thermosetting polymer precursor into a pellet; and

a first heating of the compressed mixture, as defined herein; and

optionally crushing, washing, or both, the resulting first heated mixture, as defined herein; and

optionally a second heating, as defined herein.

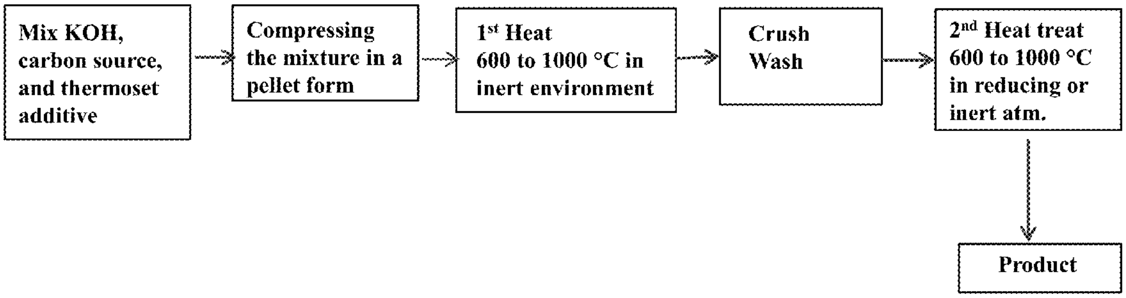
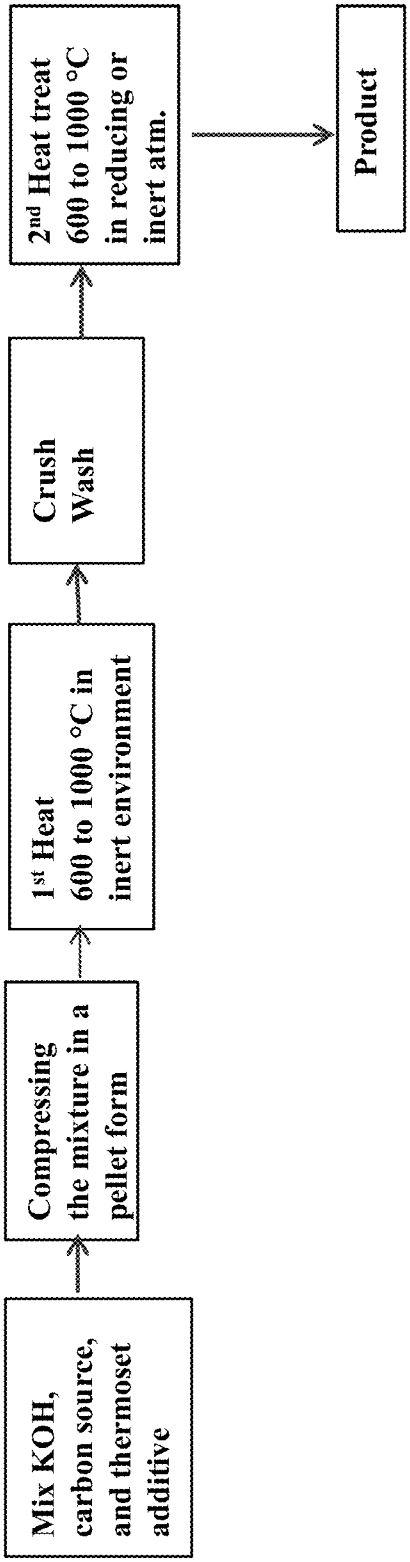


Fig. 1


Mix KOH, carbon source, and thermoset additive
Compressing the mixture in a pellet form
1st Heat 600 to 1000 °C in inert environment
Crush Wash
2nd Heat treat 600 to 1000 °C in reducing or inert atm.
Product

