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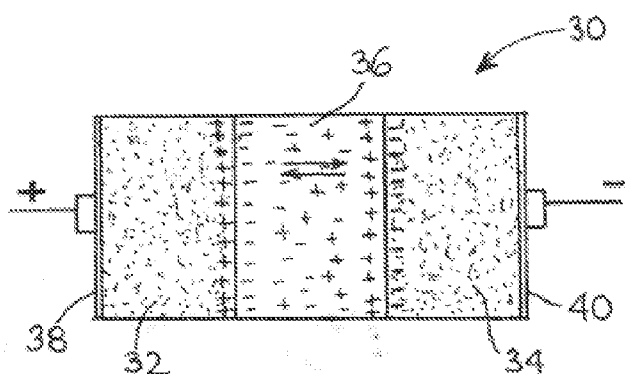


FIG. 1

(57) Abstract: A carbon pyrolyzate material is described, which is comprised at least partially of pyrolyzed pitch, wherein the carbon pyrolyzate material has: a nitrogen Brunauer-Emmett-Teller (N₂ BET) surface area measured at 77° Kelvin, which is in a range of from 1450 m² per gram of carbon material to 3000 m² per gram of carbon pyrolyzate material; ash content as determined by ASTM 2866-94 of less than 0.15% by weight, based on weight of the carbon pyrolyzate material; and metals content as determined by particle-induced x-ray emission (PIXE) spectrometry, of less than 500 ppm by weight, based on weight of the carbon pyrolyzate material. Such carbon pyrolyzate material is usefully employed in the fabrication of electrode double layer capacitor (EDLC) electrodes, and in other energy supply and storage devices, as well as in adsorbent applications, e.g., for storage and dispensing of gases.

CARBON PYROLYZATE MATERIAL, AND EDLC CARBON ELECTRODE COMPRISING SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The benefit of United States Provisional Patent Application No. 62/146,760 filed April 13, 2015 in the names of Mackenzie King, Melissa A. Petruska, and Dana A. Totir for “EDLC CARBON ELECTRODE” is claimed under the provisions of 35 USC 119. The disclosure of United States Provisional Patent Application No. 62/146,760 is hereby incorporated herein by reference, in its entirety, for all purposes.

FIELD

[0002] The present disclosure relates to carbon materials that are suitable for forming electrochemical double layer capacitor (EDLC) carbon electrodes and for constructing electrochemical energy devices, as well as methods of making and using such carbon materials, EDLC carbon electrodes and electrochemical energy devices.

DESCRIPTION OF THE RELATED ART

[0003] As the limits of lithium rechargeable batteries are realized in various mobile electronic device applications, electrochemical double layer capacitors (EDLCs) are being increasingly viewed as potentially useful components in such applications, due to their characteristics of extended lifetime ($>10^6$ cycles), high power density capability (>10 kilowatts/liter), and low power electronics overhead requirements.

[0004] Despite such ostensible advantages, however, it is generally acknowledged that for most mobile or volume-constrained electronics applications, the energy density of EDLCs will need to be substantially increased over currently achievable levels in order for EDLCs to be commercially successful in high volume industrial and consumer applications, such as regenerative braking systems for vehicles, wind power systems, and quick start-up photocopiers. Current EDLCs and related hybrids have achieved energy densities on the order of 10 watt-

hours/liter (Wh/L), but such energy density is approximately two orders of magnitude below the energy density that is achievable by conventional lithium-ion batteries.

[0005] Accordingly, power density and efficiency of EDLCs need to be improved substantially for energy harvesting applications, and energy density needs to be correspondingly increased for use of EDLCs in applications in which space is at a premium. Equation (1) below states the relationship between stored energy, E , in Joules, capacitance, C , in Farads, and voltage, V , in volts:

$$(1) \quad E = \frac{1}{2} CV^2.$$

This equation reflects the trade-offs that are involved in enhancing performance characteristics of EDLCs. As an example, increasing the capacitance of the energy storage medium to correspondingly increase energy density may be desirable in some applications, but in others the increase in capacitance will adversely affect the time constant RC (resistance $\times$ capacitance, as governing the characteristic response time of the capacitor) to an extent rendering the capacitor deficient or even useless for its intended purpose. It is important in this respect that the energy storage medium be of high purity and capable of accommodating high levels of voltage, in order to maximize energy storage capability of the EDLC device.

[0006] Carbon is used extensively in EDLC devices due to its low cost and advantageous physical properties, including conductivity, high surface area for reversible charge storage, and the good long-term durability. Most natural and synthetic carbons used in EDLC applications are provided to the integrated device manufacturer in a particulate form. In a typical processing scheme, the carbon particles are blended with binder, electrically conductive carbon black, and water, to form a slurry. Pyrolyzed coconut shell carbons that have been acid or water washed are used extensively in EDLC applications due to their low cost, but such carbons lose significant capacity during cycling due to their impurities content. For example, iron is a significant impurity that catalyzes side reactions during cycling of EDLCs, resulting in gaseous or other detrimental products that cause a decrease in cell efficiency and capacity, leading ultimately to early failure of the EDLC device.

[0007] The foregoing deficiencies of EDLC devices relating to carbon-based electrodes are shared by other electrochemical devices such as metal ion batteries, metal air batteries, and metal ion capacitors, which likewise utilize electrodes containing carbon.

[0008] In consequence of the foregoing, the art continues to seek improvements in carbon materials, and electrodes and device structures incorporating same, e.g., EDLC device structures, as well as in associated processes of manufacturing and use thereof.

SUMMARY

[0009] The present disclosure relates to carbon materials useful in forming electrochemical double layer capacitor (EDLC) carbon electrodes and constructing electrochemical energy devices, and related methods of making and using such carbon materials, EDLC carbon electrodes and electrochemical energy devices.

[0010] In one aspect, the disclosure relates to an electrochemical double layer capacitor (EDLC) electrode carbon material, comprising a pyrolyzate of at least one of poly(vinylidene chloride), poly(vinylidene chloride) copolymer, and pitch, and having the following characteristics: (i) a nitrogen Brunauer-Emmett-Teller (N_2 BET) surface area measured at 77° Kelvin, which is in a range of from 1450 m² per gram of carbon material to 2300 m² per gram of carbon material; (ii) a nitrogen Dubinin-Radushkevich micropore volume measured at 77° Kelvin, which is in a range of from 0.55 cc per gram of carbon material to 1 cc per gram of carbon material, and at least 94% of which is constituted by pores larger than 0.6 nm, as determined by Gurvich-based neopentane capacity at neopentane pressure of 450 mmHg, neopentane liquid density of 0.613 g/mL, neopentane kinetic diameter of 0.62 nm, and temperature of 273° Kelvin; (iii) particulate form in which at least 97% by weight of particles have particle size in a range of from 1 to 20 μ m; (iv) ash content as determined by ASTM 2866-94 of less than 0.15% by weight, based on weight of the carbon material; and (v) metals content as determined by particle-induced x-ray emission (PIXE) spectrometry, of less than 500 ppm by weight, based on weight of the carbon material, and, independently, iron content as determined by PIXE spectrometry, of less than 10 ppm by weight, based on weight of the carbon material.

[0011] In another aspect, the disclosure relates to an EDLC electrode comprising the EDLC electrode carbon material of the present disclosure.

