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Supercapacitor comprising silicon oxycarbide thin film layer and method for manufacturing the same

[0001]

The present invention relates to a supercapacitor and a method for manufacturing the same, and more particularly, to a supercapacitor having improved power density and a method for manufacturing the same.

[0002]

The rapid growth of renewable energy sources (solar, wind and mechanical energy harvesting) is driving the demand for sustainable energy storage technologies in our everyday lives.

[0003]

Among the available energy storage devices, including lithium - and sodium - ion batteries (LIBs and SIBs, respectively), supercapacitors have attracted attention due to their high power density, intermediate energy density, and long cycle life (compared to LIBs and SIBs).

[0004]

The development of novel electrode materials with high capacitance, heat resistance, high conductivity, high surface area and excellent electrochemical stability is an excellent way to improve the performance of supercapacitors, and recent research is being conducted to improve the energy/power performance of electrochemical energy storage (EES) through the development of novel separators with high ionic conductivity, to elucidate the role of different solvents and electrolytes, and to develop novel nanostructured materials for high - capacity electrodes.

[0005]

Accordingly, the inventors of the present invention conducted repeated research to further improve the energy density of supercapacitors, and as a result, discovered that a supercapacitor can exhibit excellent energy density and power density by including a silicon oxycarbide thin film layer, leading to the present invention.

[0006]

The present invention has been made to solve the problems of the prior art, and provides a supercapacitor with improved energy density and power density and a method for manufacturing the same.

[0007]

In order to solve the above problems, the present invention provides a method for manufacturing a supercapacitor, including a reaction step of reacting siloxene and alginate to obtain silicon oxycarbide; a slurry preparation step of mixing the silicon oxycarbide, a conductive carbon material, and a binder to produce an electrode material slurry; and a thin film layer preparation step of coating the electrode material slurry on a substrate and drying it to produce a silicon oxycarbide thin film layer.

[0008]

In addition, the present invention provides a method for manufacturing a supercapacitor, characterized in that the siloxene is manufactured by immersing a precursor containing calcium silicide in acid to dissolve calcium.

[0009]

In addition, a method for manufacturing a supercapacitor is provided, characterized in that the acid is a strong acid having a temperature of 4 ° C or lower.

[0010]

In addition, a method for manufacturing a supercapacitor is provided, characterized in that the weight ratio of the siloxene and alginate is 1:5 to 1:20.

[0011]

In addition, the present invention provides a method for manufacturing a supercapacitor, characterized in that the reaction step includes a grinding step of grinding siloxene and alginate into fine powder; an annealing step of heating the fine powder at a heating rate of 1 to 5 ° C and annealing it at 180 to 220 ° C for 1 to 5 hours; and a heat treatment step of heating the annealed fine powder at a heating rate of 5 to 20 ° C and heat - treating it at 850 to 950 ° C for 4 to 8 hours.

[0012]

In addition, a method for manufacturing a supercapacitor is provided, characterized in that the heat treatment step is performed in an inert gas atmosphere.

[0013]

In addition, the present invention provides a method for manufacturing a supercapacitor, characterized in that the electrode material slurry contains 60 to 96 wt% of the silicon oxycarbide.

[0014]

In addition, the present invention provides a method for manufacturing a supercapacitor, wherein the silicon oxycarbide has a diffraction peak of 20 to 30 ° .

[0015]

In addition, the present invention provides a method for manufacturing a supercapacitor, wherein the silicon oxycarbide has peaks at 1390 to 1430 cm^{- 1} and 1600 to 1700 cm^{- 1} when analyzed by FT - IR.

[0016]

In addition, a method for manufacturing a supercapacitor is provided, wherein the silicon oxycarbide has a Brunauer - Emmett - Teller (BET) surface area of 5.00 to 6.00 m²/g.

[0017]

In addition, the present invention provides a method for manufacturing a supercapacitor, wherein the silicon oxycarbide has an O/Si atomic ratio of 1 to 1.5 and a C/Si atomic ratio of 1.5 to 2.5 as confirmed by XPS analysis.

[0018]

In addition, the method for manufacturing a supercapacitor further includes a step of arranging a separator and a step of injecting an electrolyte after the step of manufacturing an electrode, and the method for manufacturing a supercapacitor is characterized in that the electrolyte includes TEABF₄ or Li₂SO₄.