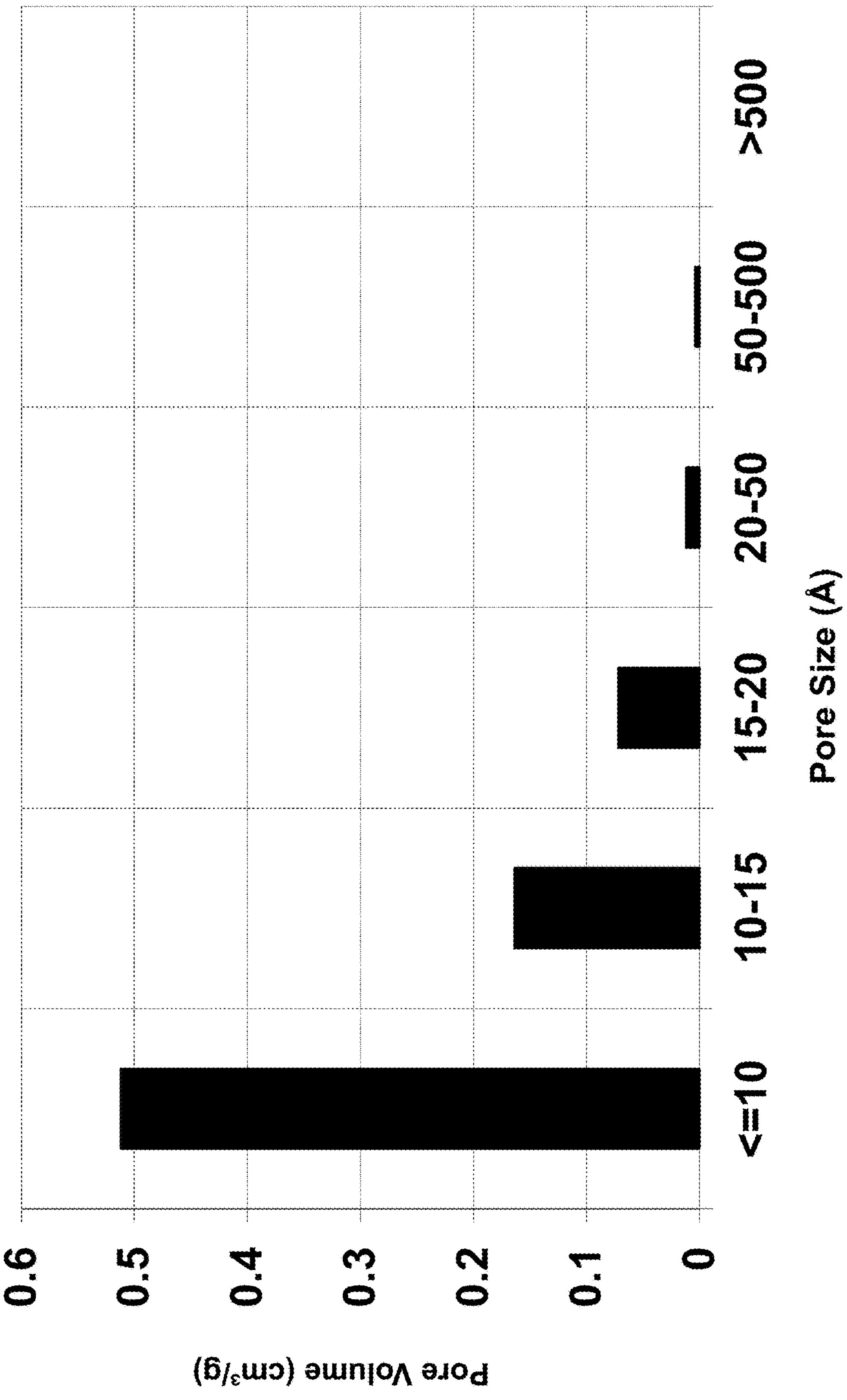

Pore Volume (cm^3/g)
0.6
0.5
0.4
0.3
0.2
0.1
0
<=10
10-15
15-20
20-50
50-500
>500
Pore Size (Å)