[0012] In another aspect, the disclosure relates to an electrochemical double layer capacitor (EDLC) electrode, comprising a carbon material having the following characteristics: (i) capacitance of greater than 27 F/gm of the electrode material as determined by IEC standard 62391-1 at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), (ii) a carbon material film density that is greater than 0.55 gram/cubic centimeter of carbon material, (iii) an Equivalent Series Resistance that exhibits less than 100% increase over a period of 1500 hours at temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), (iv) a capacitance retention of greater than 80% over a period of 1500 hours at

temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), and (v) current density of up to 50 milliamps per Farad, as based on a 3000 Farad capacitor at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN).

[0013] In a further aspect, the disclosure relates to an electrochemical double layer capacitor (EDLC) electrode carbon material, comprising a pyrolyzate of at least one of poly(vinylidene chloride), poly(vinylidene chloride) copolymer, and pitch, having the following characteristics: (i) a nitrogen Brunauer-Emmett-Teller (N₂ BET) surface area measured at 77° Kelvin, which is in a range of from 1450 m² per gram of carbon material to 2300 m² per gram of carbon material; (ii) a nitrogen Dubinin-Radushkevich micropore volume measured at 77° Kelvin, which is in a range of from 0.55 cc per gram of carbon material to 1 cc per gram of carbon material, and at least 94% of which is constituted by pores larger than 0.6 nm, as determined by Gurvich-based neopentane capacity at neopentane pressure of 450 mmHg, neopentane liquid density of 0.613 g/mL, neopentane kinetic diameter of 0.62 nm, and temperature of 273° Kelvin; (iii) particulate form in which at least 97% by weight of particles have particle size in a range of from 1 to 20 µm; (iv) ash content as determined by ASTM 2866-94 of less than 0.15% by weight, based on weight of the carbon material; (v) metals content as determined by particle-induced x-ray emission (PIXE) spectrometry, of less than 500 ppm by weight, based on weight of the carbon material, and, independently, iron content as determined by PIXE spectrometry, of less than 10 ppm by weight, based on weight of the carbon material; (vi) capacitance of greater than 27 F/gm of the carbon material as determined by IEC standard 62391-1 at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN); (vii) a carbon material film density that is greater than 0.55 gram/cubic centimeter of carbon material; (viii) an Equivalent Series Resistance that exhibits less than 100% increase over a period of 1500 hours at temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN); (ix) a capacitance retention of greater than 80% over a period of 1500 hours at temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN); and (x) current density of up to 50 milliamps per Farad, as based on a 3000 Farad capacitor at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN).

[0014] In a further aspect, the disclosure relates to an EDLC device, comprising an EDLC electrode of the present disclosure.

[0015] A further aspect of the disclosure relates to an electrochemical energy device, comprising the EDLC electrode carbon material of the present disclosure.

[0016] A still further aspect of the disclosure relates to a method of making the EDLC electrode carbon material of the present disclosure, comprising pyrolyzing a pyrolyzable precursor comprising at least one precursor material selected from the group consisting of at least one of poly(vinylidene chloride), poly(vinylidene chloride) copolymer, and pitch, under pyrolysis conditions for sufficient time to produce the pyrolyzate with the aforementioned characteristics.

[0017] Yet another aspect of the disclosure relates to a method of storing energy, comprising providing an EDLC device of the present disclosure, and inputting storable energy to the device.

[0018] Other aspects, features and embodiments of the disclosure will be more fully apparent from the ensuing description and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1 is a schematic representation of an electrochemical energy device comprising an arrangement of carbon electrodes forming an EDLC conformation with electrolyte therebetween, according to one embodiment of the present disclosure.

DETAILED DESCRIPTION

[0020] The present disclosure relates to carbon materials, and electrodes and device structures formed therefrom, as well as methods of making and using same.

[0021] As used herein and in the appended claims, the singular forms "a", "and", and "the" include plural referents unless the context clearly dictates otherwise.

[0022] As used herein, the following porosity terms shall have the following meanings: the term "pore size" refers to pore diameter or equipment dimension; the term "nanopores" refers to pores that do not exceed 100 nm in pore size; the term "micropores" refers to pores that are less than 2 nm in pore size; the term "mesopores" refers to pores having pore size in a range of from 2 nm to 50 nm; and "macropores" refers to pores that are greater than 50 nm in pore size, e.g., in a range of from 50 nm to 1000 nm, or in other suitable range in which pore size is greater than 50 nm.

[0023] In various embodiments of the present disclosure, the disclosure relates to a carbon material useful in electrochemical double layer capacitor (EDLC) devices is described, including a pyrolyzate of at least one of poly(vinylidene chloride), poly(vinylidene chloride) copolymer, and pitch, having the following characteristics: (i) a nitrogen Brunauer-Emmett-Teller (N_2 BET) surface area measured at 77° Kelvin, which is in a range of from 1450 m² per gram of carbon material to 2300 m² per gram of carbon material; (ii) a nitrogen Dubinin-Radushkevich micropore volume measured at 77° Kelvin, which is in a range of from 0.55 cc per gram of carbon material to 1 cc per gram of carbon material, and at least 94% of which is constituted by pores larger than 0.6 nm, as determined by Gurvich-based neopentane capacity at neopentane pressure of 450 mmHg, neopentane liquid density of 0.613 g/mL, neopentane kinetic diameter of 0.62 nm, and temperature of 273° Kelvin; (iii) particulate form in which at least 97% by weight of particles have particle size in a range of from 1 to 20 μ m; (iv) ash content as determined by ASTM 2866-94 of less than 0.15% by weight, based on weight of the carbon material; and (v) metals content as determined by particle-induced x-ray emission (PIXE) spectrometry, of less than 500 ppm by weight, based on weight of the carbon material, and, independently, iron content as determined by PIXE spectrometry, of less than 10 ppm by weight, based on weight of the carbon material.

[0024] As set out herein, EDLC performance values dependent on voltage and electrolyte compositions are determined under an applied voltage of 2.7 volts in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN).

[0025] The method used to determine capacitance herein is the IEC 62391-1 standard (page 15) method, in which the specific capacitance is the measured cell capacitance ($C_{\text{cell}} = (I \cdot \Delta t) / \Delta V$) divided by the total amount of carbon in the cell, with the cell being operated at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN).

[0026] ELDC device performance values described herein, which are dependent on ELDC device size, are based on a 3000 Farad capacitor device.

[0027] EDLC electrode densities described herein are based solely on the carbon in the electrode, and do not include current collectors or metallizations of such carbon material.

[0028] The disclosure, as variously set out herein in respect of features, aspects and embodiments thereof, may in particular implementations be constituted as comprising, consisting, or consisting essentially of, some or all of such features, aspects and embodiments, as well as elements and components thereof being aggregated to constitute various further implementations of the disclosure. The disclosure correspondingly contemplates such features, aspects and

embodiments, or a selected one or ones thereof, in various permutations and combinations, as being within the scope of the present disclosure.

[0029] The Gurvich-based neopentane capacity determination referred to herein is described in Carbon 2014, Vol. 74, p. 22.

