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DESCRIPTION WO2023282638A1

11 Graphene - based two - dimensional heterostructure supercapacitor and its manufacturing method

[0001]

16 Cross - reference to related applications

[0002]

20 This application claims the benefit of priority to Korean Patent Application No. 2021 -0089081, filed July 7, 2021, the contents of which are incorporated herein by reference in their entirety.

[0003]

26 The present disclosure relates to a method for preparing a siloxane - rGO heterocomposite comprising a two - dimensional electrically conductive siloxane sheet and a reduced graphene oxide sheet, a supercapacitor comprising the siloxane - rGO heterocomposite, and a method for preparing the same.

[0004]

- 33 High performance electrochemical energy storage systems (ESS), such as lithium ion batteries (LIBs) and supercapacitors (SCs), have attracted increasing attention from researchers in basic scientific research and industrial fields.
- ³⁶ The rapid charge/discharge rates, high power density (P), and long cycle life of supercapacitors make them suitable for a wide range of applications such as AC line

filtering, uninterruptible power supplies (UPS), and recovery of regenerative braking energy (RRBE) in electric vehicles (EVs).

- 40 This necessitates the development of SCs with high energy density and high power density (> 10 kW/kg).
- 44 It should have the properties to improve the energy density without reducing the power density of the supercapacitor, to reach the energy density level of lithium - ion batteries, and to have extreme temperature resistance.

[0005]

- 50 These characteristics are highly recommended for application as energy storage systems for electric vehicles.
- 52 A unique strategy to improve the energy density of supercapacitors is to use electrolytes with a wide operating voltage window (OVW) and high capacitance (C) electrodes (E=0.5 CV²). To widen the operating voltage window of supercapacitors, ionic/organic electrolytes (OVW of 3.0 V or higher) are preferable to aqueous electrolytes.

[0006]

- 60 High capacitance electrodes are another important factor in increasing the energy density dominated by low dimensional nanostructured materials.
- 62 Here, two dimensional materials (2DMs) have been considered as excellent choices for supercapacitor electrodes because of their structural advantages, including (i) 2D ion transport channels, (ii) easy ion accessibility across the entire sheet surface, and (iii) high in - plane electronic conductivity. Due to these structural advantages, two dimensional materials such as graphene sheets, transition metal dichalcogenides, MXenes, metallenes, siloxenes, and metal - organic frameworks have been investigated as promising supercapacitor electrodes. Challenges in using two dimensional materials as supercapacitor electrodes include their low out - of - plane conductivity and their tendency to aggregate and restack in nature. This results in limited ion accessibility to the internal electrically active sites, thus hindering the electrochemical properties. To overcome these problems, various strategies have been attempted, such as binder - free electrode design, decoration of nanocrystals on sheets, and heteroatom doping. In this strategy, the construction of 2D/2D heterostructures composed of two different nanosheets with different charge - storage mechanisms is very important to realize high capacitance with excellent rate performance.

wide range of fields.

83 The discovery of a number of different two - dimensional materials has greatly improved the functionality and speed of development in applications by combining different properties. Using two or more two - dimensional materials, different semiconductor layers can be created just one atomic thickness. As transistors get smaller, more of them can be placed on each chip, naturally producing faster processors. Additionally, graphene - based heterostructures used to aid in energy generation and storage could be used to create highly efficient and flexible solar and fuel cells. These heterostructures are very useful for developing next - generation batteries and supercapacitors, which promise fast charging and extended energy output. Therefore, there is a need in the art for supercapacitors with improved properties based on such heterostructures and methods for manufacturing the same.

[0008] 98 [Prior art literature]

[0009] 102 [Patent Document]

[0010] 106 1. Republic of Korea Patent No. 10 - 2235565

[0011]

110 2. Republic of Korea Patent No. 10 - 1820030

[0012]

The purpose of the present disclosure is to provide a supercapacitor exhibiting excellent electrostatic capacity, high energy - to - power ratio, and operating performance over a wide temperature range, and a method for manufacturing the same, by using reduced graphene oxide (rGO) and siloxene as electrode active materials.

[0013]

122 In order to achieve the above object, the present disclosure provides a method for producing a siloxene - rGO heterocomposite, including the steps of: adding calcium silicide (CaSi₂) to a graphene oxide dispersion in which graphene

oxide (GO) and a dispersant are stirred; generating siloxene sheets as calcium is desorbed from the calcium silicide (CaSi₂), partially reducing graphene oxide to generate a reduced graphene oxide (rGO), and adsorbing the siloxene sheets onto the surface of the rGO to generate siloxene - rGO; adding hydrazine hydrate to the siloxene - rGO to obtain a siloxene - rGO heterocomposite; and drying the siloxene - rGO heterocomposite.

[0014]

137 The weight ratio of the above graphene oxide and calcium silicide can be 1:0.8 to 1.2.

[0015]

141 The step of generating the above siloxane - rGO may be a simultaneous reaction in which a reaction in which a siloxane sheet is formed on the surface of graphene oxide and a partial reduction reaction of graphene oxide occur simultaneously.

[0016]

147 In the above simultaneous reaction, hydrogen gas generated during the formation of siloxane sheets can act as a reducing agent for graphene oxide.

[0017]

152 Drying of the above siloxane - rGO heterocomposite can be performed at a temperature of 80 to 120 ° C.

[0018]

157 The above siloxane - rGO heterocomposite can be used for any one purpose selected from supercapacitor electrodes, secondary battery electrodes, and electrochemical sensor materials.

[0019]

163 The above siloxane - rGO heterocomposite may have a BET surface area of 10 to 1000 m²/g and mesopores with an average pore size of 10 to 60 nm.

[0020]

168 In addition, the present disclosure provides a method for manufacturing a supercapacitor, including the steps of: preparing an electrode material in a slurry

form by mixing a siloxane - rGO heterocomposite, a dispersant, and a binder; preparing an electrode for a supercapacitor using the electrode material; and preparing a supercapacitor using the electrode.

[0021]

178 After the step of manufacturing the above siloxane - rGO electrode, a step of disposing a separator and a step of injecting an electrolyte are further included, and the electrolyte may include tetraethylammonium tetrafluoroborate (TEABF₄), which is an ionic/organic electrolyte.

[0022]

185 In addition, the present disclosure provides a supercapacitor including two or more electrodes including an electrode material mixed with a siloxane - rGO heterocomposite, a dispersant, and a binder, a separator positioned between the electrodes, and an electrolyte.

[0023]

¹⁹² The above supercapacitor can have an energy density of 10 to 100 Wh/kg and a power density of 10,000 to 20,000 W/kg.

[0024]

197 The above supercapacitor can have a capacitance of 4.5 to 70.9 F/g.

[0025]

201 The above supercapacitor has temperature resistance in the range of - 20 to 100 ° C and can have increased capacitance at high temperatures.

[0026]

206 The above supercapacitor can have a voltage rise of 2.0 to 2.5 V in a regenerative braking system (RBS).

[0027]

211 The present disclosure provides a supercapacitor formed with a heterostructure by hybridizing a two - dimensional material including a graphene or reduced graphene oxide (rGO) sheet having double - layer electrostatic capacitance (EDLC) properties

and a siloxane sheet having pseudocapacitance properties.

[0028]

221 Figure 1 shows a schematic diagram for preparing a siloxane - rGO heterocomposite.

[0029]

225 Figure 2 shows comparative X - ray diffraction patterns of siloxane, rGO, and siloxane - rGO formed during the process of preparing siloxane - rGO heterocomposites. (a) XRD spectra of CaSi₂ and siloxane sheets from which calcium is removed from the CaSi₂ and hydrazine - treated siloxane sheets, (b) XRD spectra of GO and rGO obtained using graphene and a modified Hummers method, (c) XRD spectra of siloxane, GO, and siloxene - rGO.

