

Description

Title of Invention: Method And Apparatus For Producing Laser-Activated Carbon

Technical Field

- 5 The present invention relates broadly, but not exclusively, to laser-activated carbon methods, and apparatuses for producing laser-activated carbon.

Background

Carbon-based materials are essential in energy storage devices due to their unique physical and chemical properties. For example, carbon blacks (CBs) are
10 commonly employed as conductive additives in electrode formulations to enhance the performance of energy storage devices by improving electrical and thermal conductivities. Other carbon nanomaterials, such as graphene, are used as both conductive additives and active material hosts on Li-S batteries.

Graphite, is the predominant carbon material used in Li-ion batteries as the anode
15 active material, due to its cycling stability, high purity, high crystallinity, low defect levels, high electrical conductivity, and thermal stability. However, graphite's theoretical Li storage capacity is limited to around 372 mAh g⁻¹.

Soft and hard carbon are two distinct forms of carbon used in "non-graphitic anodes". The theoretical capacity of soft carbon (SC) ranges between 200 mAh g⁻¹
20 and 300 mAh g⁻¹ depending on its structure and quality. As the anode in supercapacitors, it provides specific capacitance between 100 F g⁻¹ and 200 F g⁻¹, high rate capability, long cycle life, and improved safety.

Hard carbon (HC) has double the theoretical capacity of graphite (744 mAh g⁻¹) in
25 Li-ion batteries. HC can efficiently accommodate larger ions due to its disordered amorphous structure, resulting in better capacity, cycle life, and overall performance than graphite in Na-ion and K-ion batteries. Composite anodes comprising mixtures of hard and soft carbon are also being explored to combine the advantageous properties of both materials.

Recovered carbon black (rCB), or pyrolysis carbon black (CBp), is a sustainable
30 and environmentally friendly material that can be used as a conductive additive in battery electrodes. Due to its structural properties and the process by which it is produced, rCB is considered a hard carbon material and has the potential to be

applied as a battery-active material, accelerating the high-value utilisation of this solid waste.

Several challenges remain in developing hard and soft carbon materials for battery technologies. High-temperature treatments for the graphitisation or activation and the control of structural properties can be costly and unsustainable. Balancing the structure and properties for battery applications requires further development.

Nevertheless, there is a continuous demand for carbon materials with enhanced properties to meet the increasing requirements of advanced energy storage devices. In particular, cost-effective and scalable production methods, that are sustainable and environmentally friendly activation processes are needed.

A need therefore exists to provide a method and apparatus for producing activated carbon having the required properties.

Summary of Invention

In one aspect, the present invention comprises a method of producing laser-activated carbon, the method comprising: providing a carbon-based material, exposing the carbon-based material to laser radiation such that the laser radiation excites electrons in the carbon-based material, the excited electrons inducing localised thermal activation reactions, wherein the thermal activation reactions cause structural and/or compositional changes in the carbon-based material to produce laser-activated carbon.

Preferably, the carbon-based material comprises: hard carbons, soft carbons, and/or a mixture of hard carbons and soft carbons.

Preferably, the structural and/or compositional changes is/are at least one of increased surface area, increased interlayer distances, increased porosity, increased graphitic carbon content, and/or enhanced surface defects.

Preferably, the carbon-based material is carbon-based powder, carbon-based liquid suspension, or carbon-based dry-coated electrode.

Preferably, the laser radiation comprises a wavelength of about 248 nm to about 660 nm.

Preferably, the laser radiation is provided at a power output of about 1 mW to about 3 W

Preferably, the laser radiation is a continuous-wave or a pulsed laser.

Preferably, laser beams comprising of the laser radiation, have a scanning speed of about $100 \mu\text{m s}^{-1}$ to about 120 mm s^{-1}

5 Preferably, the laser beams comprising of the laser radiation, have a beam size of about $1 \mu\text{m}$ to about 1 cm .

Preferably, the method is integrable in a fluidised bed reactor, a circulating fluidised bed reactor, a rotating drum reactor, a batch reactor, and/or a Downer reactor.