[0030] In one aspect, the disclosure relates to an electrochemical double layer capacitor (EDLC) electrode carbon material, comprising a pyrolyzate of at least one of poly(vinylidene chloride), poly(vinylidene chloride) copolymer, and pitch, having the following characteristics: (i) a nitrogen Brunauer-Emmett-Teller (N_2 BET) surface area measured at 77° Kelvin, which is in a range of from 1450 m² per gram of carbon material to 2300 m² per gram of carbon material; (ii) a nitrogen Dubinin-Radushkevich micropore volume measured at 77° Kelvin, which is in a range of from 0.55 cc per gram of carbon material to 1 cc per gram of carbon material, and at least 94% of which is constituted by pores larger than 0.6 nm, as determined by Gurvich-based neopentane capacity at neopentane pressure of 450 mmHg, neopentane liquid density of 0.613 g/mL, neopentane kinetic diameter of 0.62 nm, and temperature of 273° Kelvin; (iii) particulate form in which at least 97% by weight of particles have particle size in a range of from 1 to 20 μm; (iv) ash content as determined by ASTM 2866-94 of less than 0.15% by weight, based on weight of the carbon material; and (v) metals content as determined by particle-induced x-ray emission (PIXE) spectrometry, of less than 500 ppm by weight, based on weight of the carbon material, and, independently, iron content as determined by PIXE spectrometry, of less than 10 ppm by weight, based on weight of the carbon material.

[0031] Such carbon material in one embodiment comprises a pyrolyzate of poly(vinylidene chloride) or poly(vinylidene chloride) copolymer. In another embodiment, the carbon material may comprise a pyrolyzate of poly(vinylidene chloride) and poly(vinylidene chloride) copolymer. In a further embodiment, the carbon material may comprise a pyrolyzate of poly(vinylidene chloride) or poly(vinylidene chloride) copolymer, with pitch. Another embodiment involves the carbon material comprising a pyrolyzate of poly(vinylidene chloride), poly(vinylidene chloride) copolymer, and pitch. The copolymer may for example comprise a comonomer selected from the group consisting of methyl acrylate (MA), vinyl chloride (VC), acrylonitrile (AN), and isobutylene (IB). In another embodiment, the carbon material comprises a pyrolyzate of a poly(vinylidene chloride) copolymer and pitch. In a still further embodiment, the carbon material comprises a pyrolyzate of pitch.

[0032] In applications in which the carbon material is a pyrolyzate of a mixture of poly(vinylidene chloride) or its copolymer and pitch, the amount of PVDC or its copolymer in the mixture may be any suitable amount, e.g., from 1 to 99 wt% PVDC or its copolymer, from 5 to 98

wt% PVDC or its copolymer, from 10 to 98 wt% PVDC or its copolymer, from 25 to 97 wt% PVDC or its copolymer, from 50 to 99.5 wt% PVDC or its copolymer, or other suitable range of the amount of PVDC or its copolymer, based on the total weight of the mixture.

[0033] The carbon material in various embodiments is of particulate form having a median diameter particle size in a range of from 4.5 to 6.5 μm , although any suitable particle sizes, particle size distributions, and forms of the carbon material may be employed in the general practice of the present disclosure. The carbon material may have any suitable porosity characteristics. In some embodiments, the porosity may comprise nanopores of specific pore size distribution. In other embodiments, at least a majority of pores in the porosity may be micropores. In still other embodiments of the carbon materials disclosed herein, the porosity may be constituted by pores of up to 3 nm, or in which at least the majority of pores are of such size. It will be appreciated that the porosity of carbon materials in the broad practice of the present disclosure may be widely varied, and that materials of specific pore sizes and pore size distributions may be determined to be suitable in such broad practice of the disclosure, e.g., by empirical tests, modeling, or other determinative methods.

[0034] The pyrolysis of pyrolyzable materials to form pyrolyzate carbons of the present disclosure may be carried out under suitable process conditions, as appropriate for achievement of carbon material having the properties herein disclosed. Appropriate process conditions may be determined empirically without undue effort.

[0035] The particulate pyrolyzate material may be activated to yield activated carbon material having the properties described herein. The activation may be carried out prior to, or subsequent to, the formation of an EDLC electrode. For such purpose, the particulate pyrolyzate may be blended with binder and conductive material, and molded or otherwise shaped to an appropriate form for use in an EDLC device. The binder utilized for such purpose may be of any suitable type, and may for example comprise a fluoropolymer, e.g., polytetrafluoroethylene, polyvinylchloride, polyvinylidene fluoride, etc. In various embodiments, the binder comprises a water soluble composition such as a carboxymethyl cellulose and styrene-butadiene rubber (CMC-SBR) composition. The conductive material likewise may be of any suitable type, and may for example comprise carbon black. The pyrolyzate, binder, and conductive component may be blended and processed to provide the final shaped electrode article.

[0036] Activation of the electrode material may be carried out at appropriate conditions to provide the electrode with appropriate properties for use in an EDLC device. Suitable conditions may be determined empirically without undue effort, and may for example involve exposing the

carbon material to oxidizing conditions in an ambient of carbon monoxide, carbon dioxide, oxygen, or steam at elevated temperature.

[0037] The disclosure thus contemplates an EDLC electrode comprising the EDLC electrode carbon material of the present disclosure, as variously described herein. The EDLC electrode in various embodiments may have an electrode density that is in a range of from 0.55 to 0.67 g per cc of the electrode. In other embodiments, the EDLC electrode may have a current density capability, measured at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), which is greater than 15 mA/cm² over 1500 hrs. at 65°C, a capacitance of greater than 27 F/gm of the electrode carbon material, as determined by IEC standard 62391-1 at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), or a current to capacitance ratio that is less than 53 mA/F over 1500 hrs. at 65°C and 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), depending on the measurement that is selected (two or all three of such measurements may be employed to characterize the EDLC electrode in specific embodiments of the disclosure). In specific embodiments, the EDLC electrode may have a gravimetric capacitance that is greater than 30 F/gm electrode carbon material over 1500 hrs. at 65°C and 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN). In other embodiments, the gravimetric capacitance of the EDLC electrode may be greater than 32, 34, 36, or more F/gm electrode carbon material, over a period of 1500 hrs. at 65°C and 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN). It will be appreciated that any combinations and permutations of the foregoing characteristics may be employed to characterize a specific EDLC electrode carbon material and EDLC electrodes within the broad scope of the present disclosure.

[0038] The EDLC electrode may be formed of a mixture of activated carbon material, the remainder being binder and electrically conductive carbon. The amount of activated carbon material in such mixture preferably is at least 75 wt%, e.g., in a range of from 75 to 95 wt%, based on the weight of the mixture. The electrode of such composition desirably has a density of greater than 0.55 g/cc of electrode material.

[0039] In various embodiments, the electrochemical double layer capacitor (EDLC) electrode may comprise a carbon material having the following characteristics: (i) capacitance of greater than 27 F/gm of the electrode material as determined by IEC standard 62391-1 at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), (ii) a carbon material film density that is greater than 0.55 gram/cubic

centimeter of carbon material, (iii) an Equivalent Series Resistance that exhibits less than 100% increase over a period of 1500 hours at temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), (iv) a capacitance retention of greater than 80% over a period of 1500 hours at temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), and (v) current density of up to 50 milliamps per Farad in a 3000 Farad capacitor at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN).