[0030]

234 Figure 3 shows the physical states of siloxane, GO, and siloxane - rGO. (a) Physical values obtained by Fourier transform infrared (FT - IR) spectroscopy, (b) FT - IR spectra.

[0031]

Figure 4 shows the elemental chemical properties of CaSi_{2,}GO, rGO, siloxane, and siloxane - rGO using X - ray photoelectron spectroscopy (XPS). (a) Core level spectra of Si 2P state of CaSi₂, siloxane, and siloxane - rGO, (b) Core level spectra of Si 2P state of siloxane and hydrazine - treated siloxane sheets, (c) Core level spectra of C 1s state of GO, rGO, and siloxane - rGO, (d) Typical XPS spectra of CaSi_{2,}GO, rGO, siloxane, and siloxene - rGO, (e) XPS spectra of Si 2P state and C 1s state of siloxane - rGO.

[0032]

250 Figure 5 shows the elemental chemical characteristics of CaSi_{2,}GO, rGO, siloxene, and siloxene - rGO using Raman spectroscopy. (a) Raman spectra for the 1000 - 2000 cm^{- 1} region of GO, rGO, and siloxene - rGO, (b) peak positions and I_D/I_G ratios of the corresponding materials analyzed in (a), (c) Raman spectra of siloxene and hydrazine - treated siloxene sheets, (d) Raman spectra for the 300 - 800 cm^{- 1} region of CaSi_{2,} siloxene and siloxene - rGO.

[0033]

259 Figure 6 shows the morphology of the siloxane - rGO and siloxane - rGO electrodes.
(a) - (d) High - resolution transmission electron microscopy (HR - TEM) images obtained at different levels of magnification, the inset in (d) is a selected area electron diffraction (SAED) image of the rGO sheets present in the heterostructure, (e) an overlay microscopy image, (f) - (h) mapping of Si, O, and C elements present in the siloxane - rGO heterostructure, (i) - (j) field emission scanning microscopy (FE - SEM) images of the siloxane - rGO electrodes obtained at different levels of magnification, (k) EDX spectrum of the siloxane - rGO electrode, (l) elemental distribution of Si and O atoms in the siloxane sheets, and (m) HR - TEM microscopy image of the rGO sheets.

[0034]

273 Figure 7 shows the surface area and pore volume analysis of siloxane, rGO, and siloxane - rGO. (a) N₂adsorption - desorption isotherm, (b) pore size distribution.

[0035]

279 Figure 8 shows the electrochemical analyses over a wide operating voltage window (OVW) of 3.0 V. (a) Cyclic voltammograms of siloxane, rGO and siloxane - rGO SSCs recorded using a scan rate of 50 mV/s, (b) - (c) comparative cyclic voltammograms of siloxane - rGO SSCs recorded using various scan rates from 5 to 1000 mV/s, (d) cyclic voltammogram of siloxane SSCs recorded using various scan rates from 5 to 1000 mV/s, (e) cyclic voltammogram of rGO SSCs recorded using various scan rates from 5 to 1000 mV/s.

[0036]

289 Figure 9 shows the effect of increasing scan rate on the capacitance characteristics of the current range. (a) Effect of scan rate on device capacitance, (b) Effect of current range on device capacitance, (c) Rate capability, (d) Power density of siloxane - rGO SSC as a function of rate capability analysis of (c).

[0037]

- 296 Figure 10 shows the electrostatic capacity characteristics by charge discharge profile analysis.
- 298 CD profiles of (a) siloxane SSCs, (b) rGO SSCs, and (c) siloxane rGO SSCs recorded at different levels of current over a range of OVW of 3.0 V.

[0038]

- 304 Figure 11 shows the long term cycling stability of siloxane SSC, rGO SSC, and siloxane rGO SSC.
- 306 10,000 Capacitance retention of (a) siloxane SSC, (b) rGO SSC, and (c) siloxane rGO SSC over a range of cycles.

[0039]

311 Figure 12 shows the self - discharge characteristics of siloxane SSC, rGO SSC, and siloxane - rGO SSC.

[0040]

316 Figure 13 shows the energy density retention of siloxane SSC, rGO SSC, and siloxane - rGO SSC.

[0041]

321 Figure 14 shows the performance comparison of SSCs using recently reported 2D materials and siloxane - rGO SSCs. (a) Comparison of capacitances, (b) Ragone plot comparing performance matrices.

[0042]

327 Figure 15 shows the energy storage characteristics of siloxane - rGO SSCs as a function of temperature. (a) Cyclic voltammograms in the temperature range of - 15 to 80 ° C, (b) effect of temperature on device capacitance, (c) Nyquist plot for temperatures from - 15 to 80 ° C, (d) electrochemical impedance (Z) plot as a function of applied frequency versus temperature, and the inset in (d) is a Bode phase angle plot.

[0043]

336 Figure 16 shows the performance matrix of siloxane - rGO SSC applied in a regenerative braking system (RBS). (a) Principle of RRBE process in electric vehicles using supercapacitors, (b) image of prototype used in RRBE study with driving and braking modes, (c) voltage versus time characteristics of siloxane - rGO SSC obtained in driving and braking modes, (d) enlarged area of the highlighted portion in (c).

[0044]

344 Figure 17 shows a practical application example for driving a multifunction electronic display (MFED).

[0045]

³⁵⁰ Figure 18 shows practical applications for lighting LEDs in RBS systems and driving electric vehicles. (a) Image of siloxane - rGO SSCs used in RBS systems, (b) lighting of LEDs of different colors, (c) image of electric vehicle charging station using solar cells, (d) image of electric vehicle charging using a laboratory - scale solar cell power plant (left) and image of siloxane - rGO SSC driving an electric vehicle for 30 seconds in standby mode (right), (e) image of electric vehicle driven more than 11 feet in only 9 seconds by the charged siloxane - rGO SSC.

[0046]

360 Hereinafter, preferred embodiments of the present disclosure are described in detail.

- 361 In explaining the present disclosure, if it is determined that a detailed description of a related known technology may obscure the gist of the present disclosure, the detailed description will be omitted.
- ³⁶⁴ Throughout the specification, whenever a part is said to "include" a component, this does not mean that it excludes other components, but rather that it may include other components, unless otherwise stated.

[0048]

370 The present inventors have applied for a patent for a supercapacitor including siloxene in order to improve the electrostatic capacity of a conventional supercapacitor (Korean Patent Registration No. 10 - 2053782, Korean Patent Publication No. 10 - 2022 - 0000212), and the above prior patent documents are incorporated herein by reference in their entirety and may be referred to in connection with the present disclosure.

[0049]

³⁷⁹ The present inventors have conducted research on the production of multicomponent electrode materials to develop a high - performance electrode having resistance over a wide temperature range while increasing the energy density without lowering the power density of the supercapacitor, and have thus provided a symmetric supercapacitor having a 2D/2D heterostructure in which siloxene and reduced graphene oxide (rGO) are laminated at the molecular level, suggesting the possibility of practical application as an energy device suitable for electric vehicles.

[0050]

389 In this disclosure, a novel supercapacitor electrode was developed by hybridizing two - dimensional materials including (i) graphene or reduced graphene oxide (rGO) sheets having double - layer electrostatic capacitance (EDLC) properties and (ii) siloxane sheets having pseudocapacitance properties.