10 In another aspect, the present invention comprises an apparatus for producing laser activated carbon material, comprising: at least one laser source configured to emit laser radiation, a module configured to support a carbon-based material in the path of the laser radiation, such that the laser radiation excites electrons in the carbon-based material, the excited electrons inducing localised thermal activation reactions, and wherein the thermal activation reactions cause structural and/or compositional changes in the carbon-based material to produce a laser-activated
15 carbon.

Preferably, the laser radiation comprises a wavelength of about 248 nm to about 660 nm .

Preferably, the laser radiation is provided at a power output of about 1 mW to about 3 W

20 Preferably, the laser radiation is a continuous-wave or a pulsed laser.

Preferably, the at least one laser source has a scanning speed of about $100 \mu\text{m s}^{-1}$ to about 120 mm s^{-1}

Preferably, the at least one laser source has a beam size of about $1 \mu\text{m}$ to about 1 cm .

25 Preferably, the apparatus further comprises a plurality of laser sources arranged in parallel and/or series.

Preferably, the module configured to support a stationary carbon-based material and/or receive the carbon-based material in the path of the laser radiation.

30 Preferably, the module comprises a fluidised bed reactor, a circulating fluidised bed reactor, a rotating drum reactor, a batch reactor, and/or a Downer reactor.

In another aspect, the present invention comprises a laser-activated carbon produced by the method disclosed herein.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

5 **Brief Description of the Drawings**

Embodiments of the invention will be better understood and readily apparent to one of ordinary skill in the art from the following written description, by way of example only, and in conjunction with the drawings, in which:

Fig. 1A is a block diagram of a method for producing laser-activated carbon.

10 Fig. 1B is a schematic diagram of an apparatus for producing laser-activated carbon.

Fig. 2A is an example embodiment of the apparatus in a laboratory.

Fig. 2B is another example embodiment of the apparatus in a laboratory.

Fig. 3 is another example embodiment of the apparatus as a modified reactor.

Fig. 4 is another example embodiment of the apparatus in a battery production line.

15 Fig. 5 shows the x-ray photoelectron spectroscopy (XPS) spectrum of the original hard carbon (Fig. 5a) and the laser-activated carbon (Fig. 5b).

Fig. 6 shows the high-resolution transmission electron microscopy (HRTEM) image of the laser-activated carbon (Fig. 6a) and the original hard carbon (Fig. 6b).

20 Fig. 7 shows x-ray diffraction (XRD) pattern of original hard carbon and laser-activated hard carbon.

Fig. 8 shows the cycling performance at 0.1 and 2 A g⁻¹ of original hard carbon and laser-activated hard carbon.

Fig. 9 shows the cycling performance at 1 A g⁻¹ of original high-purity hard carbon and laser-activated high-purity hard carbon.

25 Fig. 10 shows fluorescence microscope images of the original recovered carbon black, laser-activated recovered carbon black, the original hard carbon, and laser-activated hard carbon under bright field (BF) and ultraviolet (UV).

Detailed Description

It will be appreciated that the method and embodiments described herein may be implemented in, or applied to, an apparatus configured to perform one or more of the steps disclosed. Such an apparatus may include one or more components, modules, or systems operable to execute the method, either in whole or in part, and may be embodied in hardware, software, or a combination thereof.

Certain terminology may be used in the following description for the purpose of reference only, and thus are not intended to be limiting.

Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of claimed subject matter. Thus, the appearances of the phrase "in one embodiment" or "an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in one or more embodiments.

Two or more steps may be performed concurrently or with partial concurrence. Further, the steps of the method may be performed in an order different from what has been disclosed. Such variation will depend on the process hardware systems chosen and on designer choice. All such variations are within the scope of the disclosure. Additionally, even though the disclosure has been described with reference to specific exemplifying embodiments thereof, many different alterations, modifications and the like will become apparent for those skilled in the art.