[0040] In another aspect, the disclosure relates to an electrochemical double layer capacitor (EDLC) electrode carbon material, comprising a pyrolyzate of at least one of poly(vinylidene chloride), poly(vinylidene chloride) copolymer, and pitch, and having the following characteristics: (i) a nitrogen Brunauer-Emmett-Teller (N₂ BET) surface area measured at 77° Kelvin, which is in a range of from 1450 m² per gram of carbon material to 2300 m² per gram of carbon material; (ii) a nitrogen Dubinin-Radushkevich micropore volume measured at 77° Kelvin, which is in a range of from 0.55 cc per gram of carbon material to 1 cc per gram of carbon material, and at least 94% of which is constituted by pores larger than 0.6 nm, as determined by Gurvich-based neopentane capacity at neopentane pressure of 450 mmHg, neopentane liquid density of 0.613 g/mL, neopentane kinetic diameter of 0.62 nm, and temperature of 273° Kelvin; (iii) particulate form in which at least 97% by weight of particles have particle size in a range of from 1 to 20 μm; (iv) ash content as determined by ASTM 2866-94 of less than 0.15% by weight, based on weight of the carbon material; (v) metals content as determined by particle-induced x-ray emission (PIXE) spectrometry, of less than 500 ppm by weight, based on weight of the carbon material, and, independently, iron content as determined by PIXE spectrometry, of less than 10 ppm by weight, based on weight of the carbon material; (vi) capacitance of greater than 27 F/gm of the electrode material as determined by IEC standard 62391-1 at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN); (vii) a carbon material film density that is greater than 0.55 gram/cubic centimeter of carbon material; (viii) an Equivalent Series Resistance that exhibits less than 100% increase over a period of 1500 hours at temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN); (ix) a capacitance retention of greater than 80% over a period of 1500 hours at temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN); and (x) current density of up to 50

milliamps per Farad in a 3000 Farad capacitor at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN).

[0041] A further aspect of the disclosure relates to an EDLC device comprising an EDLC electrode of a type as variously described herein, e.g., at least one electrode, or more than one electrode. The EDLC device may for example include 2 electrodes according the present disclosure. In other embodiments, wherein at least one such electrode of the present disclosure is employed, the other electrode(s) may be of differing type(s).

[0042] The disclosure therefore contemplates an electrochemical energy device, comprising an EDLC electrode carbon material of a type as variously described herein. In a particular implementation, such electrochemical energy device may comprise two electrodes, each comprising the EDLC electrode carbon material, a current collector in contact with each of the two electrodes, and a separator element between the two electrodes.

[0043] According to one method aspect of the present disclosure, a method is provided for making the EDLC electrode carbon material of a type as variously described herein. Such method comprises pyrolyzing a pyrolyzable precursor comprising at least one precursor material selected from the group consisting of at least one of poly(vinylidene chloride), poly(vinylidene chloride) copolymer, and pitch, under pyrolysis conditions for sufficient time to produce the pyrolyzate with the aforementioned characteristics.

[0044] The present disclosure further comprises a method of storing energy, including providing an EDLC device according to the present disclosure, and inputting storable energy to the device. In a preferred implementation of such method, the energy storage density of the EDLC device is at least 7.4 watt-hr/liter, as based on a 3000 Farad EDLC device.

[0045] The carbon materials of the present disclosure enable the fabrication of EDLC devices, for operation with a suitable electrolyte, e.g., 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), or other suitable electrolytic species and solvent. The resulting EDLC device has the ability to preserve energy and power capabilities to within 80% of initial values after operation for a period of 1500 hours at temperature of 65°C, as well as the ability to preserve energy and power capabilities while being cycled at current densities of 53 milliAmps per Farad and lower, as based on a 3000 Farad device.

[0046] Electrolytes utilized in electrochemical energy devices of the present disclosure may be of any suitable type, as regards the electrolytic species and the solvent medium, and may for example include quaternary ammonium salts and alkyl ammonium salts of varying types, in organic solvent media such as acetonitrile, tetrahydrofuran, gamma-butyrolactone, propylene carbonate, diethyl carbonate, and the like.

[0047] Accordingly, in various embodiments of the present invention, EDLC devices are contemplated, in which the device includes at least one electrode of the present disclosure, i.e., in which the multiple electrodes may be the same as or different from one another, provided that there is at least one electrode of the present disclosure in the device. The EDLC device may utilize any suitable electrolyte media, e.g., 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), or other suitable electrolytic species and solvent. The electrodes of the present disclosure is used in such devices may be characterized as having one or more of the following characteristics: (i) capacitance of greater than 27 F/gm of the electrode material as determined by IEC standard 62391-1 at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), (ii) a carbon material film density that is greater than 0.55 gram/cubic centimeter of carbon material, (iii) an Equivalent Series Resistance that exhibits less than 100% increase over a period of 1500 hours at temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), (iv) a capacitance retention of greater than 80% over a period of 1500 hours at temperature of 65°C and voltage of 2.7V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), and (v) current density of up to 50 milliamps per Farad, as based on a 3000 Farad capacitor at 2.7 V in organic electrolyte comprising 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN). In various embodiments, the Equivalent Series Resistance may be in a range of from 0.1 milliohm to 0.2 milliohm, as based on a 3000 Farad capacitor.

[0048] Referring now to the drawing, FIG. 1 is a schematic representation of an electrochemical energy device comprising an arrangement of carbon electrodes forming an EDLC conformation with electrolyte therebetween, according to one embodiment of the present disclosure.

[0049] The electrochemical energy device 30 of FIG. 1 comprises an arrangement of carbon electrodes 32 and 34 forming an EDLC conformation with electrolyte 36 therebetween, according to another embodiment of the present disclosure. Electrode 32 is metallized on an outer face thereof to constitute current collector 38 thereon, and electrode 34 is correspondingly metallized on an outer face thereof to constitute current collector 40 thereon.

[0050] Regardless of the specific configuration (e.g., spiral, flat, etc.) employed for the electrochemical energy device, the carbon pyrolyzates with their associated metallization elements form electrodes that are electrically coupled to respective terminals, and upon addition of suitable electrolyte form EDLC cells. The electrolyte may comprise a liquid-phase electrolyte, of an organic or aqueous character, or may comprise a solid state electrolyte material.

[0051] The carbon material of the present disclosure thus can be used to fabricate electrodes that have the capacity to handle high current densities, that exhibit high current efficiency, that possess low capacity fade during repetitive cycling, and that otherwise exhibit high capacitance, high power, and high energy density, and accommodate high voltages in electrochemical double layer capacitor devices.

[0052] EDLC devices of the present disclosure utilizing suitable electrolyte media, e.g., 1M tetraethyl ammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN), or other suitable electrolytic species and solvent, afford high performance in terms of efficiency, capacitance of carbon material, capacitance of electrode material, carbon material film density, Equivalent Series Resistance capacitance retention, and current density in large capacitor formats.

[0053] In various embodiments of the present disclosure, the disclosure relates to a carbon pyrolyzate material comprised at least partially of pyrolyzed pitch, wherein the carbon pyrolyzate material has: a nitrogen Brunauer-Emmett-Teller (N₂ BET) surface area measured at 77° Kelvin, which is in a range of from 1450 m² per gram of carbon material to 3000 m² per gram of carbon pyrolyzate material; ash content as determined by ASTM 2866-94 of less than 0.15% by weight, based on weight of the carbon pyrolyzate material; and metals content as determined by particle-induced x-ray emission (PIXE) spectrometry, of less than 500 ppm by weight, based on weight of the carbon pyrolyzate material.

[0054] Such carbon pyrolyzate material is suitably formed by pyrolysis of pitch, or a pyrolyzable composition comprising pitch and other pyrolyzable material, under such time and temperature conditions as to produce a pyrolyzate of desired characteristics, which optionally may be further processed under suitable activation conditions to provide a product pyrolyzate material of appropriate character for the end use application for which the carbon pyrolyzate material is intended.