Fig. 2

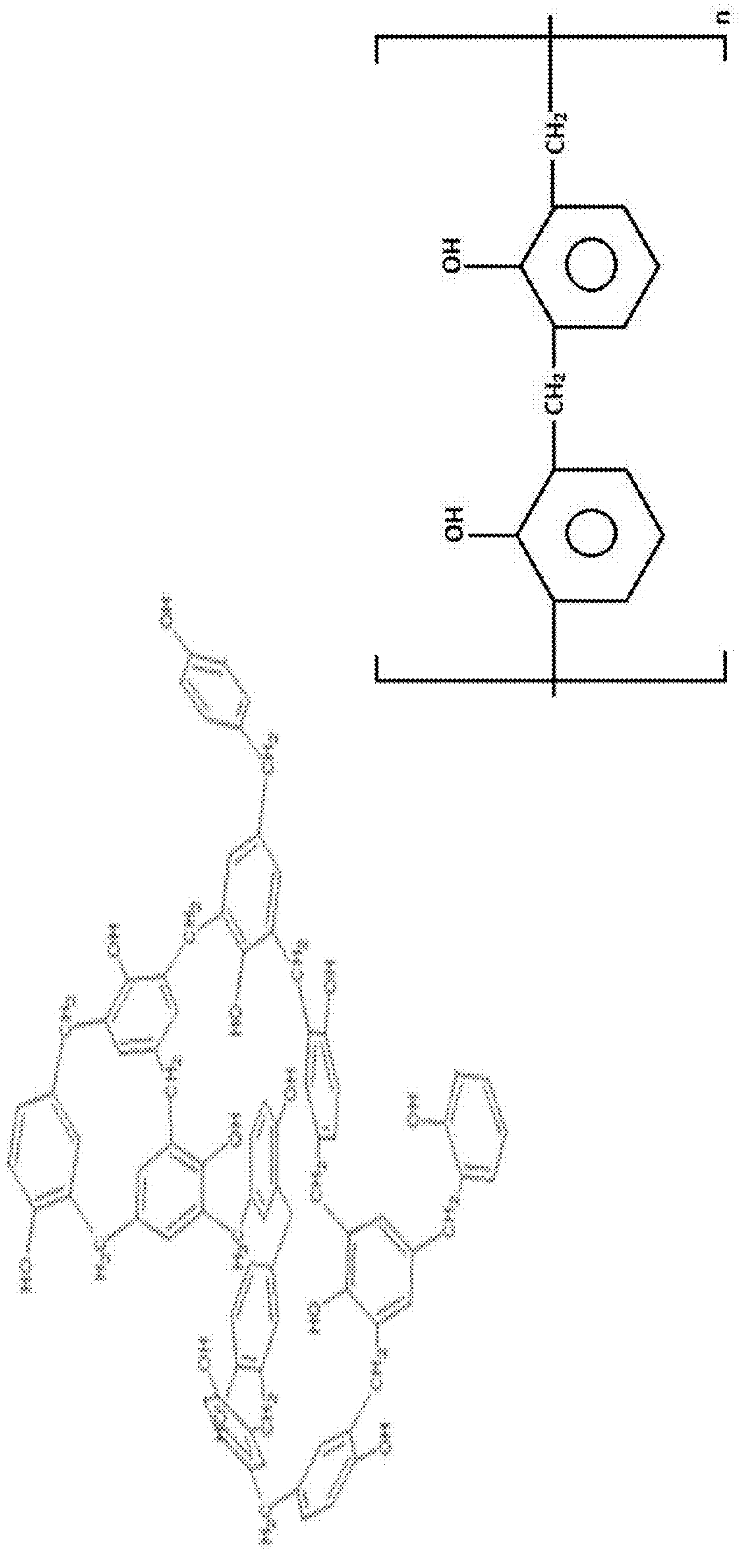


Fig. 3

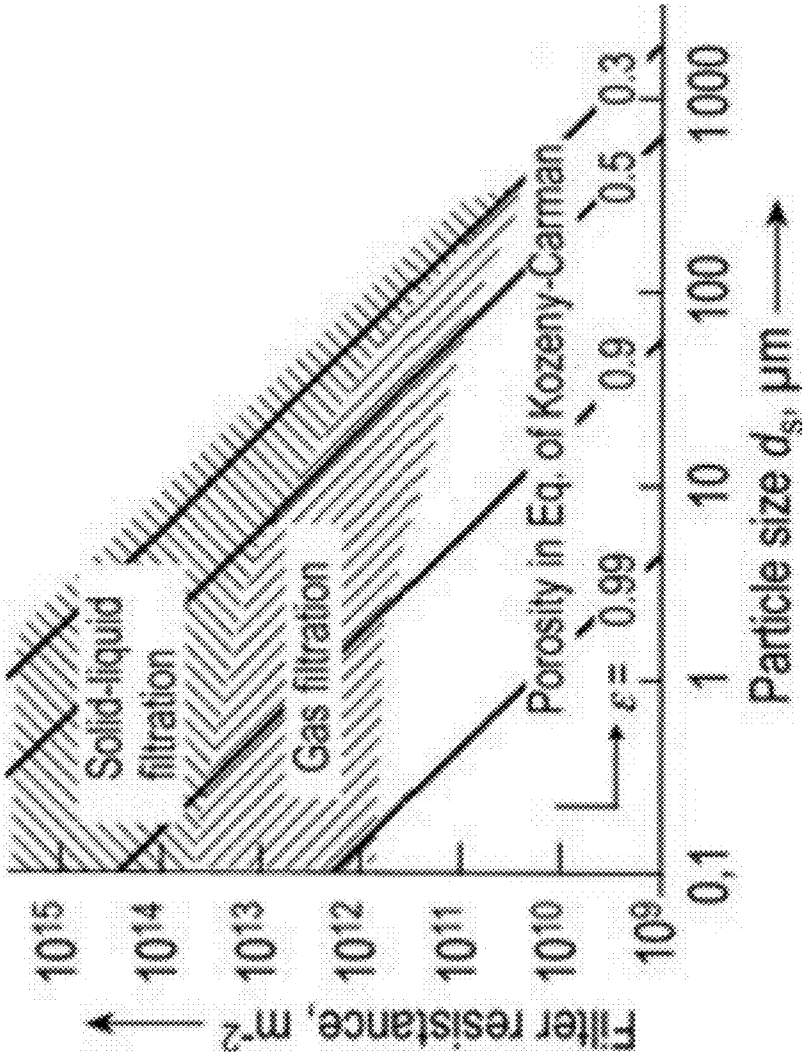

Filter resistance, m^-2
10^15
10^14
10^13
10^12
10^11
10^10
10^9
0.1
1
10
100
1000
Particle size d_s, μm
Solid-liquid filtration
Gas filtration
Porosity in Eq. of Kozeny-Carman
ε = 0.99
0.9
0.5
0.3

Fig. 4

CARBON ACTIVATION METHOD AND ENERGY STORAGE DEVICE THEREOF

CROSS-REFERENCE TO RELATED CO-PENDING APPLICATIONS

[0001] The present application is related to commonly owned and assigned U.S. application Serial Nos. USSN Application Ser. No. 61/894,990 filed on Oct. 24, 2013, and U.S. Application Ser. No. 61/858,902 filed on Jul. 26, 2013, entitled CARBON FOR HIGH VOLTAGE EDLCS" now U.S. Pat. No. ______ (not available; notice of allowance), which mentions: a method of forming activated carbon, comprising: carbonizing a carbon precursor by heating the carbon precursor at a carbonization temperature effective to form a carbon material; and activating the carbon material by heating the carbon material at an activation temperature while exposing the carbon material to carbon dioxide, wherein the carbon precursor comprises phenolic Novolac resin, but does not claim priority thereto.