[0019]

In order to solve the above another problem, the present invention provides a supercapacitor characterized by including two or more electrodes containing electrode materials including silicon oxycarbide, a conductive carbon material and a binder, a separator positioned between the electrodes, and an electrolyte.

[0020]

In addition, the supercapacitor is provided, characterized in that it has an energy density of 10 to 25 mJ/cm² and a power density of 5,000 to 20,000 W/kg.

[0021]

The present invention relates to a supercapacitor and a method for manufacturing the same, and can provide a supercapacitor and a method for manufacturing the same, which can exhibit excellent energy density and power density by including a silicon oxycarbide thin film layer.

[0022]

Figure 1 is a schematic diagram showing a method for producing a silicon - oxy - carbide (silicon oxycarbide) thin film layer through a carbon - thermal reaction between a siloxene sheet and a sodium alginate biopolymer at 900 ° C.

[0023]

Figure 2 shows TGA curves of siloxene, alginate and siloxene - alginate powder mixtures.

[0024]

Figure 3 is a TGA curve of a silicon oxycarbide thin film layer manufactured by carbon heat.

[0025]

Figure 4 is a drawing showing the physicochemical properties of a silicon oxycarbide thin film layer, wherein (A) is an X-ray photoelectron spectroscopy (XPS) measurement spectrum of siloxene, alginate-derived carbon, and a silicon oxycarbide thin film layer, (B) is a comparative XPS spectrum of the Si(2p) state in siloxene and silicon oxycarbide, (C) is a comparative XPS spectrum of the O(1s) state existing in siloxene, carbon, and silicon oxycarbide, and (D) is a comparative XPS spectrum of the C(1s) state existing in carbon and silicon oxycarbide.

[0026]

FIG. 5 is a diagram showing the physicochemical properties of a silicon oxycarbide thin film layer, wherein (A) is an X-ray diffraction pattern of silicon oxycarbide, (B) is a Fourier-transform infrared spectroscopy (FT-IR) spectrum of alginate-derived carbon and silicon oxycarbide, (C) is a Raman spectrum of the silicon oxycarbide thin film layer, (D) to (H) are high-resolution transmission electron microscope images of the silicon oxycarbide thin film layer obtained at various magnifications, (H) is a SAED pattern of the silicon oxycarbide thin film layer, and (I) to (L) are elemental maps of the silicon oxycarbide, wherein (I) is an overlay image, (J) is an elemental map of Si atoms, (K) is an elemental map of O atoms, and (L) is an elemental map of C atoms.

[0027]

Figure 6 shows the laser Raman spectra of siloxene sheets, alginate-derived carbon, and silicon oxycarbide thin film layers.

[0028]

Figure 7 is the N_2 adsorption-desorption isotherm curve of silicon oxycarbide powder.

[0029]

Figure 8 is a drawing showing the electrochemical analysis of a silicon oxycarbide electrode in 1 M Li_2SO_4 using a three-electrode battery, in which, in the cyclic voltammogram of the silicon oxycarbide electrode, (A) is a cyclic voltammogram according to the operating potential window of -1.0 to 1.0 V, (B) is a cyclic voltammogram according to the operating potential window of -1.0 to 0.0 V, (C) is a cyclic voltammogram according to the operating potential window of 0.0 to 1.0 V, (D) is a cyclic voltammogram according to the scan rate of 100 mVs⁻¹, (E) is a Nyquist plot of the silicon oxycarbide electrode, and (F) is a charge-discharge (CD) profile of the silicon oxycarbide electrode.