1

- 396 Siloxane rGO symmetric supercapacitors (siloxane rGO SSCs) fabricated using 1 M tetraethylammonium tetrafluoroborate (TEABF₄) electrolyte exhibited superior performance metrics compared to those reported for state of the art SSCs due to the 2D/2D heterostructure.
- 400 The excellent energy to power ratio and operation over a wide temperature range (- 15 to 80 ° C) of the siloxane - rGO SSCs have been demonstrated in this disclosure to demonstrate their feasibility as advanced EES systems for capturing regenerative braking energy in electric vehicles.

[0052]

407 Accordingly, the present disclosure provides a siloxane - rGO heterocomposite comprising a two - dimensional electrically conductive siloxane sheet and a reduced graphene oxide sheet, a supercapacitor comprising the siloxane - rGO heterocomposite, and a method for preparing the same.

[0054]

414 Hereinafter, a siloxane - rGO heterocomposite according to the present disclosure and a supercapacitor including the siloxane - rGO heterocomposite and a method for manufacturing the same are described in detail.

[0055]

In one aspect, the present disclosure relates to a method for preparing a siloxene rGO heterocomposite, the method for preparing a siloxene - rGO heterocomposite comprising: a step of adding calcium silicide (CaSi < sub > 2 </sub >) to a graphene oxide dispersion in which graphene oxide (GO) and a dispersant are stirred; a step of generating a siloxene sheet as calcium is desorbed from the calcium silicide (CaSi < sub > 2 </sub >), partially reducing the graphene oxide to generate a reduced graphene oxide (rGO), and allowing the siloxene sheet to be adsorbed on the surface of the rGO to generate siloxene - rGO; a step of adding hydrazine hydrate to the siloxene - rGO to obtain a siloxene - rGO heterocomposite; and a step of drying the siloxene - rGO heterocomposite.

[0056]

441 FIG. 1 is a schematic diagram illustrating a process for preparing a siloxane - rGO heterocomposite according to the present disclosure as one embodiment.

[0057]

- ⁴⁴⁶ In one embodiment of the present disclosure, graphene oxide is formed by oxidizing graphite using a strong acid such as nitric acid, sulfuric acid, or hydrochloric acid, and has a hydroxyl group and an epoxy group on the surface and includes oxygen containing functional groups such as a carboxyl group and a ketone group at the end.
- 450 Because of these oxygen functional groups, graphene oxide becomes hydrophilic, and when graphene oxide is placed in water and treated with ultrasonic waves, graphene oxide, which has a frame composed of carbon atoms, is easily exfoliated, and a large amount of stable dispersion can be obtained.
- 454 However, since the sp² hybrid structure is broken during the oxidation process, the excellent physical properties unique to graphene, including electrical conductivity, are lost.
- 457 Therefore, when graphene oxide is subsequently treated with a reducing agent or high heat, the oxygen functional groups are removed and the sp² hybrid structure is restored, generating reduced graphene oxide, thus restoring its original physical properties.

[0058]

- ⁴⁶⁴ In one embodiment of the present disclosure, the siloxane sheet is produced by removing calcium from calcium silicide and becomes a material having a two dimensional linear structure and a direct bandgap including surface - linked Si chains having functional groups mainly composed of oxygen, hydrogen and hydroxyl groups.
- ⁴⁶⁹ The structure of siloxane sheets is greatly affected by experimental conditions such as reaction time, temperature, and solvent used.
- 471 The siloxane sheet formed in the Kautsky type of the present disclosure has a planar Si - silicon structure with Si₆ rings and various functional groups on the upper surface area, and it was confirmed that it can be utilized as an excellent electrode material for a supercapacitor by proving high energy storage characteristics in the previous patent of the present inventors (Korean Patent No. 10 - 2053782).

[0059]

⁴⁸¹ The above method for preparing the siloxane - rGO heterocomposite may be performed by mechanical or ultrasonic mixing.

[0060]

486 In the step of adding calcium silicide (CaSi₂) to the graphene oxide dispersion in which the above graphene oxide and dispersant are stirred, the weight ratio of the graphene oxide and calcium silicide may be 1:0.8 to 1.2, and preferably, the weight ratio is ideally 1:1.

[0061]

- ⁴⁹³ 1 g of graphene oxide forms 0.6 g of graphene sheet, and 1 g of calcium silicide forms 0.55 to 0.65 g of siloxane sheet.
- ⁴⁹⁵ Thus, finally, 0.6 g of siloxane sheets and 0.6 g of graphene sheets are randomly stacked to form a 2D/2D heterostructure.

[0062]

- 500 Since the double layer capacitance (EDLC) increases as the amount of graphene oxide increases and the pseudocapacitance increases as the amount of calcium silicide increases, a ratio of 1:0.8 to 1.2 can be used to balance the charge storage of the two capacitances, and a weight ratio of 1:1 can be preferably used.
- 504 Since this change in ratio leads to different types of supercapacitive characteristics such as high double layer capacitance or high pseudocapacitance, it is ideal for the 2D heterostructure electrode of the present disclosure to have 50% double layer capacitance (EDLC) and 50% pseudocapacitive electrode.

[0063]

- ${\scriptstyle 511}$ The above dispersant may be hydrochloric acid (HCl) at 4 ° C or lower.
- 512 Using cold hydrochloric acid, the calcium of calcium silicate slowly dissolves, generating hydrogen gas, which induces a phase reaction change that activates the hydroxyl groups of the siloxane sheets.

[0064]

518 The step of generating the above siloxane - rGO may be a simultaneous reaction in which a reaction in which a siloxane sheet is formed on the surface of graphene oxide and a partial reduction reaction of graphene oxide occur simultaneously, and the simultaneous reaction is such that a siloxane sheet is generated by hydrogen gas generated when calcium ions are desorbed from calcium silicide, and the hydrogen gas acts as a reducing agent for graphene oxide to generate reduced graphene oxide (rGO).

[0065]

531 In this specification, the term "simultaneous reaction" means that the oxidation and reduction do not proceed separately in stages, but that the reduction reaction proceeds simultaneously with the oxidation reaction, and that the oxidation reaction proceeds simultaneously with the reduction reaction.

[0066]

- ⁵³⁸ In the step of obtaining the above siloxene rGO heterocomposite, after adding hydrazine hydrate, additional reduction of partially reduced graphene oxide and formation of a siloxene - rGO heterostructure are achieved by ultrasonic irradiation, and the content of the hydrazine hydrate may be 3 to 8 ml per 100 g of the siloxene - rGO heterocomposite, and preferably 5 ml per 100 g of the siloxene - rGO heterocomposite.
- 544 The above hydrazine hydrate can reduce graphene oxide to graphene within the above content range, and if it is out of this range, the effect is reduced or it is not economical.

[0067]

550 In one embodiment of the present disclosure, while the siloxane sheet is manufactured by the simultaneous reaction, the reduced graphene oxide is manufactured and the formation of siloxane - rGO is induced through a sonochemical reaction using hydrazine hydrate as a reducing agent, thereby providing a fast and simple process in - situ by omitting a separate heat treatment step for the reduction of the graphene oxide.

[0068]

- ⁵⁵⁹ In the step of drying the siloxane rGO heterocomposite, the drying of the siloxane rGO heterocomposite may be performed at 80 to 120 °C for 8 to 16 hours, preferably at 90 to 110 °C for 10 to 14 hours, and more preferably at 100 °C for 12 hours.
- 563 If the drying conditions of the above siloxane rGO heterocomposite are lower than 80 ° C and less than 8 hours, the adsorbed water cannot be removed, and if they are higher than 110 ° C and more than 16 hours, the problem of the 2D heterostructure

shrinking occurs.