[0002] The entire disclosure of each publication or patent document mentioned herein is incorporated by reference.

BACKGROUND

[0003] The disclosure generally relates to the field of energy storage devices.

SUMMARY

[0004] In embodiments, the disclosure provides a method of making activated carbon, which method provides improved efficiency and cost benefits.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] In embodiments of the disclosure:

[0006] FIG. **1** shows an exemplary flow diagram summary for the disclosed method of making activated carbon.

[0007] FIG. **2** shows an exemplary pore size distribution of the activated carbon of the present methods.

[0008] FIG. **3** shows exemplary chemical structure representations for a phenol formaldehyde based compound such as a phenolic Novolac resin.

[0009] FIG. **4** shows a graph of filter resistance versus particle size.

DETAILED DESCRIPTION

[0010] Various embodiments of the disclosure will be described in detail with reference to drawings, if any. Reference to various embodiments does not limit the scope of the invention, which is limited only by the scope of the claims attached hereto. Additionally, any examples set forth in this specification are not limiting and merely set forth some of the many possible embodiments of the claimed invention.

[0011] In embodiments, the disclosed method of making and using provide one or more advantageous features or aspects, including for example as discussed below. Features or aspects recited in any of the claims are generally applicable to all facets of the invention. Any recited single or multiple feature or aspect in any one claim can be combined or permuted with any other recited feature or aspect in any other claim or claims.

DEFINITIONS

[0012] "Include," "includes," or like terms means encompassing but not limited to, that is, inclusive and not exclusive.

[0013] "About" modifying, for example, the quantity of an ingredient in a composition, concentrations, volumes, process temperature, process time, yields, flow rates, pressures, viscosities, and like values, and ranges thereof, or a dimension of a component, and like values, and ranges thereof, employed in describing the embodiments of the disclosure, refers to variation in the numerical quantity that can occur, for example: through typical measuring and handling procedures used for preparing materials, compositions, composites, concentrates, component parts, articles of manufacture, or use formulations; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of starting materials or ingredients used to carry out the methods; and like considerations. The term "about" also encompasses amounts that differ due to aging of a composition or formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a composition or formulation with a particular initial concentration or mixture.

[0014] "Optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not.

[0015] The indefinite article "a" or "an" and its corresponding definite article "the" as used herein means at least one, or one or more, unless specified otherwise.

[0016] Abbreviations, which are well known to one of ordinary skill in the art, may be used (e.g., "h" or "hrs" for hour or hours, "g" or "gm" for gram(s), "mL" for milliliters, and "rt" for room temperature, "nm" for nanometers, and like abbreviations).

[0017] Specific and preferred values disclosed for components, ingredients, additives, dimensions, conditions, times, and like aspects, and ranges thereof, are for illustration only; they do not exclude other defined values or other values within defined ranges. The articles and methods of the disclosure can include any value or any combination of the values, specific values, more specific values, and preferred values described herein, including explicit or implicit intermediate values and ranges.

[0018] Electrical energy storage is needed in many applications, such as electric/hybrid vehicles, portable electronic devices, power systems, etc. Batteries of various kinds have been used for most applications. In recent years, electrochemical double layer capacitors (EDLCs, a.k.a. ultracapacitors or supercapacitors) have emerged as an alternative to batteries in applications that require high power, long shelf life, and long cycle life. Energy storage in an EDLC is achieved by separating and storing electrical charges in the electrochemical double layer at the interface between a solid surface and an electrolyte. Activated carbon (or active carbon) is the most widely used material in EDLCs because the carbon has a very large surface area, good electrical and ionic conductivity, excellent chemical stability, and low cost.

[0019] Typically activated carbon can be prepared by carbonizing a carbonaceous precursor in an inert atmosphere (e.g., N_2 or Ar), at a high temperature (commonly hundreds of degrees Celsius), followed by physical (e.g., using CO_2 or steam) or chemical (e.g., using KOH, K_2CO_3, NaOH, Na_2CO_3, $AlCl_3$, $ZnCl_2$, $MgCl_2$, or H_3PO_4, etc.) activation. Precursors include natural materials (such as coal, nut shells, wood, biomass, etc.) and synthetic materials (mostly polymers such as phenolic resin, poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), etc.). Activated carbons derived from non-lignocellulosic sources, such as wheat flour, cornmeal, corn starch, etc., have been described (see commonly owned and assigned U.S. Pat. Nos. 8,318,356 and 8,784,764). For EDLC applications, a chemical activation process yields a carbon product having superior performance compared to a physical activation process. The most significant of the chemical activation processes involves alkali activation, i.e., reaction of either KOH or NaOH with the carbon because this process yields carbon with the highest electrical performance properties. However, this process poses some significant safety and equipment issues which limit the utility. The activation takes place in at from 700 to 900° C., and since KOH melts at about 400° C., a significant amount of potassium metal vapor is generated, which has two consequences. First, the furnace can easily corrode reducing the furnace life and may cause a safety hazards that needs to be addressed via expensive safety measures. A silicon carbide lined furnace may be used to reduce corrosion issue. However the cost of the furnace is then significantly higher. Second, the reaction of alkali and carbon typically generates foam during activation due to the release of several gasses. At activation temperatures, the gases released can include, for example, CO, CO_2, H_2O, and H_2. These gases can cause severe foaming of the batch mixture. The extent of foaming limits the use of the space in the reactor vessel, such as to from about 10 to 30 vol %. So that only a minor amount of the reactor vessel, e.g., about 20 vol %, can be filled with the feed reactants, which can severely limit the output of the batch reactor and can increase processing costs and product costs.