[0030]

Figure 9 is a diagram showing the electrochemical analysis of silicon oxycarbide symmetric supercapacitors (symmetric supercapacitors) using 1 M Li₂SO₄ and 1 M TEABF₄ electrolytes, where (A) is the cyclic voltammogram of 1 M Li₂SO₄ at a scan rate of 100 mV s⁻¹, (B) and (C) are the cyclic voltammograms of 1 M Li₂SO₄ at a scan rate of 5 to 500 mV s⁻¹, (D) is the effect of scan rate on the specific capacitance of silicon oxycarbide symmetric supercapacitors in 1 M Li₂SO₄, and (E) is the cyclic voltammogram of silicon oxycarbide symmetric supercapacitors in a scan rate of 200 mV s⁻¹ at different operating voltages of 0.0 to 2.0 V. Cyclic voltammograms of supercapacitors (F) and (G) Cyclic voltammograms of silicon oxycarbide symmetric supercapacitors using 1 M TEABF₄ and 1 M TEABF₄ at scan rates from 5 to 1,000 mVs⁻¹, (H) Effect of scan rate on the specific capacitance of silicon oxycarbide symmetric supercapacitors at 1 M TEABF₄, (I) and (J) Nyquist plots of silicon oxycarbide symmetric supercapacitors at 1 M Li₂SO₄ and 1 M TEABF₄, (K) Bode phase angle plots of silicon oxycarbide symmetric supercapacitors at 1 M Li₂SO₄ and 1 M TEABF₄, (L) 1 M Specific capacitance of silicon oxycarbide symmetric supercapacitors as a function of applied frequency at Li₂SO₄ and 1M TEABF₄,

[0031]

Figure 10 shows the specific capacitance of silicon oxycarbide symmetric supercapacitors for different operating potential windows recorded using cyclic voltammetry (CV) scans at a scan rate of 200 mVs⁻¹.

[0032]

Figure 11 is a diagram showing the electrochemical analysis of silicon oxycarbide symmetric supercapacitors in 1 M Li₂SO₄ and 1 M TEABF₄, where (A) and (B) are galvanostatic CD profiles of silicon oxycarbide symmetric supercapacitors as a function of applied current from 0.5 to 10 mA in 1 M Li₂SO₄ and 1 M TEABF₄, (C) is the effect of discharge current plotted on the specific capacitance of silicon oxycarbide symmetric supercapacitors in 1 M Li₂SO₄ and 1 M TEABF₄, and (D) and (E) are graphs showing the electrochemical properties of silicon oxycarbide symmetric supercapacitors plotted over 5,000 continuous charge-discharge cycles in 1 M Li₂SO₄ or 1 M TEABF₄. The cyclic stability of the supercapacitor, (F) is the rate capability of the silicon oxycarbide symmetric supercapacitor using 1M TEABF₄,

[0033]

271 Figure 12 (A) is a field-emission scanning electron microscope photograph of silicon oxycarbide, (B) is an overlay image of the silicon oxycarbide electrode before the electrochemical test, (C) is an image of the elemental distribution measurement of Si atoms present in the silicon oxycarbide electrode, (D) is an image of the elemental distribution measurement of O atoms present in the silicon oxycarbide electrode, (E) is an image of the elemental distribution measurement of C atoms present in the silicon oxycarbide electrode, (F) is an image of the elemental distribution measurement of F atoms present in the silicon oxycarbide electrode,

[0034]

282 Figure 13 (A) is a field-emission scanning electron micrograph of silicon oxycarbide, (B) is an overlay image of the silicon oxycarbide electrode before the electrochemical test, (C) is an image of the elemental distribution of Si atoms present in the silicon oxycarbide electrode after the cyclic test in 1 M Li₂SO₄, (D) is an image of the elemental distribution of O atoms present in the silicon oxycarbide electrode after the cyclic test in 1 M Li₂SO₄, (E) is an image of the elemental distribution of C atoms present in the silicon oxycarbide electrode after the cyclic test in 1 M Li₂SO₄, (F) is an image of the elemental distribution of S atoms present in the silicon oxycarbide electrode after the cyclic test in 1 M Li₂SO₄, and (G) is an image of the elemental distribution of F atoms present in the silicon oxycarbide electrode after the cyclic test in 1 M Li₂SO₄. Image of element distribution measurement in atoms,

[0035]