For purposes of clarity, the same or similar reference numbers will be used in the drawings to identify similar elements. However, for the sake of convenience, certain features present or annotated with reference numerals in some figures of the present disclosure are not shown or annotated with reference numerals in other figures of the present disclosure. Unless the context clearly requires otherwise, these omissions should not be interpreted to mean that features omitted from the drawings of one figure could not be equally incorporated or implemented in the configurations of the disclosed methods, apparatus and systems related to or embodied in other figures. Conversely, unless the context clearly requires otherwise, it should not be assumed that the presence of certain features in some figures of the present disclosure means that the disclosed methods, apparatus and systems related to or embodied in such figures must necessarily include these features.

The present invention provides a method for producing laser-activated carbon. The laser-activated carbon may be used in energy storage devices. With reference to Fig. 1A, the method comprises providing 10 a carbon-based material. The method further comprises exposing 20 the carbon-based material to laser radiation such that the laser radiation excites electrons in the carbon-based material. The excited electrons induce localised thermal activation reactions. The localised thermal activation reactions are induced on the carbon-based material. The energy from the laser interacts with the carbon-based material, exciting electrons and creating molecular motions that dissipate as heat. The localised temperature may reach up to 2500 K in less than 0.1 s. The thermal activation reactions cause structural and/or compositional changes in the carbon-based material. The structural and/or compositional changes may be at a structural level rather than a morphology level of the carbon-based material surface.

In an embodiment, the carbon-based material may comprise hard carbons, soft carbons, and/or a mixture of hard carbons and soft carbons. The hard carbons may be amorphous and contain a disordered microstructure. The hard carbons may have a turbostratic layer arrangement. The hard carbons may have numerous pores and defects in its structure. The mixture of hard carbons and soft carbons may include recovered carbons (e.g. recovered carbon blacks), carbon nano-objects, carbon fibre and nanofiber, activated carbon, and carbon blacks.

In an embodiment, the structural and/or compositional changes may be at least one of the following: increased surface area, increased porosity, increased interlayer distances, increased graphitic carbon content, increased porosity, and enhanced surface defects. The method optimises the material for use in energy storage devices. The structural and/or compositional changes may serve as ion active sites, for example for alkali ions, Li^+ , Na^+ , or K^+ . The enhanced surface defects may be controlled. Examples of enhanced surface defects may be carbon vacancies, and/or hydrogen heteroatoms. The structural and/or compositional changes may improve adsorption of ions, particularly alkali metal ions, resulting in lower ionic diffusion impedance and/or higher specific capacity performance than non-activated carbon. The method does not require organic solvents, or generate significant waste, reducing the processing cost.

In an embodiment, the carbon-based material may be in powder form, liquid suspension form, or dry-coated electrode.

In an embodiment, the laser radiation may have a wavelength of about 248 nm to about 660 nm. Preferably, the laser radiation may have a wavelength of about 248 nm,

450 nm, 532 nm, and/or 660 nm. In an embodiment, the laser radiation may be provided at a power output of about 1 mW to about 3 W. In an embodiment, the laser radiation may have a power density output of about $45 \text{ mW } \mu\text{m}^{-2}$. The laser radiation may be a continuous-wave or a pulsed laser. The wavelengths, power output and/or the speed of the laser radiation may be adjustable. The continuous-wave radiation may be provided by at least one laser source having multiple wavelengths. The pulsed laser radiation may be provided by at least one laser source, for example an Excimer Laser.

In an embodiment, laser beams comprising the laser radiation, may have a scanning speed of about $100 \text{ } \mu\text{m s}^{-1}$ to about 120 mm s^{-1} . Preferably, the laser beam may have a scanning speed of about $200 \text{ } \mu\text{m}^{-2}$. In an embodiment, the laser beam may have a beam size of about $1 \text{ } \mu\text{m}$ to about 1 cm. Preferably, the beam size may be about 1 cm by about 3 cm.

In an embodiment, the method may be integrable in a fluidised bed reactor, a circulating fluidised bed reactor, a rotating drum reactor, a batch reactor, and/or a Downer reactor. The method is versatile and adaptable, suitable for integration into existing processes, production lines, and/or reactor types.