[0020] Commonly owned and assigned WO2015/017200 (PCT/US2014/047728), mentions a method to address the foam issue. Fats, oils, fatty acids, or fatty acid esters are used as an additive in the alkali, carbon reaction mixture to minimize foaming. When these additives react with the alkali they can produce alcohol and/or water by-products. These by-products can be undesirable because they can lead to increased potassium metal vapor generation.

[0021] Another known preparative activation method (commonly owned and assigned WO2011/110543; U.S. Pat. No. 8,927,103, to Kirschbaum) involves: mixing an inert (i.e. non-reactive) hydrophilic polymer (e.g., polyether); forming a pellet of the carbon, the KOH, and the polymer; and heating the pellet in an inert environment to activate the carbon. The method reduces K volatilization due to reduced geometric surface area of the pellet or briquette compared to free powder, which briquetting reduces the corrosion issue by internal containment, and leads to lower costs. The method is applicable only to a very fine particle sizes, for example, 5 microns or less, and does not work with large particle size carbon (e.g., 100 micron) needed for an industrially viable process.

[0022] In embodiments, the disclosure provides a method of making activated carbon comprising:

[0023] compressing a mixture comprising an alkali metal hydroxide, a carbon source, and a solid thermosetting polymer precursor into a pellet; and

[0024] a first heating of the compressed mixture at from 600 to 1,000° C., for from 10 minutes to 24 hours, for example, 850° C. for 2 hrs.

[0025] The “solid” aspect of the thermosetting polymer precursor refers to the phase state of the precursor at ambient temperatures.

[0026] In embodiments, the method can further comprise washing the resulting compressed first heated mixture.

[0027] In embodiments, the method can further comprise a second heating of the resulting compressed, first heated, and washed mixture, at from 600 to 1000° C., for from 10 minutes to 24 hours, for example, 650 to 700° C. such 675° C., for from 2 to 10 hrs, such as 5 hrs.

[0028] In embodiments, the method can further comprise placing the compressed pellet into a closed container having a vent, e.g., a galvanized paint can having a press-fit seal and having a lid having a 5 mm diameter hole) prior to the first heating.

[0029] In embodiments, the method can further comprise crushing the resulting compressed and heated activated carbon product prior to the washing.

[0030] In embodiments, the first heating can be accomplished, for example, in a container that is open to an external atmosphere, such as a crucible in a furnace having ambient air or an inert atmosphere.

[0031] In embodiments, the alkali metal hydroxide can be, for example, powdered KOH, powdered NaOH, and like powdered alkali metal hydroxides, the carbon source can be, for example, powdered green coke, and the thermosetting polymer precursor can be, for example, a mixture of a phenolic resin and a cross-linking agent.

[0032] In embodiments, the alkali metal hydroxide and the carbon source can be, for example, in a weight ratio of from 1:1 to 4:1, such as 2:1, including intermediate values and ranges.

[0033] In embodiments, the thermosetting polymer precursor to the mixture of the KOH and the powdered green coke can be, for example, in a weight ratio of from 1:2 to 1:20, such as 1:10, including intermediate values and ranges.

[0034] In embodiments, the second heating can be accomplished, for example, in a forming gas, in an inert gas, or in a combination thereof.

[0035] In embodiments, the washing can be accomplished, for example, successively with water and then a dilute aqueous acid, or concurrently with a mixture of water and a dilute aqueous acid.

[0036] In embodiments, the carbon source can have, for example, a median particle size of from 1 to 200 microns, such as from 2 to 175, 5 to 150, 10 to 125, 20 to 100, and like particle sizes, including intermediate values and ranges.

[0037] In embodiments, the disclosure provides a method of making activated carbon, which method provides improved efficiency and cost benefits.

[0038] In embodiments, the disclosure provides a method for the economic preparation of alkali activated carbon. In embodiments, the method uses a chemically reactive, oligomeric, solid additive in combination with an alkali and a carbon source material.

[0039] In embodiments, the disclosure provides a method where the solid additive is used as a binder for pelletizing a mixture of the carbon source and the alkali reactant (e.g., KOH).

[0040] In embodiments, as the temperature is increased during ramp up in a first heating step, a crosslinking reaction of the reactive oligomer (i.e., the phenolic resin) with itself and the other components of the mixture takes place in from 70 to 120° C. The crosslinking of the reactive oligomer is followed by the activation reaction in a second heating at, for example, 600 to 1000° C. The crosslinked oligomer product also goes through the carbonization and activation to yield a high performance nanostructured carbon increasing the activated carbon yield, which is in contrast to an entirely sacrificial material such as an polyethylene glycol.