[0055] In applications in which the carbon pyrolyzate material is formed from a pyrolyzable composition comprising pitch and other pyrolyzable material, the other pyrolyzable material may be of any suitable type, and may for example comprise: one or more of polyacrylonitrile, polyfurfuryl alcohol, polyvinylbutyral, polyvinylchloride, polyvinylidene fluoride, polyvinylidene chloride, polyvinylidene chloride copolymer (with any suitable comonomer, e.g., methyl acrylate (MA), vinyl chloride (VC), acrylonitrile (AN), or isobutylene (IB), etc.), polyvinylidene fluoride, polyvinylidene fluoride copolymer (with any suitable comonomer, e.g., methyl acrylate (MA), vinyl chloride (VC), acrylonitrile (AN), or isobutylene (IB), etc.), or other synthetic resins; one or more of natural source materials such as coal, coconut shells, peach pits, cellulosic materials, etc.; pyrolyzable carbon cryogel materials of a type as described for example in Feaver et al. U.S.

Patents 8,404,384 and 9,112,230; blends, mixtures, and compositions of any two or more of the foregoing pyrolyzable materials. As one illustrative sample, the pyrolyzable composition may comprise pitch, polyacrylonitrile, and cellulosic material. As another illustrative example, the pyrolyzable composition may comprise pitch and pyrolyzable carbon cryogel material. As yet another illustrative example, the pyrolyzable composition may comprise pitch, polyvinylidene chloride copolymer, and cellulosic material.

[0056] In such pyrolyzable compositions comprising pitch and other pyrolyzable material, the relative proportions of the pitch and other component(s) of the composition may be varied as necessary or desirable for a given end use application of the resulting carbon pyrolyzate material. For example, the amount of pitch in the pyrolyzable composition may range from 1% to 100% by weight, based on total weight of the composition, or in a range of from 2% to 99%, 5% to 95%, 10% to 90%, 20% to 85%, 25% to 80%, 30% to 75%, 35% to 70%, 40% to 65%, or 45% to 60%, on the same weight percentage basis. In general, the amount of pitch in the pyrolyzable composition may be in a range whose lower value is selected from any of 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5%, 5%, 7%, 8%, 10%, 12%, 15%, 18%, 20%, 22%, 25%, 28%, 30%, 35%, 40%, 50%, 60%, 70%, 80%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, and 99%, and whose upper value is greater than the lower value of the range and is selected from any of 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5%, 5%, 7%, 8%, 10%, 12%, 15%, 18%, 20%, 22%, 25%, 28%, 30%, 35%, 40%, 50%, 60%, 70%, 80%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.8%, 99.9%, 99.95%, and 99.99%.

[0057] Pyrolysis of the pyrolyzable composition to form such pitch-based carbon pyrolyzate materials may be conducted at any suitable temperature and for any suitable time, as necessary or desirable to form the pyrolyzate of desired character. For example, pyrolysis temperatures may be in a range of 600°C to 1100°C, or higher, and the pyrolysis time may be in a range of from 2 to 50 hours, or more, it being understood that the time and temperature of the pyrolysis may be readily determined within the skill of the art, based on the disclosure herein, to achieve the desired pyrolysis reaction product.

[0058] In like manner, optional activation of the pitch-based carbon pyrolyzate may be carried out at appropriate conditions involving exposure to oxidizing conditions, e.g., in an ambient of carbon monoxide, carbon dioxide, oxygen, steam, or other ambient, at appropriate temperature and pressure conditions to effectuate the activation of the pyrolysis reaction product.

[0059] The pyrolysis and optional activation may be conducted to provide porosity of the pitch-derived carbon pyrolyzate material of character appropriate to the end use application for

which the carbon pyrolyzate material is intended. For example, the pyrolysis and optional activation may be conducted to provide a pitch-derived carbon pyrolyzate material having a majority ($> 50\%$) of its pore volume constituted by pores having a pore size in a range of from 0.5 to 10 nm. In other embodiments, the pyrolysis and optional activation may be conducted to provide a pitch-derived carbon pyrolyzate material having a nitrogen Dubinin-Radushkevich micropore volume measured at 77° Kelvin, which is in a range of from 0.55 cc per gram of carbon material to 1 cc per gram of carbon material, and at least 94% of which is constituted by pores larger than 0.6 nm, as determined by Gurvich-based neopentane capacity at neopentane pressure of 450 mmHg, neopentane liquid density of 0.613 g/mL, neopentane kinetic diameter of 0.62 nm, and temperature of 273° Kelvin. Other embodiments may provide pitch-derived carbon pyrolyzate materials of other pore size and pore size distribution characteristics, as appropriate to the end use application for which the carbon pyrolyzate material is intended.

[0060] In various embodiments, the pitch-derived carbon pyrolyzate material may be constituted by appropriate selection of the pitch and any co-pyrolyzable component(s) so that the carbon pyrolyzate material has an iron content as determined by PIXE spectrometry, of less than 10 ppm by weight, based on weight of the carbon pyrolyzate material. In other embodiments, the pitch-derived carbon pyrolyzate material may be constituted by appropriate selection of the pitch and any co-pyrolyzable component(s) so that the carbon pyrolyzate material contains less than 50 ppm by weight of halogen (chlorine, fluorine, bromine, or iodine), based on total weight of the carbon pyrolyzate material, e.g., less than 40 ppm, 35 ppm, 30 ppm, 25 ppm, 20 ppm, 15 ppm, 10 ppm, 5 ppm, 1 ppm, 0.5 ppm, or 0.1 ppm, on the same total weight basis, as appropriate to the end use application for which the carbon pyrolyzate material is intended. For example, it may be desirable to minimize the presence of halo components such as chlorine or fluorine in specific applications, in connection with avoidance of corrosion issues, ionic transport issues, and other issues that may be associated with presence of such components.

[0061] The foregoing parts per million values in specific embodiments may relate to concentrations of chlorine alone, or fluorine alone, or may represent combined concentrations of chlorine and fluorine, where both of such halo constituents are present. In applications in which the co-pyrolyzable component(s) that are pyrolyzed with pitch comprise chlorine-containing precursors, such as polyvinyl chloride, polyvinylidene chloride, copolymers of vinylidene chloride and vinyl chloride, polyvinylidene chloride copolymers including a monomer selected from the group consisting of methyl acrylate (MA), vinyl chloride (VC), acrylonitrile (AN), and isobutylene (IB), etc., it may be desirable to process the pyrolyzable composition at an appropriate temperature, pressure, and ambient composition to cause chlorine to be liberated

during the pyrolysis, as hydrogen chloride vapor, chlorine gas, or other gaseous compounds of chlorine that may be produced during the pyrolysis operation.

[0062] More generally, the pitch-derived carbon pyrolyzate material may be of any suitable form, and may for example be of particulate, granular, powder, or other divided form, or of monolithic, or other form, with any suitable confirmation and dimensional character. For example, the pitch-derived carbon pyrolyzate material may be in a form of particles having a median diameter particle size in a range of from 2 to 10 μm , or from 4 to 7 μm , or in other suitable range appropriate to the end use of the material.