Fig. 1B shows an apparatus 50 for producing laser activated carbon material. The apparatus 50 comprises at least one laser source 51 configured to emit laser radiation 52. The apparatus 50 further comprises a module 55 configured to support a carbon-based material 56 in the path of the laser radiation 52, such that the laser radiation 52 excites electrons in the carbon-based material 56, the excited electrons induce localised thermal activation reactions. The module 55 may comprise of a material that is non-reactive to the carbon-based material 56 and/or the laser radiation 52. The thermal activation reactions cause structural and/or compositional changes in the carbon-based material 106 to produce a laser-activated carbon.

In an embodiment, the laser radiation 52 comprises a wavelength of about 248 nm to about 660 nm. Preferably, the laser radiation 52 may have a wavelength of about 248 nm, 450 nm, 532 nm, and/or 660 nm. In an embodiment, the laser radiation 52 is provided at a power output of about 1 mW to about 3 W. In an embodiment, the laser radiation 52 may have a power density output of about $45 \text{ mW } \mu\text{m}^{-2}$. The wavelengths, power output and/or the speed of the at least one laser source 51 may be adjustable.

In an embodiment, the at least one laser source 51 has a scanning speed of about $100 \mu\text{m s}^{-1}$ to about 120 mm s^{-1} . In an embodiment, the at least one laser source 51 has a beam size of about $1 \mu\text{m}$ to about 1 cm . In an embodiment, the at one laser source 51 may be a continuous-wave laser source or a pulsed laser source. The at least one laser source 51 may have multiple wavelength options. The pulsed laser source may be an Excimer Laser, for example.

In an embodiment, the apparatus 50 comprises a plurality of laser sources 51 arranged in parallel and/or series. The arrangement of the at least one laser source 51 allows for coverage of the area of the carbon-based material 56 and the appropriate treatment time. The apparatus 50 may further comprise at least one beam expander configured to increase a diameter of the laser radiation 52.

Variations of the apparatus may be envisaged, for example, the module 55 may be a receptacle configured to support carbon-base material 56 in powder form. The carbon-based powder may be in liquid suspension form.

In an embodiment, the module 55 is configured to support a stationary carbon-based material 56 in the path of the laser radiation 52. Fig. 2A shows an example embodiment of the apparatus 100. The apparatus 100 may be a laboratory set-up. The module 105 may be a platform, for example. The module 105 may comprise at least one fastener configured to secure the carbon-based material 106. The at least one laser source 101 may be set up to directly irradiate the carbon-based material 106. In another embodiment, the apparatus 100 further comprises at least one mirror and/or a beam splitter configured to direct the laser radiation 102 at the carbon-based material 106.

Fig. 2B shows another example embodiment of the apparatus 200. The apparatus may be a laboratory set-up. In an embodiment, the apparatus 200 may comprise at least one beam expander configured to increase a diameter of the laser radiation 202. A beam expander may be used to increase the coverage area of the carbon-based material 206.

Fig. 3 shows an example embodiment of the apparatus 300. The apparatus 300 may be a modified reactor. The module 305 may be configured to receive the carbon-based material 306 into the path of the laser radiation 302. The module 305 may be a chamber configured to receive the carbon-based material 306 in powder form via a gas flow. The gas flow rate may control the speed of the carbon-based powder 306. At least one laser source 301 may be positioned to irradiate the carbon-based powder

306. The at least one laser source may comprise a plurality of laser sources 402 arranged in parallel and/or series. The apparatus may be configured to separate the laser-activated carbon 307 produced from the carbon-based material 306.

Fig. 4 shows another example embodiment of the apparatus 400. The apparatus 400
 5 may be in a battery production line. The module 405 may be configured to receive the carbon-based material 406 via a transport system, for example, a conveyor system. The carbon-based material 406 may be a dry carbon-based material, for example dry electrodes, coated over a current collector. The laser-activated carbon 407 may be densified by calendering. The at least one laser source may comprise a plurality of
 10 laser sources 402 arranged in parallel and/or series to ensure complete coverage of the electrode area and laser treatment time. The treatment time or scanning speed, may be controlled by adjusting the speed of the transport system.