[0041] Notable differences between the presently disclosed method and the aforementioned method disclosed in commonly owned and assigned U.S. Pat. No. 8,927,103 (Kirschbaum) include, for example: the binder used in the presently disclosed methods is a reactive, solid, water-insoluble, crosslinkable, thermosetting polymer precursor, in contrast to a sacrificial inert polymer as in U.S. Pat. No. 8,927,103.

[0042] In the compression or pelletization aspect of the presently disclosed methods, the pelletization can use a carbon source having a median particle size of 100 microns, or more, to fashion pellets, which is a significantly larger particle size compared to an apparent particle size upper limit of about 5 to 10 microns in the aforementioned U.S. Pat. No. 8,927,103.

[0043] The solid oligomeric additive in the disclosed methods is subsequently carbonized and activated in situ to become part of the activated carbon product.

[0044] Other sacrificial or fugitive additives mentioned in the prior art can adversely interfere with the carbon activation so that either the KOH: carbon ratio, or the activation temperature has to be increased to compensate for such additives.

[0045] In embodiments, the disclosed methods are advantaged for at least the following reasons:

[0046] the methods can eliminate foaming by, for example, greater than 50 vol %;

[0047] the methods can permit about a significant (e.g., 2×) increase in the useful material produced for a given activation furnace in the same amount of time;

[0048] the methods provide an increased production rate;

[0049] the methods provide a low cost activated carbon; and

[0050] the methods provide for efficient processing of 100 microns or larger carbon source particles that enable practical industrial scale manufacture.

[0051] In embodiments, the present disclosure provides methods that use a solid reactive pre-polymer, such as a cross-linkable Novolac phenolic resin, which when added to a mixture of a suitable carbon source and alkali (such as KOH) can: eliminate foaming without introducing by-products or contaminants (e.g., fats); and permit the use of a large particle size carbon (e.g., 100 microns).

[0052] In embodiments, the disclosed methods use a crosslinkable solid additive in combination with a mixture of alkali and carbon. In embodiments, the solid reactive thermosetting polymer precursor additive can be, for example, a phenolic resin, such as a Novolac (e.g., available from Plenco). This resin is different from phenolic Resols, which can be a solid or aqueous solution containing about 30% water. Although phenolic Resols could also be used, the disclosed method preferably does not use a Resol resin, which has limited shelf life because the Resol resins continue to polymerize at even ambient temperatures (see www.plenco.com/phenolic-novolac-resol-resins).

[0053] The Novolac resin binds well with the mixture of KOH powder and the carbon powder, and can form chemical bonds with itself in a curing or cross-linking reaction. The Novolac resin goes through a softening stage at about 65 to 105° C., followed by the crosslinking reaction, which crosslinking is complete at about 120° C. After the cure (i.e., the 120° C.) the crosslinked polymer resin is strongly bonded the other ingredients. Another significant property of the Novolac resin additive is that on sufficiently high heating during the subsequent activation process in an inert environment, as presently disclosed, the resin maintains a robust fused pellet formed in the compression or pelletization step.

[0054] Although not bound by theory, the carbon particle size is not a significant constraint for the disclosed method since, for example, a 100 microns carbon particle size powder or larger can be easily and readily processed. The additional carbon content that arises from carbonization of the Novolac resin additive during the disclosed methods can also be contemporaneously activated in situ to a high performance carbon, which result increases the activated carbon net yield, and avoids additional or unnecessary steps for removal of the Novolac resin.

[0055] In embodiments, the disclosure provides a method for producing activated carbon via chemical activation. The methods involve mixing a carbonized precursor ("carbon source") of activated carbon with an alkali source such as KOH and a reactive solid thermosetting polymer precursor additive. The carbonized precursor can be obtained from a natural or a synthetic source. Natural sources include lingocellulosic material such as coconut shell flour, walnut shell flour, etc., and non-lignocellulosic sources such as wheat flour, corn flour, or other carbon sources such as green coke, needle coke, coal, charcoal, and like known carbon sources. Alkali sources can include, for example, KOH, NaOH, or like alkali compounds.

[0056] The thermosetting polymer precursor additive can be, for example, a chemically reactive resin, preferably a solid, water insoluble, and cross-linkable phenolic resin. An example resin is a phenol formaldehyde based compound such as a phenolic Novolac resin, having representative structures shown in FIG. **3**.

[0057] Novolac resins can include a crosslinking agent such as hexamethylenetetramine, also known as hexa, hexamine, or HMTA, and like crosslinking agents or additives, or mixtures thereof.

[0058] Novolac resins are amorphous (i.e., not crystalline), are solid at 25° C., and will soften and flow at from 150° to 220° F. (65 to 105° C.). The number average molecular weight (M_n) of a suitable phenol Novolac resin can be, for example, from 250 to 900, including intermediate values and ranges.

[0059] The disclosed methods are summarized below.

[0060] Referring again to the Figures, FIG. **1** is summary flow diagram of the disclosed method of making.

[0061] FIG. **2** shows an exemplary pore size distribution of the activated carbon of the present methods.

[0062] FIG. **3** shows exemplary chemical structures for a phenol formaldehyde based compound such as a phenolic Novolac resin.