Figure 14 (A) is a field - emission scanning electron microscope image of silicon oxycarbide, (B) is an overlay image of the silicon oxycarbide electrode before the electrochemical test, (C) is an image of the elemental distribution measurement of Si atoms in the silicon oxycarbide electrode after the cyclic test in 1 M TEABF₄, (D) is an image of the elemental distribution measurement of O atoms in the silicon oxycarbide electrode after the cyclic test in 1 M TEABF₄, (E) is an image of the elemental distribution measurement of C atoms in the silicon oxycarbide electrode after the cyclic test in 1 M TEABF₄, (F) is an image of the elemental distribution measurement of N atoms in the silicon oxycarbide electrode after the cyclic test in 1 M TEABF₄, (G) is an image of the elemental distribution measurement of B atoms in the silicon oxycarbide electrode after the cyclic test in 1 M TEABF₄, and (H) is an image of the elemental distribution measurement of B atoms in the silicon oxycarbide electrode after the cyclic test in 1 M TEABF₄. Image of elemental distribution measurement of F atoms present in silicon oxycarbide electrode after cyclic testing at TEABF₄.

[0036]

Figure 15 is a Ragone plot of a silicon oxycarbide symmetric supercapacitor using 1M Li₂SO₄electrolyte.

[0037]

Figure 16 (A) is a Ragone plot of a silicon oxycarbide symmetric supercapacitor in TEABF₄, and (B) is a diagram showing a multi - function electronic display powered by a fully charged silicon oxycarbide of TEABF₄.

[0038]

Hereinafter, preferred embodiments of the present invention will be described in detail.

In explaining the present invention, if it is determined that a detailed description of a related known technology may obscure the gist of the present invention, the detailed description will be omitted.

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.

[0040]

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 No. 10 - 2053782), and all of the contents described in the above prior literature can be referenced in the present invention.

[0041]

In addition, the inventors of the present invention have conducted repeated research to further improve the energy density of supercapacitors, and as a result, have discovered that supercapacitors can exhibit excellent energy density and power density by including a silicon oxycarbide thin film layer, leading to the present invention.

[0042]

Accordingly, the present invention relates to a method for manufacturing a supercapacitor, including a reaction step of reacting siloxene and alginate to obtain silicon oxycarbide; a slurry preparation step of mixing the silicon oxycarbide, a conductive carbon material, and a binder to produce an electrode material slurry; and a thin film layer preparation step of coating the electrode material slurry on a substrate and drying it to produce a silicon oxycarbide thin film layer.

[0043]

Hereinafter, a method for manufacturing a supercapacitor according to the present invention will be described in detail.

[0044]

The above reaction step is a step of obtaining silicon oxycarbide by reacting siloxene and alginate.

[0045]

The above siloxene can be manufactured by immersing a precursor containing calcium silicide in an acid to dissolve calcium, and the acid can be a strong acid having a temperature of 4 ° C or lower, and preferably can be hydrochloric acid. In addition, it is advantageous to proceed with the reaction efficiently and obtain siloxene of the desired form by maintaining a temperature of 0 to 2 ° C. while vigorously mixing under the hydrochloric acid.

[0046]

385 The production of the above siloxene can be carried out for 40 to 96 hours, preferably for 60 to 80 hours, and the reaction can be carried out efficiently and relatively completely within the above time range, and if the time range is exceeded, the reaction is not complete, making it difficult to produce the desired siloxene.

[0047]

392 The manufacturing of the above siloxene can be checked to see the progress of the reaction as the black color of calcium silicide changes to the yellow color of siloxene. After the reaction is complete, the siloxene can be recovered by washing with water and ultrasonic waves, separating it from water, and then drying it (siloxene drying step).

397 During this cleaning process, ultrasound can be performed at 15 to 25 kHz.

398 In addition, the above drying (siloxene drying step) can be performed at a drying temperature of 60 to 90 ° C. for 6 to 20 hours, and in this case, drying can be performed efficiently without damaging the siloxene and removing the reaction residue.

[0048]

405 In the above reaction step, the weight ratio of the siloxene and the alginate may be 1:5 to 1:20, and preferably 1:10 to 1:15.

407 If it is out of the above range, it may be difficult to manufacture silicon oxycarbide, and in the present invention, the alginate may be sodium alginate, potassium alginate, magnesium alginate, triethanolamine alginate or propylene glycol alginate, and preferably sodium alginate.