[0069]

573 The siloxane - rGO heterocomposite manufactured by the above manufacturing method can be used for any one purpose selected from among supercapacitor electrodes, secondary battery electrodes, and electrochemical sensor materials.

[0070]

⁵⁷⁹ The above siloxane - rGO heterocomposite may have a surface area of 10 to 1000 m^{2/}g calculated by the Brunauer - Emmett - Teller (BET) method and an average pore diameter of 10 to 60 nm measured by the Horvath - Kawazoe (HK) method, and may have mesoporous characteristics, and may improve ion accessibility during an electrochemical charge storage process within the above range.

[0071]

588 In another aspect, the present disclosure relates to a method for manufacturing a supercapacitor, comprising: a step of manufacturing an electrode material slurry by mixing a siloxane - rGO heterocomposite, a dispersant, and a binder; a step of manufacturing an electrode for a supercapacitor using the electrode material; and a step of manufacturing a supercapacitor using the electrode.

[0072]

⁵⁹⁶ The description of the above siloxane - rGO heterocomplex is the same as described above.

[0073]

601 The above dispersant may be at least one selected from the group consisting of dimethyl sulfoxide (DMSO), dimethylformamide (DMF), n - methyl - 2 - pyrrolidone (NMP), dimethylacetamide (DMAC), and triethyl phosphate (TEP), and the above binder may be at least one selected from the group consisting of polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyvinyl alcohol (PVA), and styrene butadiene (SBR).

[0074]

 ${\scriptstyle\it 610}$ The above dispersant may be n - methyl - 2 - pyrrolidone (NMP), and 0.4 to 0.6 mL of

NMP may be used per 100 mg of the siloxane - rGO heterocomposite to form a homogeneous slurry.

[0075]

617 The above binder may be polyvinylidene fluoride (PVDF), and may be added in an amount of 1 to 20 parts by weight, preferably 3 to 7 parts by weight, per 100 parts by weight of the siloxane - rGO heterocomposite.

[0076]

623 When the above dispersant and binder are within the above range, the stable performance and capacity characteristics of the electrode material can be further improved.

[0077]

- 629 The step of manufacturing an electrode for a supercapacitor using the above electrode material can be manufactured by coating the electrode material on a substrate or pressing it with a roll press.
- 632 At this time, the pressing pressure of the press can be 1 to 20 ton/cm² and the temperature of the roll can be 40 to 150 to improve the electrode density and control the electrode thickness.

[0078]

638 When within the above range, the electrochemical properties of the electrode material can be maintained and homogeneously compressed.

[0079]

- 643 Even when mixed together in the above step, the siloxane rGO heterocomplex has siloxane sheets adsorbed on the rGO surface, so the layered siloxane - rGO maintains a state of being spaced apart from each other, preventing restacking.
- 646 In this way, the electrode shape can be formed by uniformly distributing them without clumping together, while maintaining the excellent properties of each of siloxane and rGO.

[0080]

652 In the step of manufacturing the above siloxane - rGO electrode, drying can be performed at a temperature of 100 to 150 ° C and can be performed for about 10

minutes to 48 hours.

656 This drying process evaporates the dispersant from the molded product while simultaneously binding the siloxane - rGO particles, thereby enhancing the strength of the electrode for supercapacitors.

[0081]

663 The heterostructure composed of two different nanosheets with different charge storage mechanisms is very important for realizing a fixed capacity with excellent rate performance, and a supercapacitor including the siloxane - rGO electrode for a supercapacitor manufactured as described above can have a fixed capacity.

[0082]

670 In one embodiment of the present disclosure, the method may further include a separator arrangement step and an electrolyte injection step after the electrode manufacturing step for the supercapacitor.

[0083]

676 The above separator is not particularly limited as long as it is a separator commonly used in the battery and capacitor fields, such as a polyethylene nonwoven fabric, a polypropylene nonwoven fabric, a polyester nonwoven fabric, a polyacrylonitrile porous separator, a poly(vinylidene fluoride) hexafluoropropane copolymer porous separator, a cellulose porous separator, kraft paper or rayon fiber.

[0084]

⁶⁸⁴ The above electrolyte preferably uses an ionic/organic electrolyte rather than an aqueous electrolyte for a wide operating voltage window (OVW) of the supercapacitor, and specifically, tetraethylammonium tetrafluoroborate (TEABF4) electrolyte can be used.

[0085]

691 In another aspect, the present disclosure provides a siloxane - rGO supercapacitor comprising two or more electrodes including an electrode material mixed with a siloxane - rGO heterocomposite, a dispersant, and a binder, a separator positioned between the electrodes, and an electrolyte. 698 The above siloxane - rGO supercapacitor uses a siloxane - rGO heterocomposite as an electrode material, and exhibits high energy density, improved capacitance, excellent cyclic stability, and applicability over a wide voltage and temperature range.

[0087]

- 704 The above mentioned siloxane rGO supercapacitor may have an energy density of 10 to 100 Wh/kg, preferably 30 to 70 Wh/kg, and in the examples of the present disclosure, it was shown to vary from 16.25 Wh/kg to 55.79 Wh/kg.
- 707 Additionally, it may have a power density of 5,000 to 20,000 W/kg, preferably 10,000 to 18,000 W/kg, and in an embodiment of the present disclosure, increased to 15,000 W/kg.
- 710 This is far superior to other silicon based symmetric supercapacitor devices, such as siloxene, graphene - P - Si SSC, and silicon nanoTRIS, which were used as conventional electrodes.

[0088]

- ⁷¹⁶ The above siloxane rGO supercapacitor can have a capacitance of 4.5 to 70.9 F/g, and preferably can have a capacitance of 44.63 F/g to 56.17 F/g.
- 718 As the scan rate increases, the cyclic voltage current also increases, indicating high speed performance.
- 720 This speed capability performance demonstrated excellent capacitance retention and power density retention while switching the current range.
- 722 In addition, it demonstrated excellent long term stability by maintaining a capacitance of more than about 112% even after more than 10,000 charge discharge cycles.

[0089]

728 In one embodiment of the present disclosure, the siloxane - rGO supercapacitor comprises a siloxane - rGO heterocomposite as an electrode material, thereby exhibiting high energy density and capacitance stability as electric double layer capacitor (EDLC) properties and slow self - discharge characteristics by reducing charge redistribution.

[0090]

736 The inventors of the present invention additionally evaluated two aspects of the siloxane - rGO supercapacitor according to the present disclosure for application to electric vehicles: 1) high - temperature capacitance performance and 2) ability to capture regenerative braking energy.

[0091]

743 Accordingly, the siloxane - rGO supercapacitor according to the present disclosure was found to have a temperature range of - 20 to 100 ° C and an increased capacitance at high temperatures.

[0092]

749 The data results presented by electrochemical impedance spectroscopy showed that the charge - transfer resistance (R_{ct}) of the siloxane - rGO supercapacitor was low at high temperatures and increased at low temperatures, and the phase angle shifted from - 50.57 ° (at - 15 ° C) to - 66.13 ° (at 80 ° C) in the low - frequency region, indicating that the capacitance characteristics increased at high temperatures.

[0093]

758 Additionally, the siloxane - rGO supercapacitor according to the present disclosure can be characterized by having a voltage rise of 2.0 to 2.5 V in a regenerative braking system (RBS).

[0094]

The voltage - time characteristics of the siloxane - rGO supercapacitor connected to a regenerative braking system (RBS) were monitored under different braking conditions. When a small braking pulse was applied to the RBS, the voltage value of the siloxane - rGO supercapacitor reached a maximum of 0.8 V (30 s) and 1.2 V (90 s), and the voltage increased to 2.2 V under rapid braking pulses.