[0063] Pitch-derived carbon pyrolyzate materials of the present disclosure may be utilized in any suitable applications. In specific embodiments, the pitch-derived carbon pyrolyzate material may be employed to form an EDLC electrode, e.g., for fuel-cell or other electrochemical energy supply application. In other embodiments, the pitch-derived carbon pyrolyzate material may be employed as a physical adsorbent material in a gas storage and dispensing vessel, in which the pitch-derived carbon pyrolyzate material is disposed for storage and dispensing of gas or gases having sorptive affinity to the carbon pyrolyzate material, wherein such gas(es) are readily reversibly adsorbed on, and subsequently desorbed from, the carbon pyrolyzate material under appropriate respective adsorption and desorption conditions. Gas storage and dispensing apparatus of such type is shown and described in Tom, et al. U.S. Patent No. 5,518,528, the disclosure of which is hereby incorporated herein by reference, in its entirety. In still other embodiments, the pitch-derived carbon pyrolyzate material may be employed as a carrier or support for catalyst or other supported agent(s) or material(s). In yet other embodiments, the pitch-derived carbon pyrolyzate material may be employed as a substrate material that is impregnated, e.g., with tungsten carbide or other suitable and pregnant material, to provide resultant ballistic materials for varying applications.

[0064] In various embodiments in which carbon pyrolyzate material is required to have electrical conductivity and electrical capacitance characteristics, pitch may be used with other pyrolyzable materials to avoid the need for use of carbon black or other conductivity enhancement materials in the pyrolyzable composition. For example, carbon black is utilized to increase electrical conductivity in pyrolyzate materials due to its conductive character, but it has no significant electrical capacitance. Pitch, however, produces a pyrolyzate that has both electrical conductivity and electrical capacitance characteristics, in addition to handling and processing advantages of pitch in relation to carbon black powder. Pitch may therefore be utilized in pyrolyzable compositions comprising pitch and co-pyrolyzable component(s) to impart advantageous electrical properties to the resultant pyrolyzate. In various embodiments, such

pyrolyzable composition of pitch and co-pyrolyzable component(s) may comprise from 0.1% to 10% pitch, based on total weight of the pyrolyzable composition. In other embodiments, such pyrolyzable composition of pitch and co-pyrolyzable component(s) may comprise from 0.1% to 5% pitch, based on total weight of the pyrolyzable composition.

[0065] As indicated earlier herein, the co-pyrolyzable component(s) of the pyrolyzable composition used to prepare carbon pyrolyzate materials of the present disclosure may be of any suitable type, and may for example comprise: one or more of polyacrylonitrile, polyfurfuryl alcohol, polyvinylbutyral, polyvinylchloride, polyvinylidene fluoride, polyvinylidene chloride, polyvinylidene chloride copolymer (with any suitable comonomer, e.g., methyl acrylate (MA), vinyl chloride (VC), acrylonitrile (AN), or isobutylene (IB), etc.), polyvinylidene fluoride, polyvinylidene fluoride copolymer (with any suitable comonomer, e.g., methyl acrylate (MA), vinyl chloride (VC), acrylonitrile (AN), or isobutylene (IB), etc.), or other synthetic resins; one or more of natural source materials such as coal, coconut shells, peach pits, cellulosic materials, etc.; pyrolyzable carbon cryogel materials of a type as described for example in Feaver et al. U.S. Patents 8,404,384 and 9,112,230; blends, mixtures, and compositions of any two or more of the foregoing pyrolyzable materials.

[0066] Carbon pyrolyzate materials of the present disclosure may comprise pitch-derived carbon pyrolyzate materials as variously described herein, in mixtures, blends, and combinations of different materials. Such mixtures, blends, and combinations may include pitch-derived carbon pyrolyzate material(s) with other materials, which may include pyrolyzates, and/or non-pyrolyzed material, e.g., binders, sealants, optically energizable materials (such as fluorescent, phosphorescent, and other emissive materials), impregnating materials, sensor or indicator materials, or any other materials whose presence in the mixture, blend, or combination is non-deleterious thereto.

[0067] In various embodiments, mixtures may be utilized in which pyrolyzed carbon and pitch are mixed with one another, e.g., with the pyrolyzed carbon being in the form of particles or granules, and with the mixture being utilized as a coating that may then be pyrolyzed to encapsulate a substrate or interior body, such as an interior electrode member, within the resultant pitch-derived carbon pyrolyzate material.

[0068] Pitch-derived carbon pyrolyzate material may be activated to increase the surface area for higher performance, in various embodiments. For example, a pitch-based carbon was activated in carbon dioxide at 900°C for 15 hours, jet milled, and characterized as exhibiting 26.3% burn off, a BET nitrogen surface area of 1523 m² per gram of the activated pyrolyzate material. The material contained 359 ppm total contaminants, and had an ash value of 0.15%. The

PIXE composition of such activated pitch-based carbon material is set out in Table 1 below, wherein “Det. Limit 95% Conf.” refers to the detection limit of the PIXE apparatus, as specified with respect to a 95% confidence interval.

[0069] Table 1 CO₂-Activated Pitch Pyrolyzate

Element Name	Energy (keV)	Det. Limit 95% Conf.	Concentration Mass	Error
* C -----			99.964%	
Na	1.041	50.720 ppm		
Mg	1.254	19.470 ppm		
Al	1.485	11.300 ppm		
Silicon	1.740	10.410 ppm	41.912 ppm	5.771 ppm
P	2.014	4.921 ppm		
Sulphur	2.308	6.241 ppm	122.705 ppm	4.282 ppm
Cl	2.623	3.443 ppm		
K	3.314	2.102 ppm		
Calcium	3.692	2.639 ppm	10.380 ppm	1.959 ppm
Sc	4.091	1.918 ppm		
Ti	4.511	2.052 ppm		
V	4.952	1.558 ppm		
Chromium	5.415	0.702 ppm	30.681 ppm	1.862 ppm
Mn	5.899	1.601 ppm		
Iron	6.405	1.154 ppm	136.406 ppm	2.578 ppm
Co	6.930	1.116 ppm		
Nickel	7.478	0.566 ppm	17.041 ppm	0.769 ppm
Cu	8.048	0.467 ppm		
Zn	8.639	0.420 ppm		
Ga	9.250	0.399 ppm		
Ge	9.887	0.358 ppm		
As	10.544	0.623 ppm		
Se	11.222	0.657 ppm		
Br	11.924	0.816 ppm		
Rb	13.395	1.094 ppm		
Sr	14.165	1.575 ppm		
Y	14.959	1.827 ppm		
Zr	15.775	2.186 ppm		
Nb	16.615	3.434 ppm		
Mo	17.480	2.915 ppm		
Tc	18.367	5.925 ppm		
Ru	19.279	5.211 ppm		
Rh	2.697	6.414 ppm		
Pd	2.839	5.852 ppm		
Ag	2.984	5.221 ppm		
Cd	3.133	5.341 ppm		
In	3.286	5.768 ppm		
Sn	3.444	4.688 ppm		
Sb	3.604	6.422 ppm		
Te	3.768	6.977 ppm		
I	3.937	5.645 ppm		
Cs	4.288	3.849 ppm		