[0063] Solid Novolac powder resin as the thermosetting polymer precursor, and a cross-linking agent, can be added to the mixture alkali and carbon in a weight ratio of 0.05 to 0.3 (polymer precursor: (KOH and carbon)). The combined mixture can then be compressed into a pellet having a desired size, for example, from a 1 cm^3 cubic pellet to a 15×10×5 cm briquette. The pellet or briquette can optionally be contained in a carrier boat or enclosed in sealable container. The carrier boat or sealable container can be, for example, a metallic or other material suitable, that can withstand the processing temperatures and conditions. The pellet can be heated in from 65 to 110° C. in air to bind the ingredients within the pellet together. Heating can alternatively be accomplished in a furnace in a suitable inert atmosphere such as nitrogen gas. The pellet, after green pressing, and before or after resin cure, can optionally be enclosed in a sealable container. Following the compressing or pelletizing step the pellet can be first heat treated in an inert atmosphere at from 600 to 1000° C. to react the reactants and to form the activated carbon. The resulting first heat treated carbon pellet was then washed with water and optionally with dilute acid to remove residual potassium compounds followed by an optional second heat treatment in an inert or reducing atmosphere, such as forming gas, to create the desired activated carbon. The heat treatment in inert or reducing environment after activation is optional and can depend on the oxygen content specification desired in the product.

[0064] Pellet formation and subsequent containerization of pellet allows the potassium vapor to be contained within the enclosed container and equipment corrosion issues to be minimized, so that an expensive corrosion resistant linings (e.g., silicon carbide) in a lined furnaces are not necessary. This reduces the process cost substantially. It is significant that the pellet maintain its integrity during the process. If the pellet disintegrates then metallic potassium emissions can increase substantially leading to corrosion and safety issues and requiring cost prohibitive equipment.

[0065] Since washing the activated carbon product in water and acid can be a significant cost step in manufacture of activated carbon, it is desirable to have a cost effective washing. The larger carbon particle size range of the carbon produced in the disclosed process is advantaged by enabling significantly higher washing and filtration rates. It is known that filtration rate is an inverse function of filtration resistance, and that filtration resistance is inversely proportional to the particle size. This happens because during filtration, particles tend to form a filter cake. A high density filter cake and smaller particle sizes increase the resistance to filtration.

[0066] FIG. **4** shows the extent of the increase in filtration resistance expected with a decrease in particle size based on filtration theory (see for example, Ripperger, et al., in Ullmann's Encyclopedia of Industrial Chemistry, Filtration, 1. Fundamentals). FIG. **4** shows that if the filtration particle size in increased from 5 to 100 microns the filtration resistance (i.e., for a solid-liquid filtration as in the present disclosure) declines by 3 to 4 orders of magnitude.

[0067] Filtration of a slurry containing small particles such as 5 microns is slow and costly due to an extremely slow filtration rate using commercially available equipment. For an industrially viable process a larger relative particle size, such as about 100 microns or more, is preferred.

EXAMPLES

[0068] Following examples describe the invention in more detail and in greater particularity.

Example 1

[0069] Two grams of KOH powder was mixed with one gram of green coke powder having a 100 micron mean particle size, and 0.3 g of solid powdered Novolac resin including a cross-linking agent or curing agent (Plenco product no. 14043) in from 7.5 to 9.5 wt %, from Plastics Engineering Company, Sheboygan, Wis. The mixture was then pressed into 1"×0.5" pellets with a lab press to a density of, e.g., 1.0 to 1.8 g/cm^3, and preferably to 1.2 to 1.3 g/cm^3. The pellets were then introduced into a furnace having a nitrogen atmosphere for a first heating including, for example, heating with a one hr hold at each of 70° C., 80° C., 90° C., and 110° C. After 4 hrs, the heating was continued to 800° C. with a two hr hold at 800° C. The pellets were then cooled to ambient (e.g., room temp.) under a nitrogen atmosphere.

[0070] Alternatively, liquid water or water vapor may be introduced into the furnace under nitrogen atmosphere at a cool down temperature below 300° C. to ambient. The pellets, if placed in a closed container (e.g., a tin coated paint can) in the above heating process, can be removed from the container. The pellets retained shape and showed excellent handling strength, that is, they were resistant to crumbling during typical manual or robotic manipulation. The integrity of the pellets is significant since it suggested that potassium vapor was contained and that the pelleting process addressed safety and corrosion issues. The pellets were then washed with water followed by 37 wt % aqueous HCl, and finally with water again to remove residual potassium compounds. The washed carbon powder was then ground to nominal 5 micron particle size, and then heat treated in 5 wt % H_2/N_2 forming gas at 675° C. for two hours then cooled. The resulting carbon powders were tested for performance in an electric double layer capacitor device. The device was made as follows: 0.85 g of each carbon sample was separately ball milled with 0.05 g of carbon black (Black Pearl 2000) for 10 min at 350 rpm. 0.10 g of DuPont 603A PTFE was added to each separate mill jar, and then milled for 20 min at 300 rpm. The resulting flakes were pulse-ground in a coffee grinder until they were powderized, i.e., free flowing powders. The powdered samples were separately pressed into sheets having a thickness of from 4.5 to 5.0 mil with a roll mill. The separate sheets were placed against a piece of an aluminum current collector, and rolled through the mill to form an electrode sheet.