[0095]

772 The above two property evaluations suggest that the siloxane - rGO supercapacitor can be used as an efficient energy storage system (EES) for electric vehicles, as it maintains supercapacitive performance over a wide temperature range and exhibits the ability to capture regenerative braking energy.

[0097]

⁷⁷⁹ In one embodiment of the present disclosure, the electrostatic capacitance was calculated according to the following mathematical expression 1.

[0099]

785 In the above mathematical expression 1,

[0100]

789 C is the capacitance (F/g), I is the discharge current (A), T_d is the time required for discharge (sec), M is the mass of the electroactive material (g), and V is the potential window (V).

[0101]

⁷⁹⁵ In one embodiment of the present disclosure, the energy density and power density were calculated according to the following mathematical expressions 2 and 3.

[0104]

soo In the above mathematical expressions 3 and 4, E is the energy density, C is the capacitance, V is the potential window, P is the power density, and T_d is the discharge time (seconds).

[0105]

806 In one embodiment of the present disclosure, the capacitance of the device with respect to frequency was calculated using EIS analysis according to the following mathematical expression 4.

[0107]

812 In the above mathematical expression 4, C is the capacitance of the device, f is the applied frequency, and z is a virtual plot of impedance.

[0108]

- 817 Hereinafter, preferred embodiments are presented to aid understanding of the present disclosure.
- 819 However, the following examples are provided only to make it easier to understand the present disclosure, and the contents of the present disclosure are not limited by the following examples.

[0111]

- 829 Calcium silicide (CaSi₂) precursor was purchased from Kojundo Chemical Research Institute, Japan.
- 831 Polyvinylidene fluoride (PVDF) was purchased from Sigma Aldrich, Korea.
- 832 Tetraethylammonium tetrafluoroborate (TEABF₄) was purchased from Alfa Aesar Chemicals, Korea.
- 834 Hydrazine hydrate, hydrochloric acid (HCI), and N methyl 2 pyrrolidone (NMP) were purchased from Daejung Chemical Co., Ltd. (Republic of Korea).

[0112]

839 Ultrasonic investigations were performed on a VCX 750 ultrasonicator (Sonics and Materials, Inc, USA, 20 kHz, 750 W) using a direct - immersion titanium horn.

[0113]

844 XRD patterns of the prepared siloxane, graphene oxide (GO), and siloxane - rGO were determined using an X - ray diffractometer system (Empyrean) with Cu - K radiation (= 1.5418 Å).

[0114]

- 850 The functional groups of siloxane, graphene oxide, and siloxane rGO were investigated using Fourier transform infrared spectroscopy (Thermo scientific FT -IR spectrometer (Nicolet 6700)).
- 853 The powder pre mixed with calcium bromide (KBr) was compressed into pellets and measured against bare KBr as a standard.

[0115]

858 Raman spectra were acquired using a LabRam HR Evolution Raman spectrometer (Horiba Jobin - Yvon, France) using an argon ion laser at a wavelength of 514 nm.

[0116]

- 863 The elemental chemical states of siloxene and reduced graphene oxide (GO) were determined by X - ray photoelectron spectrometry (ESCA - 2000, VG Microtech Ltd.).
- 866) was used to analyze the surface morphology and element distribution

measurements, and analyses were conducted using a field emission scanning electron microscope (JSM - 6700F, JEOL Instruments) and a high - resolution transmission electron microscope (JEM - 2011, JEOL).

[0117]

874 Nitrogen adsorption/desorption isotherms (77 K) of the manufactured siloxane, graphene oxide, and siloxane - rGO were measured using a NOVA 2000 system (Quantachrome, USA).

[0118]

880 Additionally, a dual - range semi - micro balance (AUW - 220D, Shimadzu) with five decimal places approximation was used to determine the active material mass loading of the electrodes manufactured for supercapacitors.

[0119]

886 Electrochemical measurements such as cyclic voltammetry (CV) at various scan rates, electrochemical impedance spectroscopy (EIS) data analysis (frequency from 0.01 Hz to 100 kHz and amplitude of 10 mV) and galvanostatic charge and discharge (CD) measurements at different current amplitudes for the siloxane - rGO symmetric supercapacitor devices were performed using an Autolab PGSTAT302N electrochemical terminal.

[0121] 895 Example

[0122] 899 1. Siloxane - rGO heterocomplex 900 manufacturing

[0123]

904 Graphene oxide was prepared by oxidizing graphite powder using a modified Hummer method using potassium permanganate and sulfuric acid. 1 g of graphene oxide (GO) was dispersed in a cold HCl solution (100 mL, 37%), and 1 g of well - pulverized calcium silicide (CaSi₂) powder was added and soaked at 0 ° C with a stirring speed of 200 rpm for 4 days.

909 As calcium of CaSi₂ de - intercalated through a topochemical reaction,

siloxane sheets were formed and adsorbed on the partially reduced rGO surface.

- *911* After the reaction was completed, the black siloxane rGO produced was separated through a centrifugal separation process using acetone and water.
- 914 The separated siloxane rGO powder was redispersed in 100 mL of water, and hydrazine hydrate solution was immediately added, followed by ultrasonication for 2 h.
- *917* The sonochemical and sonochemical reactions of siloxane and graphene oxide are well represented in the schematic diagram in Fig. 1.
- ⁹¹⁹ The heterostructured siloxane rGO was separated by centrifugation and then dried at 100 ° C for 12 h.

[0125]

924 2. Fabrication of coin - type symmetric supercapacitor devices

[0126]

- 928 A homogeneous slurry was prepared by grinding 5 wt% polyvinylidene fluoride (PVDF) and 95 wt% siloxane - rGO hetero powder dispersed in N - methyl - 2 pyrrolidone (NMP) using a mano mortar and pestle, and the homogeneous slurry was coated on an aluminum (AI) substrate using a doctor blade to secure a uniform electrode thickness of 25 to 50 μm. Subsequently, the coated slurry was dried in an oven at 80 ° C for 12 hours to evaporate the solvent.
- 934 The siloxane rGO electrode coated aluminum foil was pressed on a rolling press machine (WCRP - 1015G) to form it into an electrode shape.
- *936* The siloxane rGO electrode thus manufactured was cut into a circle with a diameter of 14 mm for the manufacture of coin cells.

[0127]

- 941 Next, the siloxane rGO electrode was dried to fabricate a supercapacitor cell.
- 942 A coin type cell (CR2032) was fabricated using two electrodes separated by a Cellguard membrane, and the cell was crimped using an Electric Coin Cell Crimping and Disassembling Machine (MTI Korea).
- 945 The electrolyte used was 1.0 M TEABF4 electrolyte, and the fabrication of the electrolyte and coin cell device was performed in a glove box with a humidity of 1 ppm and lower than air.

[0129]

951 As comparative examples that can be compared with the siloxane - rGO heterocomposites manufactured in the above examples, siloxane sheets, hydrazine - treated siloxane sheets, GO sheets, and rGO sheets were used, and as comparative examples that can be compared with the siloxane - rGO supercapacitor (hereinafter referred to as siloxane - rGO SSC), siloxane supercapacitors (hereinafter referred to as siloxane SSCs) and rGO supercapacitors (hereinafter referred to as rGO SSCs) were used.

[0131]

963 Experimental Results

[0132]

967 1. Physicochemical properties of siloxane - rGO heterocomposites and siloxane - rGO electrodes

[0133]

972 The siloxane - rGO powders were characterized using X - ray diffraction (XRD), Fourier transform infrared spectroscopy (FT - IR), X - ray photoelectron spectroscopy (XPS), Raman spectroscopy, high - resolution transmission electron microscopy (HR - TEM), and field emission scanning electron microscopy (FE -SEM) along with elemental mapping analysis.