Ba	4.466	5.392 ppm
La	4.648	6.332 ppm
Ce	4.841	4.212 ppm
Pr	5.034	2.847 ppm
Nd	5.230	4.544 ppm
Pm	5.431	10.580 ppm
Sm	5.632	2.625 ppm
Eu	5.841	3.547 ppm
Gd	6.050	2.685 ppm
Tb	6.271	6.977 ppm
Dy	6.492	9.659 ppm
Ho	6.725	1.058 ppm
Er	6.945	3.676 ppm
Tm	7.182	2.678 ppm
Yb	7.416	4.183 ppm
Lu	7.655	1.325 ppm
Hf	7.899	1.118 ppm
Ta	8.149	1.797 ppm
W	8.398	1.430 ppm
Re	8.652	1.286 ppm
Os	8.911	1.012 ppm
Ir	9.174	0.839 ppm
Pt	9.443	1.130 ppm
Au	9.712	1.132 ppm
Hg	9.989	1.077 ppm
Tl	10.267	1.191 ppm
Pb	10.551	1.555 ppm
Bi	10.838	1.390 ppm
Th	12.968	2.843 ppm
U	13.616	3.761 ppm

[0070] Another pitch-derived carbon pyrolyzate material, but without activation, was jet milled, and characterized as having a BET nitrogen surface area of ~1300 m² per gram of pyrolyzate material. Such material contained 193 ppm by weight, based on total weight of the carbon pyrolyzate material, of impurities, including 27 ppm of iron. The PIXE composition of such non-activated pitch-based carbon material is set out in Table 2 below.

[0071] Table 2 Non-Activated Pitch Pyrolyzate

Element Name	Energy (keV)	Det. Limit 95% Conf.	Concentration Mass	Error
* C -----			99.981%	
Na	1.041	76.040 ppm		
Mg	1.254	19.310 ppm		
Al	1.485	10.700 ppm		
Silicon	1.740	9.966 ppm	32.854 ppm	5.444 ppm
P	2.014	4.486 ppm		
Sulphur	2.308	5.534 ppm	120.013 ppm	3.804 ppm
Cl	2.623	2.948 ppm		

K	3.314	1.960 ppm		
Calcium	3.692	1.663 ppm	10.381 ppm	1.570 ppm
Sc	4.091	1.675 ppm		
Ti	4.511	1.090 ppm		
V	4.952	1.103 ppm		
Cr	5.415	0.846 ppm		
Mn	5.899	0.627 ppm		
Iron	6.405	0.373 ppm	27.243 ppm	1.120 ppm
Co	6.930	0.517 ppm		
Nickel	7.478	0.430 ppm	1.826 ppm	0.331 ppm
Cu	8.048	0.374 ppm		
Zn	8.639	0.382 ppm		
Ga	9.250	0.313 ppm		
Ge	9.887	0.263 ppm		
As	10.544	0.308 ppm		
Se	11.222	0.305 ppm		
Br	11.924	0.817 ppm		
Rb	13.395	0.945 ppm		
Sr	14.165	1.399 ppm		
Y	14.959	1.606 ppm		
Zr	15.775	1.208 ppm		
Nb	16.615	2.306 ppm		
Mo	17.480	3.216 ppm		
Tc	18.367	4.067 ppm		
Ru	19.279	3.556 ppm		
Rh	20.216	5.487 ppm		
Pd	21.176	4.285 ppm		
Ag	2.984	6.360 ppm		
Cd	3.133	4.418 ppm		
In	3.286	5.140 ppm		
Sn	3.444	3.929 ppm		
Sb	3.604	5.189 ppm		
Te	3.768	4.867 ppm		
I	3.937	2.748 ppm		
Cs	4.288	3.637 ppm		
Ba	4.466	3.652 ppm		
La	4.648	4.164 ppm		
Ce	4.841	3.611 ppm		
Pr	5.034	1.631 ppm		
Nd	5.230	2.843 ppm		
Pm	5.431	2.309 ppm		
Sm	5.632	1.360 ppm		
Eu	5.841	2.113 ppm		
Gd	6.050	1.333 ppm		
Tb	6.271	2.990 ppm		
Dy	6.492	3.997 ppm		
Ho	6.725	0.779 ppm		
Er	6.945	1.717 ppm		
Tm	7.182	1.393 ppm		
Yb	7.416	1.619 ppm		
Lu	7.655	0.923 ppm		

Hf	7.899	0.801 ppm
Ta	8.149	0.753 ppm
W	8.398	0.816 ppm
Re	8.652	1.172 ppm
Os	8.911	0.972 ppm
Ir	9.174	0.912 ppm
Pt	9.443	0.581 ppm
Au	9.712	0.928 ppm
Hg	9.989	0.651 ppm
Tl	10.267	0.665 ppm
Pb	10.551	0.764 ppm
Bi	10.838	1.166 ppm
Th	12.968	2.231 ppm
U	13.616	2.406 ppm

[0072] In specific embodiments, the pitch-derived carbon pyrolyzate materials of the present disclosure, as variously described herein, may be utilized in fabrication of electrochemical double layer capacitor (EDLC) electrodes and other devices and products, and may comprise pyrolyzates of any of the pyrolyzable compositions variously described herein. The EDLC electrodes, devices comprising same, and other devices and products described herein, may be characterized by any of the same ranges and parametric characteristics as variously specified herein for corresponding EDLC electrodes and devices, and other devices and products, comprising the non-pitch-based carbon pyrolyzate materials described herein.

[0073] While the disclosure has been set forth herein in reference to specific aspects, features and illustrative embodiments, it will be appreciated that the utility of the disclosure is not thus limited, but rather extends to and encompasses numerous other variations, modifications and alternative embodiments, as will suggest themselves to those of ordinary skill in the field of the present disclosure, based on the description herein. Correspondingly, the disclosure as hereinafter claimed is intended to be broadly construed and interpreted, as including all such variations, modifications and alternative embodiments, within its spirit and scope.

THE CLAIMS

What is claimed is:

1. A carbon pyrolyzate material comprised at least partially of pyrolyzed pitch, wherein the carbon pyrolyzate material has: a nitrogen Brunauer-Emmett-Teller (N₂ BET) surface area measured at 77° Kelvin, which is in a range of from 1450 m² per gram of carbon material to 3000 m² per gram of carbon pyrolyzate material; ash content as determined by ASTM 2866-94 of less than 0.15% by weight, based on weight of the carbon pyrolyzate material; and metals content as determined by particle-induced x-ray emission (PIXE) spectrometry, of less than 500 ppm by weight, based on weight of the carbon pyrolyzate material.
2. The carbon pyrolyzate material of claim 1, having an iron content as determined by PIXE spectrometry, of less than 10 ppm by weight, based on weight of the carbon pyrolyzate material.
3. The carbon pyrolyzate material of claim 1, wherein the concentration of said pyrolyzed pitch is 100% by weight, based on weight of the carbon pyrolyzate material.
4. The carbon pyrolyzate material of claim 1, comprising pyrolyzed pitch and pyrolyzate of pyrolyzable material selected from the group consisting of: one or more of polyacrylonitrile, polyfurfuryl alcohol, polyvinylbutyral, polyvinylchloride, polyvinylidene fluoride, polyvinylidene chloride, polyvinylidene chloride copolymer, polyvinylidene fluoride, and polyvinylidene fluoride copolymer; one or more of natural source materials selected from the group consisting of coal, coconut shells, peach pits, and cellulosic materials; pyrolyzable carbon cryogel materials; and blends, mixtures, and compositions of any two or more of the foregoing pyrolyzable materials.
5. The carbon pyrolyzate material of claim 1, comprising a pyrolyzate of:
 - (i) pitch, polyacrylonitrile, and cellulosic material;
 - (ii) pitch and pyrolyzable carbon cryogel material; or
 - (iii) pitch, polyvinylidene chloride copolymer, and cellulosic material.