In an embodiment, the module 55 comprises a: fluidised bed reactor, a circulating fluidised bed reactor, a rotating drum reactor, a batch reactor, and/or a Downer
 15 reactor.

The present invention further provides a laser-activated carbon material produced by the method/apparatus described herein. In an embodiment, to produce laser-activated hard carbon (LAHC) electrodes, laser radiation were applied directly to dry electrodes. The dry electrodes comprised of 63% HC, 7% conductive carbon, and 30% organic
 20 binder coated with a mass loading of 2.1 mg onto Cu or Al current collectors. Recovered carbon black (rCB) obtained from the pyrolysis of end-of-life tyres was used as HC active material. The laser radiation had a wavelength of about 532 nm, power density output of about $45 \text{ mW } \mu\text{m}^{-2}$, and scanning speed of about $200 \text{ } \mu\text{m s}^{-1}$. The experiment was undertaken at room temperature in air.

Referring to Fig. 5, the x-ray photoelectron spectroscopy (XPS) spectrum of the carbon region (C1s) indicates the structural and compositional changes generated by the laser radiation on the rCB material. Fig. 5a shows the original HC material presents strong peaks at about 284.5 eV and about 285.5 eV, corresponding to the $\text{sp}^2 \text{ C}=\text{C}$ bonds from the basal structure and $\text{C}-\text{O}$ functional terminal groups, respectively. In contrast,
 30 Fig. 5b shows the LAHC presents a larger number of defects characterised by the decrease of the $\text{sp}^2 \text{ C}=\text{C}$ peak and the rise of $\text{sp}^3 \text{ C}-\text{C}$ bonds at about 285.0 eV. Moreover, the peak at about 288.4 eV related to $\text{C}-\text{O}$ bonds decreased considerably.

Fig. 6 shows the high-resolution transmission electron microscopy (HRTEM) images of the LAHC (Fig. 6a) and the original HC (Fig. 6b). Fig. 6a shows regions of LAHC,

revealing the formation of graphitic clusters formed by the laser radiation compared with the original HC shown in Fig. 6B. The formation of graphitic clusters contribute to the improved crystallinity.

Fig. 7 shows the x-ray diffraction (XRD) of the LAHC has an improved crystallinity compared with the HC. The lattice spacing on the graphitic clusters of the LAHC was found to range from about 0.35 nm to about 0.37 nm, which is larger than the typical graphite value. In contrast, the original HC material shows a near-complete amorphous structure by HRTEM, in Fig. 6b, and XRD, in Fig. 7.

Fig. 8 shows the stability of the original HC and LAHC measured at 0.1 A g^{-1} for 100 cycles (Fig. 8a) and at 2 A g^{-1} for 400 cycles (Fig. 8b). The results show that both original HC and LAHC have a higher specific capacity than the theoretical capacity of graphite, which is 372 mAh g^{-1} . Additionally, LAHC showed a specific capacity of 516 mAh g^{-1} , which is 9% higher than the original HC, which has a specific capacity of 473 mAh g^{-1} . At a mass loading of about 1.5 mg cm^{-2} , both the original HC and LAHC showed a stable trend for 400 cycles, even at 2 A g^{-1} . At the 400th cycle, the LAHC exhibited a capacity of 101.8 mAh g^{-1} with about 68% capacity retention, which is higher than the 52.6 mAh g^{-1} capacity of the original HC, which retained less than 30% of its capacity.

In another embodiment, laser radiation was applied to activate carbon composite materials commonly used for making battery electrodes. To ensure the applicability of the laser-activated HC produced by the method as electrodes, a high-purity HC material was processed into an electrode in the same manner as rCB. The laser radiation had a wavelength of about 532 nm, power density output of about $45 \text{ mW } \mu\text{m}^{-2}$, scanning speed of about $200 \text{ } \mu\text{m s}^{-1}$, and the experiment was undertaken at room temperature in air. Fig. 9 shows at 1 A g^{-1} , the LAHC (Lasered) demonstrated better capacity performance than the original HC (Pristine), following a similar trend to the LAHC rCB of Fig. 8. This further confirmed the feasibility of the method disclosed herein.