[0134]

- 980 Referring to Fig. 2a, the XRD pattern of the siloxane sheet derived from CaSi₂ and the hydrazine - treated siloxane sheet shows a broad peak at 23.3 ° and shows that the surface functional groups were removed.
- ⁹⁸³ In Fig. 2b, the 10 ° diffraction peak observed in the GO sheet disappeared in the rGO sheet, indicating that GO was reduced to rGO.
- 985 The siloxane rGO XRD pattern in Fig. 2c shows that the 11.3 ° diffraction peak of siloxane and the 10.4 ° diffraction peak of GO disappear, and a broad peak at 23.3 ° is observed, indicating the formation of a heterostructure of siloxane - rGO re stacked through random interstratification.

[0135]

992 Referring to the FT - IR physical values of the GO sheet, siloxane sheet, and siloxane - rGO heterocomposite in FIG. 3a and the FT - IR spectrum in FIG. 3b, the peaks appearing at 1,061, 1,572, 1,732, and 2,127 cm^{- 1} of the siloxane - rGO heterocomposite correspond to the vibration bands corresponding to the Si - O - Si and OSi₂ Si - H groups of the siloxane sheet and the peaks of the vibration bands corresponding to the C=O and C - C groups of the rGO sheet, thereby maintaining these functional groups.

1002 This demonstrates the presence of Kautsky - type siloxane in the heterostructure. 1005 In contrast, other surface functional groups disappeared, further confirming the

formation of heterostructures of siloxane - rGO through these changes.

[0136]

- 1010 Figures 4 and 5 show the elemental chemical states of the siloxane rGO heterocomposite.
- 1012 Referring to Fig. 4a, the Si 2p spectra of CaSi_{2,}siloxene and siloxene - rGO powders confirm (i) the disappearance of the Si - Si state (99.5 eV) and (ii) the maintenance of the Si - O - Si state (102.5 eV) of siloxene - rGO.
- 1015 This is due to the reaction between the hydrazine treated siloxane and the siloxane sheets in Fig. 4b.
- 1017 Additionally, referring to Fig. 4c, the C 1s spectrum of the siloxane rGO powder shows that the C - O surface groups attached to GO are removed compared to the spectra of GO and rGO.
- 1020 Comparing the XPS survey spectra of CaSi_{2,}siloxane, GO, rGO, and siloxane - rGO powders in Fig. 4d, the fabricated siloxane - rGO heterostructure shows obvious changes.
- 1023 XPS results for the siloxane rGO powder collected after the topochemical reaction showed a weak Si - Si network on the siloxane sheets (Fig. 4e) and partial reduction of GO before hydrazine treatment (Fig. 4f).

[0137]

- 1029 Referring to Figures 5a and 5b, the Raman spectra and related physical values (G and D band positions and I_D/I_G ratio) of GO, rGO, and siloxane - rGO are summarized to demonstrate the re - graphitization process.
- 1032 By Raman analysis, the restoration of sp² network (rGO sheets) in the heterostructure and the transformation of Si - Si into Si - O - Si network (siloxane sheets) were confirmed.
- 1035 Referring to the Raman spectra of CaSi₂, siloxane, hydrazine treated siloxane, and siloxane - rGO powders in Figs. 5c and 5d, the Raman signatures such as Si - O - Si (498 cm^{- 1}) and Si - Si (524 cm^{- 1}) of siloxane sheets were merged into a single peak at 518 cm^{- 1} (Si -O - Si) of siloxane - rGO.
- 1040 Raman spectra of the siloxane rGO heterostructure with different laser powers (10 to 50 mW) are shown in Fig. 5e.
- 1042 The Raman signatures of rGO are clear from the first order scattering of the E_{2g} mode (G band, 1,582 cm^{- 1}) and defects (D band

at 1,350 cm^{- 1}), but the signature of the siloxane band (at 518 cm^{- 1}) was observed only at high laser power.

1046 In the hydrazine - treated siloxane sheets, the Si - Si network and S - H groups were removed, and the G - band positions of the rGO sheets and siloxane - rGO heterostructure shifted to a lower wavenumber at 1,598 cm < sup > - 1 </sup > compared with that of the GO sheets, indicating that a better reduction reaction occurred.

[0138]

- 1056 Referring to Figure 6, HR TEM images of randomly stacked siloxane rGO heterocomposites show the growth of siloxane sheets on the rGO surface (Figures 6a - d).
- 1059 This demonstrates the role of rGO as a layered conductive substrate for the growth of siloxane.
- 1061 The selected area electron diffraction (SAED) image inserted in Fig. 3d shows the hexagonal diffraction spots of the rGO sheets present in the heterostructure.
- 1063 Elemental mappings shown in Figures 6e h show the formation of a heterostructure in which two different sheets are randomly stacked.
- 1065 Additionally, FE SEM images of the molded siloxane rGO electrode (Fig. 6i j) showed laterally aligned sheets, and EDS spectrum in Fig. 6k showed the presence of Si, C, O, and F elements in the siloxane - rGO electrode.
- 1068 In addition, Fig. 6I shows that Si and O elements are uniformly distributed throughout the siloxane sheet (lateral size approximately 0.7 × 2.0 μm²) with an O/Si ratio of 1.34, and Fig. 6m confirms the formation of rGO sheets after the sonochemical reduction reaction.

[0139]

- 1075 Siloxane rGO heterocomposites can enhance ion accessibility in electrochemical charge storage process due to the presence of mesoporous fraction.
- 1077 Referring to Figure 7, the specific surface area and pore size of the siloxane rGO heterocomposite can be known.
- 1079 The N₂ adsorption desorption isotherms in Fig. 7a show the presence of type - IV characteristic curves (according to IUPAC standard) for siloxane sheets, rGO sheets, and siloxane - rGO heterocomposites in the relative partial pressure range of 0.1 to 0.95.
- 1083 The BET calculated surface areas of these materials were 47.77, 169.27, and 136.65 m²/g, respectively.
- 1085 Figure 7b shows that the average pore diameter of these materials using the HK method is in the range of 25 to 40 nm.

[0141]

1091 2. Electrochemical properties of siloxane - rGO supercapacitors

[0142]

- 1095 Referring to the cyclic voltammograms in Fig. 8, the siloxane rGO supercapacitors show a linear increase in the current range with increasing scan rate. The cyclic voltammograms of siloxane SSCs, rGO SSCs, and siloxane - rGO SSCs recorded over a voltage operating window of 3.0 V at a scan rate of 50 mV/s (Fig. 8a), and the cyclic voltammograms of siloxane SSCs, rGO SSCs, and siloxane - rGO SSCs recorded using different scan rates from 5 to 1000 mV/s (Fig. 8b – e), a typical rectangular - shaped cyclic voltammogram was observed for all the SSCs, with notable differences in the area.
- ¹¹⁰³ The area of the cyclic voltammogram is higher for siloxane rGO SSCs than for siloxane SSCs and rGO SSCs, highlighting the enhanced charge storage properties.

[0143]

- 1108 Also, referring to Fig. 9, the effect of increasing the scan speed on the capacitance characteristics of the current range is shown.
- 1110 In Fig. 9a, the device capacitance of siloxane rGO SSC recorded at a scan rate of 5 mV/s was 56.17 F/g, which was higher than that of siloxane SSC (4.89 F/g) and rGO SSC (37.55 F/g).
- 1113 The device capacitance of the siloxane rGO SSC recorded at an applied current of 1 mA in Fig. 9b was 44.63 F/g, which was higher than that of the siloxane SSC (1.79 F/g) and rGO SSC (30.46 F/g).