6. The carbon pyrolyzate material of claim 1, comprising a pyrolyzate of pitch and polyvinylidene chloride.

7. The carbon pyrolyzate material of claim 1, comprising a pyrolyzate of pitch and polyvinylidene chloride-methyl acrylate copolymer.

8. The carbon pyrolyzate material of claim 1, comprising a pyrolyzate of a pyrolyzable composition comprising pitch and other pyrolyzable material, wherein the amount of pitch in the pyrolyzable composition is in a range of from 2% to 99%, 5% to 95%, 10% to 90%, 20% to 85%, 25% to 80%, 30% to 75%, 35% to 70%, 40% to 65%, or 45% to 60%, based on total weight of the pyrolyzable composition.

9. The carbon pyrolyzate material of claim 1, comprising a pyrolyzate of a pyrolyzable composition comprising pitch and other pyrolyzable material, wherein the amount of pitch in the pyrolyzable composition is in a range whose lower value is selected from any of 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5%, 5%, 7%, 8%, 10%, 12%, 15%, 18%, 20%, 22%, 25%, 28%, 30%, 35%, 40%, 50%, 60%, 70%, 80%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, and 99%, and whose upper value is greater than the lower value of the range and is selected from any of 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5%, 5%, 7%, 8%, 10%, 12%, 15%, 18%, 20%, 22%, 25%, 28%, 30%, 35%, 40%, 50%, 60%, 70%, 80%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.8%, 99.9%, 99.95%, and 99.99%.

10. The carbon pyrolyzate material of claim 4, wherein the polyvinylidene chloride copolymer or polyvinylidene fluoride copolymer is a copolymer of a comonomer selected from the group consisting of methyl acrylate (MA), vinyl chloride (VC), acrylonitrile (AN), and isobutylene (IB).

11. The carbon pyrolyzate material of claim 1, comprising porosity in which a majority of pore volume of the carbon pyrolyzate material is constituted by pores having a pore size in a range of from 0.5 to 10 nm.

12. The carbon pyrolyzate material of claim 1, having a nitrogen Dubinin-Radushkevich micropore volume measured at 77° Kelvin, which is in a range of from 0.55 cc per gram of carbon material to 1 cc per gram of carbon material, and at least 94% of which is constituted by

pores larger than 0.6 nm, as determined by Gurvich-based neopentane capacity at neopentane pressure of 450 mmHg, neopentane liquid density of 0.613 g/mL, neopentane kinetic diameter of 0.62 nm, and temperature of 273° Kelvin.

13. The carbon pyrolyzate material of claim 1, containing less than 50 ppm by weight of halogen, based on total weight of the carbon pyrolyzate material.

14. The carbon pyrolyzate material of claim 4, containing less than 50 ppm by weight of halogen, based on total weight of the carbon pyrolyzate material.

15. The carbon pyrolyzate material of claim 1, containing halogen below at least one of 40 ppm, 35 ppm, 30 ppm, 25 ppm, 20 ppm, 15 ppm, 10 ppm, 5 ppm, 1 ppm, 0.5 ppm, and 0.1 ppm, based on total weight of the carbon pyrolyzate material.

16. The carbon pyrolyzate material of claim 1, in a form selected from the group consisting of particulate, granular, powder, and monolithic forms.

17. The carbon pyrolyzate material of claim 1, in a particulate form having a median diameter particle size in a range of from 2 to 10 μm .

18. The carbon pyrolyzate material of claim 1, in a particulate form having a median diameter particle size in a range of from 4 to 7 μm .

19. An EDLC electrode comprising the carbon pyrolyzate material of claim 1.

20. A gas storage and dispensing apparatus, comprising the carbon pyrolyzate material of claim 1, in a gas storage and dispensing vessel.

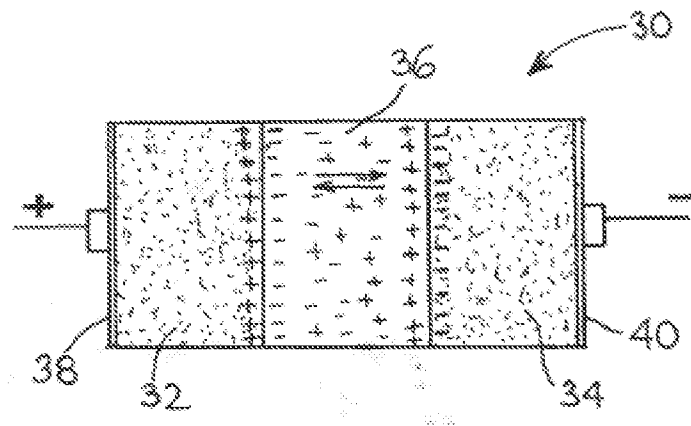


FIG. 1

A. CLASSIFICATION OF SUBJECT MATTER**C01B 31/02(2006.01)i, H01G 11/34(2013.01)i, B01J 20/20(2006.01)i**

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)

C01B 31/02; B01J 21/18; B01J 37/02; H01G 11/34; B01J 20/20

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: carbon, pyrolyzate, pitch, polyacrylonitrile (PAN), cellulosic material, polyvinylidene chloride (PVDC), copolymer, porosity, surface area, pore size, pore volume, electric double layer capacitor (EDLC)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HUANG, CHENG-WEI et al., "Electric double layer capacitors based on a composite electrode of activated mesophase pitch and carbon nanotubes," Journal of materials Chemistry, 2012, vol. 22, no. 15, pages 7314-7322 See page 7315, left column, lines 1-4; page 7315, left column, line 13-right column, line 11; page 7316, right column, lines 5-7 and 17-19; page 7319, left column, lines 16-17; figures 2, 4; and table 1.	1-3, 11-13, 15-20
Y		4-10, 14
Y	DZIURA, ALEKSANDRA et al., "Saran-derived carbons for CO ₂ and benzene sorption at ambient conditions," Industrial & Engineering Chemistry Research, 2014, vol. 53, no. 40, pages 15383-15388 See abstract; page 15384, left column, lines 27 and 28; and page 15384, left column, line 39-right column, line 11.	4, 7-10, 14
Y	GU, WENTIAN et al., "Review of nanostructured carbon materials for electrochemical capacitor applications: advantages and limitations of activated carbon, carbide-derived carbon, zeolite-templated carbon, carbon aerogels, carbon nanotubes, onion-like carbon, and graphene," WIREs Energy and Environment, 2014, vol. 3, no. 5, pages 424-473 See page 428, right column, lines 20-52; and table 1.	5, 6

☒ 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

"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

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18 July 2016 (18.07.2016)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/027032

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KIM, Y.J. et al., "Correlation between the pore and solvated ion size on capacitance uptake of PVDC-based carbons," Carbon, 2004, vol. 42, nos. 8-9, pages 1491-1500 See abstract; page 1492, left column, line 15-right column, line 18; and figures 6-8.	1-20
A	SIMON, PATRICE et al., "Materials for electrochemical capacitors," Nature Materials, 2008, vol. 7, no. 11, pages 845-854 See abstract; and page 847, left column, lines 2-9.	1-20
A	US 2008-0254972 A1 (ISTVAN, RUDYARD LYLE et al.) 16 October 2008 See abstract; and claims 1-78.	1-20

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International application No.

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datePatent family
member(s)Publication
date

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