[0049]

414 In addition, the reaction step may include a grinding step of grinding siloxene and alginate into fine powder; an annealing step of heating the fine powder at a heating rate of 1 to 5 ° C and annealing it at 180 to 220 ° C for 1 to 5 hours; and a heat treatment step of heating the annealed fine powder at a heating rate of 5 to 20 ° C and heat - treating it at 850 to 950 ° C for 4 to 8 hours.

[0050]

422 The above - mentioned pulverizing step is a step of pulverizing siloxene and alginate into a fine powder so that they are mixed, and the above - mentioned annealing step is a step of removing the influence of heat history and pores remaining in the

internal structure of siloxene and alginate, and the pulverized fine powder may be heated at a heating rate of 1 to 5 ° C and performed at 180 to 220 ° C for 1 to 5 hours, and preferably may be heated at a heating rate of 1 to 3 ° C and performed at 190 to 210 ° C for 1 to 3 hours.

[0051]

The above heat treatment step is a step for removing a functional group attached to the edge of siloxene and carbonizing the raw polymer to produce silicon oxycarbide. The heat treatment may be performed at 850 to 950 ° C for 4 to 8 hours by heating at a heating rate of 5 to 20 ° C, and preferably, the heat treatment may be performed at 880 to 920 ° C for 5 to 7 hours by heating at a heating rate of 5 to 15 ° C. If the above temperature and time conditions are exceeded during heat treatment, the functional group attached to the edge of siloxene may not be easily removed, and carbonization may not occur, making it difficult to manufacture silicon oxycarbide.

[0052]

The above heat treatment step can be performed in an inert gas atmosphere, and preferably can be performed in an argon (Ar) gas atmosphere.

[0053]

In the present invention, the slurry preparation step is a step of preparing an electrode material slurry by mixing silicon oxycarbide, a conductive carbon material, and a binder. The silicon oxycarbide may be silicon oxycarbide prepared by the method described above, and the characteristics of the silicon oxycarbide are described in detail below.

[0054]

The conductive carbon material may include at least one selected from carbon black, graphene, and carbon nanotubes, and the binder may include at least one selected from the group consisting of PVDF (Polyvinylidene Fluoride), PTFE (Polytetrafluoroethylene), PVA (Polyvinyl Alcohol), and SBR (Styrene Butadiene).

[0055]

The electrode material slurry may contain 60 to 96 wt% of the silicon oxycarbide, preferably, the electrode material slurry may include 70 to 96 wt% of the silicon oxycarbide, 2 to 15 wt% of the conductive carbon material, and 2 to 15 wt% of the binder, and more preferably and more specifically, the electrode material slurry may include 86 to 94 wt% of the silicon oxycarbide, 3 to 7 wt% of the conductive carbon material, and 3 to 7 wt% of the binder, and within the above range, the stability performance and capacity characteristics of the supercapacitor can be further improved.

[0056]

In the present invention, the thin film layer manufacturing step is a step of manufacturing a silicon oxycarbide thin film layer by coating an electrode material slurry on a substrate and drying it.

[0057]

The above thin film layer manufacturing step can be performed at a drying temperature of 60 to 90 ° C. for 6 to 20 hours, or at a drying temperature of 75 to 85 ° C. for 10 to 16 hours. In this case, a silicon oxycarbide thin film layer can be manufactured while maintaining the characteristics of silicon oxycarbide and having characteristics such as strength required for a supercapacitor electrode, and the silicon oxycarbide thin film layer can be used as an electrode of a supercapacitor.

[0058]

The method for manufacturing the above supercapacitor may further include a step of arranging a separator and a step of injecting an electrolyte after the step of manufacturing the thin film layer. At this time, the separator and the electrolyte may be applied if they are generally applied to a supercapacitor. For example, the electrolyte may include $TEABF_4$ or Li_2SO_4.

[0059]

In the present invention, the silicon oxycarbide may have the following characteristics.

The above silicon oxycarbide may have a diffraction peak of 20 to 30 ° , and may have peaks at 1390 to 1430 cm^{-1} and 1600 to 1700 cm^{-1} when analyzed by FT - IR (Fourier - transform infrared spectroscopy), and preferably may have peaks at 1400 to 1420 cm^{-1} and 1640 to 1670 cm^{-1}.