[0071] A 14 mm punch was used to punch electrodes from the electrode sheet. The punched electrodes were dried overnight at 120° C. in a vacuum oven. After transferring the electrodes to a glovebox, they were fashioned into a standard aluminum/stainless steel casing for the positive/negative electrodes in a coin cell with 90 microL of 1.2 M triethylmethyl ammonium tetrafluoroborate (TEMA-TFB) in acetonitrile (AN) electrolyte composition and a cellulose separator. The coin cells were tested according to standard electrochemical procedures to measure performance. The carbon had a measured capacitance performance of 110 F/cc in the EDLC button cell.

Example 2

[0072] Example 1 was repeated with the exception that a different percentage (i.e., a doubled amount) of the same Novolac resin binder was used. Two grams of KOH powder was mixed with one gram of green coke powder having a 100 micron mean particle size, and 0.6 g of the Plenco solid powdered phenolic Novolac resin. As in the other inventive pellet examples, the pellet maintained excellent integrity with excellent strength and handle-ability during and after the method. The pellets were also processed into cells as Example 1. The carbon had a measured capacitance performance of 115 F/cc in the EDLC coin cell.

Example 3

[0073] Example 1 was repeated with the exception that the carbon source particles to be heat activated in the pellet had a nominal particle size of about five microns. The pellets maintained excellent strength and integrity, and the carbon had a measured capacitance performance of 108 F/cc. This result, in conjunction with the results of Examples 1 and 2, demonstrates that the method can also be used with smaller carbon source particle sizes.

Comparative Example 4

[0074] Example 1 was repeated with the exception that Novolac resin was replaced with a polyethylene glycol (Sigma-Aldrich, Cat. No. P3015, average molecular weight 200)(see the aforementioned U.S. Pat. No. 8,927,103 (WO2011110543A1), to original assignee SGL, now assigned to Corning, Inc.). A pellet was made with KOH and green coke carbon as Example 1. The particle size of the selected green coke carbon was 100 microns. The pellet was heated with the same schedule as Example 1. After the furnace was cooled to ambient temperature and the door was opened, it was observed that the pellets disintegrated or crumbled indicating that the polyethylene glycol binder was unsatisfactory for achieving stable pellets, workable particle size (e.g., 100 microns), and cost reductions of the disclosed method.

[0075] The disclosed methods have demonstrated the industrial viability of preparing nanoporous activated carbon by chemical activation of a suitable carbon source that includes a phenolic resin additive system. The Comparative Example 4 demonstrated that the method disclosed in U.S. Pat. No. 8,927,103 was unsatisfactory for preparing activated carbon having a larger particle size using a pellet or briquet method since the pellet or briquet would easily crumble when handled or transported prior to the first heating. Table 1 provides a summary of the examples.

TABLE 1

Summary of Examples.

Example	Green Coke Particle Size (microns)	Binder Type	Weight Ratio (Green Coke + KOH):Binder	EDLC capacitance (F/cc)
1	100	Novolac phenolic resin	10:1	110
2	100	Novolac phenolic resin	10:2	115
3	5	Novolac phenolic resin	10:1	108
Comp. 4	100	PEG	10:1	N.M.[1]

[1] not measured.

[0076] The disclosure has been described with reference to various specific embodiments and techniques. However, many variations and modifications are possible while remaining within the scope of the disclosure.

What is claimed is:

1. A method of making activated carbon comprising:
compressing a mixture comprising an alkali metal hydroxide, a carbon source, and a solid thermosetting polymer precursor into a pellet; and
a first heating of the compressed mixture at from 600 to 1,000° C., for from 10 mins to 24 hours.

2. The method of claim **1** further comprising washing the resulting compressed and first heated mixture.

3. The method of claim **2** further comprising a second heating of the compressed, first heated, and washed mixture, at from 600 to 1000° C., for from 10 mins to 24 hours.

4. The method of claim **1** further comprising placing the compressed pellet into a closed container having a vent prior to the first heating.

5. The method of claim **2** further comprising crushing the compressed and first heated product prior to the washing.

6. The method of claim **1** wherein the first heating is accomplished in an container open to an external atmosphere.

7. The method of claim **1** wherein the alkali metal hydroxide is powdered KOH, the carbon source is powdered green coke, and the thermosetting polymer precursor is a mixture of a phenolic resin and a cross-linking agent.

8. The method of claim **7** wherein the alkali metal hydroxide and the carbon source is in a weight ratio of from 1:1 to 4:1.

9. The method of claim **7** wherein the mixture of a phenolic resin and a cross-linking agent to the mixture of the KOH and the powdered green coke is in a weight ratio of from 1:2 to 1:20.

10. The method of claim **1** wherein the second heating is accomplished in a forming gas, in an inert gas, or in a combination thereof.

11. The method of claim **2** wherein washing is accomplished successively with water, and a dilute aqueous acid, or concurrently with water and a dilute aqueous acid.

12. The method of claim **1** wherein carbon source has a median particle size of from 1 to 200 microns.

13. The method of claim **1** wherein carbon source has a median particle size of from 10 to 150 microns.

14. The method of claim **1** wherein carbon source has a median particle size of from 90 to 110 microns.

15. The method of claim **1** wherein compressing eliminates foaming of the mixture when heated.

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