[0144]

1119 The rate capability performance of the siloxane - rGO SSC (Fig. 9c) shows excellent retention of capacitance and power density while switching the current range (1-10 mA) (Fig. 9d) and vice versa.

[0145]

- 1125 To evaluate the performance metrics of the siloxane rGO SSCs, charge discharge (CD) analysis using the galvanostatic method is shown in Fig. 10.
- 1127 The CD profiles of the manufactured SSCs show an enhancement in charge storage capacity in the order of siloxane SSC (Fig. 10a) < rGO SSC (Fig. 10b) < siloxane rGO SSC (Fig. 10c), which is attributed to the heterostructure of siloxane - rGO.

[0146]

1134 The electrical activation effect of siloxane - rGO SSCs was also observed in the long - term stability performance.

[0147]

- 1139 Referring to Fig. 11, in charge discharge cycle tests over 10,000 times, the siloxane SSC and rGO SSC were found to maintain capacitances of 96.59% and 90.35%, respectively (Fig. 11a and Fig. 11b).
- 1142 As shown in Figures 11c and 11d, the siloxane rGO SSC showed a trend in which the capacitance increased to 118% at 2,500 cycles, then gradually decreased to 115.5% at 5,000 cycles, and then stabilized at 112.2% at 10,000 cycles.

[0148]

- 1148 The self discharge characteristics of supercapacitors are one of the most important characteristics when considering practical applications.
- 1150 To evaluate the self discharge characteristics of the siloxane rGO SSC, the SSC was charged to 3.0 V using the chrono method for 10 min, and then the open circuit voltage was measured for 2 h, as shown in Fig. 12a.
- ¹¹⁵³ All the fabricated siloxane SSCs, rGO SSCs, and siloxane rGO SSCs exhibited a voltage drop due to ohmic drop at the beginning of the self discharge cycle.
- 1155 Initially, the discharge rate was fast and then slowed down as time increased, and it was confirmed that the voltage drop and discharge rate of the siloxane - rGO SSC were the slowest.
- 1158 This indicates that a diffusion controlled Faraday process is involved in self discharge.
- 1160 Siloxane rGO SSCs exhibit better self discharge characteristics than siloxane SSCs and rGO SSCs, which is attributed to the reduced faradaic leakage and charge redistribution due to the heterostructure.

[0149]

- 1166 The effect of these heterostructured electrodes on the device capacitance performance is well illustrated in Fig. 13.
- 1168 Due to its high capacitance and wide voltage operation window, the siloxane rGO SSC exhibits an energy of 55.79 Wh/kg, which is significantly higher than that of the siloxane SSC (2.23 Wh/kg) and rGO SSC (38.07 Wh/kg) at the corresponding power density of 1,500 W/kg<sup/>.
- ¹¹⁷² The energy density of the siloxane rGO SSCs varied from 16.25 Wh/kg to 55.79 Wh/kg, and the power density increased from 1,500 W/kg to 15,000 W/kg,

respectively.

- 1176 This indicates that the energy density retention of siloxane rGO SSC (29.12%) is higher than that of siloxane SSC (22.86%) and rGO SSC (11.92%), which have a 10 - fold increase in power density value.
- 1180 Referring to FIG. 14b, the siloxane rGO SSC according to the present disclosure exhibits higher capacitance performance than other recently reported silicon and Si - hybrid based supercapacitors.

[0150]

- 1186 Tables 1 and 2 below compare gravimetric and areal measurements of state of the - art supercapacitors using organic/ionic liquid electrolytes with silicon oxycarbide symmetric supercapacitor devices.
- 1189 The data in Table 1 provide evidence for the superior power performance of the siloxane - rGO heterostructure symmetric supercapacitors compared to other supercapacitor systems using electrodes such as graphene, rGO, coPIL - RGO, MoS₂, MXene, and siloxane.
- 1193 The data in Table 2 show that the areal energy power performance index of the siloxane - rGO heterostructure symmetric supercapacitors is higher than that of other silicon - based symmetric supercapacitors.

[0151]

1199 S.No.
1200 Electrodes for SC Electrodes for SC
1201 Electrolyte
1202 Voltage Window(V)
1203 Energy density Energy density (Wh/kg)
1204 Power density (W/kg)
1205 1
1206 Activated carbon
1207 BMPY - TFSI
1208 0.0 to 3.0
1209 25
1210 5000

2

1214 Nanocarbon 1215 EMIM - TFSI 1216 0.0 to 3.0 1217 46

3

1222 Super 30, Norit
1223 Pyr < sub > 14 < /sub > TFSI
1224 0.0 to 3.5
1225 30
1226 10000

4

1230 Porous graphene macrofoam
1231 TEABF < sub > 4 < /sub >
1232 0.0 to 2.5
1233 23.5
1234 312

5

```
1238 Graphene / V < sub > 2 < /sub > O < sub > 5 ( < /sub > Graphene /
V < sub > 2 < /sub > O < sub > 5 < /sub > )
1240 LiClO < sub > 4 < /sub > /PC
1241 0.0 to 2.5
1242 32
1243 1374
```

6

1247 Poly (ionic liquid) - modified reduced graphene (rGO)
1248 [MPPy] [TFSI]
1249 0.0 to 3.0
1250 40
1251 2100

7

```
1255 BDA/rGO
1256 TEABF < sub > 4 < /sub >
1257 0.0 to 2.7
1258 34
1259 10000
```

8

1263 Tris - rGO 1264 TEABF < sub > 4 < /sub > 1265 0.0 to 2.7 1266 32 1267 1000

9

1271 Graphene - CMK - 5
1272 EMIMBF4
1273 0.0 to 3.5
1274 60.7
1275 10000
1276 9
1277 Exfoliated MoS₂(Exfoliated MoS₂)
1278 TEABF₄
1279 0.0 to 3.0
1280 18.43
1281 7500

10

1285 Few layered MoS₂ (Few layered MoS₂)
1286 TEABF₄
1287 0.0 to 3.0
1288 20.31
1289 7500

11

1293 HT - Siloxene 1294 EMIMBF < sub > 4 < /sub > 1295 0.0 to 3.0 1296 6.64 1297 15000

12 ¹³⁰¹ Ti₃C₂T_x/MWCNT//rGO ASC 1302 Et < sub > 4 < /sub > NBF < sub > 4 < /sub >
1302 0.0 to 2.0
1304 20
1305 1000

13

1309 Reduced graphene oxide 1310 [SET < sub > 3 < /sub >] [TFSI] / GO 1311 0.0 to 2.5 1312 17.7 1313 875

14

1317 Siloxene - rGO SSC 1318 TEABF₄ 1319 0.0 to 3.0 1320 55.79 1321 15000

[0152]

1325 S.No. 1326 Electrodes for SC Electrodes for SC 1327 Electrolyte 1328 Voltage Window(V) 1329 Energy density Energy density (Wh/kg) 1330 Power density (W/kg) 1331 **1** 1332 Graphene coated - P - Si 1333 EMIMBF₄ 1334 0.0 to 2.7 1335 10 1336 65000 1337 2 1338 Oxide - coated silicon nanowire 1339 [BMIM[NTf₂] 1340 - 0.6 to 1.0 1341 0.23 1342 651 1343 **3**

```
1344 Graphene - P - Si
1344 PVA - H < sub > 2 < /sub > SO < sub > 4 < /sub >
1346 - 0.9 to 1.2
1347 25
1348 54000
1349 4
1350 Graphene - P - Si
1351 PVA - H < sub > 2 < /sub > SO < sub > 4 < /sub >
1352 - 0.9 to 1.2
```