[0060]

Additionally, the silicon oxycarbide may have a Brunauer - Emmett - Teller (BET) surface area of 5.00 to 6.00 m²/g, and preferably 5.40 to 5.80 m²/g.

[0061]

Among the properties that can vary depending on the reaction conditions or methods in silicon oxycarbide that can be manufactured by various methods, the characteristics of the silicon oxycarbide of the present invention are shown.

[0062]

In addition, in the present invention, the silicon oxycarbide may have an O/Si atomic ratio of 1 to 1.5, preferably 1.2 to 1.4, as confirmed by XPS analysis, and a C/Si atomic ratio of 1.5 to 2.5, preferably 1.9 to 2.2, through which it can be seen that Si (silicon), O (oxygen), and C (carbon) are homogeneously distributed within the silicon oxycarbide thin film layer.

[0063]

According to another aspect of the present invention, a supercapacitor is disclosed, characterized by including two or more electrodes containing an electrode material including silicon oxycarbide, a conductive carbon material and a binder, a separator positioned between the electrodes, and an electrolyte.

[0064]

In the present invention, the silicon oxycarbide may have the following characteristics.

The above silicon oxycarbide may have a diffraction peak of 20 to 30 ° , and may have peaks at 1390 to 1430 cm⁻¹ and 1600 to 1700 cm⁻¹ when analyzed by FT-IR (Fourier-transform infrared spectroscopy), and preferably may have peaks at 1400 to 1420 cm⁻¹ and 1640 to 1670 cm⁻¹.

[0065]

Additionally, the silicon oxycarbide may have a Brunauer-Emmett-Teller (BET) surface area of 5.00 to 6.00 m²/g, and preferably 5.40 to 5.80 m²/g.

[0066]

Among the properties that can vary depending on the reaction conditions or methods in silicon oxycarbide that can be manufactured by various methods, the characteristics of the silicon oxycarbide of the present invention are shown.

[0067]

When the silicon oxycarbide according to the present invention is applied as an electrode material, it can provide excellent performance in terms of stability and electrostatic capacity.

[0068]

The supercapacitor according to the present invention can have an energy density of 10 to 25 mJ/cm², preferably 12 to 22 mJ/cm², and can have a power density of 5,000 to 20,000 W/kg, preferably 6,000 to 18,000 W/kg. This is a much higher value compared to other silicon - based symmetric supercapacitor devices, such as siloxene, SiC nanowires, and silicon nanotris, which were used as conventional electrodes.

[0069]

In the experimental results of the present invention, the inventors of the present invention investigated in detail the supercapacitor characteristics of silicon oxycarbide, and confirmed the characteristics of a silicon oxycarbide - based symmetric supercapacitor applicable in a wide voltage range of 2.0 V or 3.0 V.

[0070]

In addition, the silicon oxycarbide symmetric supercapacitor device showed excellent cyclic stability in which more than 86% of the capacitance was maintained even after more than 5,000 charge - discharge cycles. These experimental results of the present invention show that the electrode material of the present invention has high energy density, excellent capacitance - to - capacitance ratio, and excellent cyclic stability when applied to a supercapacitor, and thus has great utility as a material for improving the characteristics of a supercapacitor.

[0071]

In the present invention, the electrostatic capacitance was calculated according to the following mathematical equations 1 and 2.

[0072]

[Mathematical Formula 1]

[0073]

C = ∫Idv/(S X M X △V)

[0074]

[Mathematical formula 2]

[0075]

C = (I X T_d) / (M X △V)

[0076]

In the above mathematical expressions 1 and 2,

[0077]

C is the capacitance (F g⁻¹), I is the discharge current (A), T_d is the time required for discharge (sec), M is the mass of the electroactive material (g), s is the scan rate (mV s⁻¹), and △V is the potential window (V).

[0078]

In the present invention, the energy density and power density were calculated according to the following mathematical equations 3 and 4.

[0079]

[Mathematical Formula 3]

[0080]

E = [C X △V²] / 2

[0081]

[Mathematical Formula 4]

[0082]

P = E / T_d

[0083]

In the above mathematical equations 3 and 4, E and P are the energy and power density of the supercapacitor device, C is the capacitance, △V is the potential window, and T_d is the discharge time (seconds).