Fig. 10 shows fluorescence microscope images which can distinguish the original HC from the laser-activated HC. Under UV excitation, the laser-activated carbon materials exhibit bright fluorescence emission due to the introduction of defects, whereas the original carbon-based materials show no fluorescence emission under UV exposure.

It will be appreciated, the method and apparatus disclosed herein may be applied in, but not limited to, the energy storage industry, battery industry, supercapacitor industry,

electrode fabrication industry, and battery active materials industry. For example, the method and apparatus disclosed may be used to produce laser-activated carbon anode active materials and/or electrodes for energy storage devices based on ions, for example Li^+ , Na^+ , K^+ , or a combination of the ions.

- 5 The method and apparatus disclosed is scalable and yields high outputs – it can produce large quantities of active material and/or electrodes. The method and apparatus disclosed does not require organic solvents or exotic technologies, nor does it generate significant waste. This reduces processing costs and aligns with the ecofriendly approaches increasingly demanded today.

Claims

1. A method of producing laser-activated carbon, the method comprising:
 - providing a carbon-based material,
 - exposing the carbon-based material to laser radiation such that the
 - 5 laser radiation excites electrons in the carbon-based material, the excited electrons inducing localised thermal activation reactions,
 - wherein the thermal activation reactions cause structural and/or compositional changes in the carbon-based material to produce laser-activated carbon.
- 10 2. The method according to claim 1, wherein the carbon-based material comprises: hard carbons, soft carbons, and/or a mixture of hard carbons and soft carbons.
3. The method according to claim 1 or 2, wherein the structural and/or compositional changes is/are at least one of increased surface area, increased
- 15 interlayer distances, increased porosity, increased graphitic carbon content, and/or enhanced surface defects.
4. The method according to any one of claims 1-3, wherein the carbon-based material is carbon-based powder, carbon-based liquid suspension, or carbon-based dry-coated electrode.
- 20 5. The method according to any one of claims 1-4, wherein the laser radiation comprises a wavelength of about 248 nm to about 660 nm, and/or wherein the laser radiation is provided at a power output of about 1 mW to about 3 W, and/or the laser radiation is a continuous-wave or a pulsed laser.
6. The method according to claim 5, wherein laser beams comprising of the laser
- 25 radiation, have a scanning speed of about $100 \mu\text{m s}^{-1}$ to about 120 mm s^{-1} and/or a beam size of about $1 \mu\text{m}$ to about 1 cm.
7. The method according to any one of claims 1-6, wherein the method is integrable in a fluidised bed reactor, a circulating fluidised bed reactor, a rotating drum reactor, a batch reactor, and/or a Downer reactor.
- 30 8. An apparatus for producing laser activated carbon material, comprising:

at least one laser source configured to emit laser radiation,

a module configured to support a carbon-based material in the path of the laser radiation, such that the laser radiation excites electrons in the carbon-based material, the excited electrons inducing localised thermal activation reactions, and

wherein the thermal activation reactions cause structural and/or compositional changes in the carbon-based material to produce a laser-activated carbon.

9. The apparatus according to claim 8, wherein the laser radiation comprises a wavelength of about 248 nm to about 660 nm, and/or wherein the laser radiation is provided at a power output of about 1 mW to about 3 W and/or the laser radiation is a continuous-wave or a pulsed laser.
10. The apparatus according to claim 8 or 9, wherein the at least one laser source has a scanning speed of about $100 \mu\text{m s}^{-1}$ to about 120 mm s^{-1} and/or a beam size of about $1 \mu\text{m}$ to about 1 cm.
11. The apparatus according to any one of claims 8-10, further comprising a plurality of laser sources arranged in parallel and/or series.
12. The apparatus according to any one of claims 8-11, wherein the module configured to support a stationary carbon-based material and/or receive the carbon-based material in the path of the laser radiation.
13. The apparatus according to any one of claims 8-12, wherein the module comprises a fluidised bed reactor, a circulating fluidised bed reactor, a rotating drum reactor, a batch reactor, and/or a Downer reactor.
14. A laser-activated carbon produced by the method according to any one of claims 1 to 7.