15

```
1356 43000
1357 5
1358 PEDOT coated SiNWs
1359 [C<sub>3</sub>mpyr] [NTf<sub>2</sub>]
1360 0.0 to 1.5
1361 10
1362 85000
1363 6
1364 Si diatom@MnO<sub>2</sub>ASC
1365 Na<sub>2</sub>SO<sub>4</sub>
1366 0.0 to 1.6
1367 23.2
1368 2220
1369 7
1370 HT - Siloxene
1371 EMIMBF<sub>4</sub>
1372 0.0 to 3.0
1373 6.64
1374 15000
1375 8
1376 Silicon carbide - MnO<sub>2</sub>ASC(Silicon carbide -
    MnO < sub > 2 < /sub > ASC)
1378 Na<sub>2</sub>SO<sub>4</sub>
1379 0.0 to 1.9
1380 30.6
1381 10000
1382 9
1383 Panasonic
1384 -
1385 2.5
```

1386 2.3 1386 514 1388 10 1389 Maxwell 1390 -1391 2.7 1392 2.5 1393 1281 1394 11 1395 Siloxene - rGO SSC 1396 TEABF < sub > 4 < / sub > 1397 0.0 to 3.0 1398 55.79 1399 15000

[0154]

1403 3. Performance evaluation for electric vehicle (EV) applications

[0155]

1407 To apply supercapacitors to electric vehicles (EVs), two major requirements are required: 1) retention of capacitance at high temperatures and 2) the ability to capture regenerative braking energy.

[0157]

1413 3 - 1. Temperature - dependent performance of siloxane - rGO SSCs

[0158]

- 1417 Referring to Figure 15, the supercapacitive performance of the siloxane rGO SSC can be confirmed over a wide temperature range of - 15 to 80 .
- 1419 The cyclic voltammograms of the siloxane rGO SSCs displayed rectangular profiles (including the change in current range) at different temperatures (- 15 and 80 ° C) (Fig. 15a).
- 1422 The effect of temperature on the capacitive performance of siloxane rGO SSCs shows that at low temperatures of - 15 and 5 ° C, the device capacitance still maintains capacitances of 9.23 and 16.45 F/g, respectively, and as the temperature increases from 5 ° C to 80 ° C, the device capacitance of siloxane - rGO SSCs increases from 16.45 to 34.86 F/g, respectively (Fig. 15b).
- 1427 Electrochemical impedance spectroscopy of siloxane rGO SSCs obtained at

different temperatures is displayed in the form of Nyquist plots (Fig. 15c).

- 1429 The data infer that the charge transfer resistance (R_{ct}) is low at high temperatures and increases with decreasing temperature, likely due to limited ion diffusion kinetics at extremely low temperatures.
- 1433 In particular, the Warburg line shifts closer to the imaginary axis of impedance as the temperature changes from - 15 °C to 80 °C, indicating an increase in the capacitance characteristics of the siloxane - rGO SSCs at elevated temperatures.
- 1436 This can be inferred from the low electrochemical impedance of siloxane rGO SSCs at high temperatures (Fig. 15d).
- 1438 In the low frequency region, the phase angle of siloxane rGO SSCs (inset in Fig. 16d) shifts from 50.57 ° (at 15 °C) to 66.13 ° (at 80 °C), further highlighting the excellent capacitance characteristics at high temperatures.
- 1441 These results suggest the applicability of siloxane rGO SSCs over a wide temperature range, which is an essential criterion for using energy storage systems (EES) in electric vehicles.

[0160]

1447 3 - 2. Regenerative braking energy capture capability of Siloxane - rGO SSC

[0161]

- 1451 Siloxane rGO SSCs could be ideal EES devices for regenerative braking systems (RBS) due to their properties of long cycle life, ultra - high power density, and virtually maintenance - free supercapacitors.
- 1454 Referring to Figure 16, the prototype RBS system (Figure 16b) consists of a wheel with two circular brakes (controlled by pistons at the top) and an electric motor (which acts as a generator to convert kinetic energy into electrical energy) to which a siloxane - rGO SSC is connected.
- 1458 Based on the braking level (manual control), the ability of the siloxane rGO SSC to store electrical energy was monitored by measuring the open circuit voltage value.
- 1460 The voltage versus time characteristics of the siloxane rGO SSCs coupled to the RBS (Fig. 16c) were monitored under different braking conditions.
- 1462 When the RBS was in idle/running mode and no braking was applied, no charging process occurred in the Siloxane rGO SSC for up to 25 seconds.
- 1464 The voltage of the siloxane rGO SSC varied as a function of the braking level applied to the RBS.
- ¹⁴⁶⁶ When a small braking force was applied to the RBS, the voltage value of the siloxane rGO SSC reached a maximum of 0.8 V (30 s) and 1.2 V (90 s).
- 1468 The voltage of the siloxane rGO SSC increased up to 2.2 V under rapid braking pulse (Fig. 16d).

[0163]

1474 Practical application examples to demonstrate the excellent performance matrix of the siloxane - rGO supercapacitor according to the present disclosure are shown in FIGS. 17 and 18.

[0164]

1480 Referring to Figure 17, a demonstration of driving a siloxane - rGO supercapacitor by connecting it to a multifunction electronic display (MFED) was monitored.
1482 We verified that all functions, including temperature, humidity, and clock, worked well for 30 minutes on a display equipped with a fully charged siloxane - rGO supercapacitor at 3.0 V.

[0165]

1488 Referring to Fig. 18, the siloxane - rGO supercapacitor was applied to LED lighting in the RBS system and driving of an electric vehicle.

1490 Figure 18b shows the implementation of different color LED lighting by the siloxane - rGO supercapacitor, and two siloxane - rGO supercapacitors connected in parallel in a laboratory - scale electric vehicle power plant were charged (left in Figure 18d), and the electric vehicle was driven for about 30 seconds in standby mode (right in Figure 18d) and demonstrated the ability to drive more than 11 feet in a short time of about 9 seconds (e).

[0167]

- 1499 The above experimental results demonstrate the utility of molecularly layered siloxane - rGO 2D/2D heterostructures as advanced electrode materials for supercapacitors using ionic liquid electrolytes.
- 1502 In addition to long cycle life, the siloxane rGO SSCs also provided high device capacitance, high energy density, and high power density along with high rate performance.
- 1505 In addition, the temperature dependent supercapacitive performance metrics of the siloxane - rGO SSCs indicated that they could operate as ideal energy devices even at a high temperature of 80 .
- 1508 Direct integration of siloxane rGO SSC and RBS (for EVs) demonstrated the ability to highly efficiently store the electrical energy generated/recovered during braking.
- 1510 The excellent energy power performance metrics, wide temperature tolerance and proven practical applications of siloxane - rGO SSCs support their use as high performance energy storage devices for regenerative braking energy capture (RRBE) applications in next - generation electric vehicles.

[0169]

- 1517 The preferred embodiments of the present disclosure have been described in detail above.
- 1519 The description of the present disclosure is for illustrative purposes only, and a person skilled in the art to which the present disclosure pertains will understand that other specific forms can be easily modified without changing the technical spirit or essential characteristics of the present disclosure.

[0170]

1526 Accordingly, the scope of the present disclosure is indicated by the claims described below rather than the detailed description above, and all changes or modifications derived from the meaning, scope, and equivalent concepts of the claims should be interpreted as being included in the scope of the present disclosure.

[0172]

1533 The supercapacitor according to the present disclosure can be utilized as an advanced energy storage system (EES) for capturing regenerative braking energy of electric vehicles due to its excellent electrostatic capacity, high energy - to power ratio, and stable operating performance over a wide temperature range.