[0084]

In the present invention, the capacitance of the device with respect to frequency was calculated using EIS analysis according to the following mathematical expression 5.

[0085]

[Mathematical Formula 5]

[0086]

C = 1/2πfz

[0087]

In the above mathematical expression 5, C is the capacitance of the device, f is the applied frequency, and z is a virtual plot of impedance.

[0089]

Hereinafter, specific examples according to the present invention will be described.

[0091]

Materials and Experimental Methods

[0092]

Calcium silicide (CaSi₂) precursor was purchased from Kojundo Chemical Research Institute, Japan.

Polyvinylidene fluoride (PVDF) was purchased from Sigma-Aldrich, Korea.

685 Tetraethylammonium tetrafluoroborate (TEABF₄) was purchased from Alfa Aesar Chemicals, Korea.
685 Hydrochloric acid (HCl), carbon black, acetonitrile, and N-methyl-2-pyrrolidone (NMP) were purchased from Daejung Chemical Co., Ltd. (Korea).
689 Ultrasonic investigations were performed on a VCX 750 ultrasonicator (Sonics and Materials, Inc, USA, 20 kHz, 750 W) using a direct-immersion titanium horn.

[0093]
694 The phase and crystallinity of the silicon oxycarbide thin film layers were determined using an X-ray diffractometer system (Empyrean) with Cu-Kα radiation (λ=1.5418Å).
697 The surface area of the manufactured silicon oxycarbide was measured using UPA-150, ASAP2010, and AutoporeIV of KBSI Jeonju Center.
699 The functional groups of siloxene, alginate-derived carbon and silicon oxycarbide were investigated using FT-IR spectroscopy (Thermo supercapacitor-oriented FT-IR spectrometer (Nicolet 6700)).
702 Raman spectra were obtained using a LabRam HR Evolution Raman spectrometer (Horiba Jobin-Yvon, France).
704 The chemical states of elements in siloxene, alginate-derived carbon and silicon oxycarbide were determined by X-ray photoelectron spectrometry (E-Supercapacitor A-2000, VG Microtech Ltd.).
707) was analyzed.
708 Surface morphology and element distribution measurements were analyzed using a high-resolution transmission electron microscope (JEM-2011, JEOL).

[0095]
713 Example

[0096]
717 1. Silicon oxycarbide (silicon oxycarbide) manufacturing

[0097]
721 Siloxene was prepared through the topochemical reaction of CaSi₂ using cold hydrochloric acid.
723 Briefly, 1 g of finely ground CaSi₂powder was immersed in HCL with vigorous stirring at 0 ° C for four days.
725 A color change from black CaSi₂ to yellow-green is observed, indicating that Ca dissolves slowly in HCL.

After the reaction was completed, the green siloxene was separated through a centrifugal separation process using acetone and water. The powder thus separated was immersed in 100 mL of water and then ultrasonicated for one hour. Afterwards, the green siloxene was separated by centrifugation and dried at 80 ° C for 12 hours.

[0098]

The above siloxene (0.4 g) and sodium alginate (5 g) were ground into a fine powder and annealed at 200 ° C for 2 hours at a heating rate of 2 ° C. Next, the temperature was increased to 900 ° C at a rate of 10 ° C, heat - treated in an Ar atmosphere for 6 hours, and then cooled to room temperature to produce silicon oxycarbide.

[0100]

2. Manufacturing of silicon oxycarbide thin film layer (working electrode)

[0101]

A homogeneous slurry was prepared by pulverizing 5 wt% carbon black, 5 wt% polyvinylidene fluoride (PVDF), and 90 wt% silicon oxycarbide dispersed in N - methyl - 2 - pyrrolidone (NMP) using a mano mortar and pestle, and the homogeneous slurry was coated on an aluminum (Al) substrate (aluminum foil) using a doctor blade to secure a uniform electrode thickness, and then the coated slurry was dried in a vacuum oven at 80 ° C to evaporate the solvent. After drying, the silicon oxycarbide electrode - coated aluminum foil was pressed on a rolling press machine (WCRP - 1015G) and the electrode was cut into a circle with a diameter of 14 mm for the manufacture of coin cells to produce a silicon oxycarbide thin film layer.

[0102]

Additionally, for the three - electrode test, a silicon oxycarbide thin film layer was fabricated using a stainless steel substrate (1x1 cm²) instead of aluminum foil.

[0104]

3. Fabrication of coin - type symmetric supercapacitor devices

[0105]

A symmetric supercapacitor device based on silicon oxycarbide was fabricated as a coin cell (CR2032) using silicon oxycarbide thin film layers (using aluminum foil) as electrodes separated by Celguard membranes and 1 M $TEABF_4$ as electrolyte. The fabricated device was crimped using an Electric Coin Cell Crimping and Disassembling Machine (MTI Korea). Electrolyte and coin cell device fabrication was performed inside a glove box with a humidity of 1 ppm and below air.

[0106]

Additionally, a coin-cell symmetric supercapacitor device was fabricated using 1 M Li_2SO_4 as the electrolyte core and a silicon oxycarbide thin film layer using a stainless steel substrate (1x1 cm^2).

[0107]

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 silicon oxycarbide symmetric supercapacitor devices were performed using an Autolab PGSTAT302N electrochemical terminal.

[0109]

Experimental Results

[0110]

Figure 1 shows the fabrication of a silicon oxycarbide thin film layer using a carbon-thermal reaction at high temperature. Siloxene (prepared via topochemical de-intercalation of calcium from $CaSi_2$) and sodium alginate were used as silicon and carbon precursors for the production of silicon oxycarbide/carbon ceramics. Siloxene sheets and sodium alginate were mixed and heated at 900 ° C to produce black silicon oxycarbide ceramic. To understand the formation mechanism of silicon oxycarbide, thermogravimetric analysis (TGA) was performed on siloxene, alginate (sodium alginate), and a mixture of siloxene and alginate (sodium alginate) powders, as shown in Fig. 2. The TGA thermogram of siloxene (Fig. 2) shows high thermal stability up to 900 °C. In contrast, the thermogram of alginate (sodium alginate) is characterized by three steps: (i) removal of OH- and CO- groups at 220 °C, (ii) carbonization starting at 270 °C, and (iii) complete conversion of alginate to carbon at 900 °C. Thermograms of powders containing a mixture of siloxene and alginate (sodium alginate) were similar to bare alginate (sodium alginate) except that the residual weight percentage was higher. The manufactured silicon oxycarbide powder was thermally stable up to 900 °C (see Fig. 3). Carbon-thermally produced silicon oxycarbide powders were characterized using X-ray photoelectron spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy, and high-resolution transmission electron microscopy along with elemental mapping analysis.

[0111]

Figure 4A shows X-ray photoelectron spectroscopy (XPS) measurements of siloxene, alginate-derived carbon, and silicon oxycarbide thin film layers. The presence of peaks corresponding to Si, O and C at 103, 530 and 284 eV, respectively, in the XPS spectrum of silicon oxycarbide indicates the carboxylothermal conversion of siloxene and alginate to silicon oxycarbide nanostructures. To elucidate the chemical states of the elements in the manufactured silicon oxycarbide, the core-level spectra of Si, O, and C were compared with those obtained from pristine siloxene and alginate-derived carbon, as shown in Figure 4(B-D). Comparison of the Si(2p) state of the exposed siloxene sheet and the silicon oxycarbide thin film layer in Figure 4B shows that the chemical state of Si has changed after the carbothermal reaction. The Si(2p) spectrum of siloxene (Fig. 4B, bottom) contains two peaks at 99 and 103 eV, which correspond to the Si-Si bonding and oxygenation/hydrogenation functions of siloxene, respectively. Interestingly, the carbothermal reaction and conversion of siloxene into silicon oxycarbide thin films was found to significantly change the bonding environment of Si. New bonding between Si, O, and C in the silicon oxycarbide thin film layer results in a Si(2p) state similar to that found in silicon oxycarbide. After carbothermal reaction, the disappearance of Si-Si bonds indicated by the XPS peak at 99 eV indicates that the siloxene-inserted groups in siloxene are converted to O-Si-O-C groups in silicon oxycarbide. The Si(2p) spectrum of the carbon-thermally prepared silicon oxycarbide thin film layer (shown in the upper part of Fig. 4B) shows the presence of four different chemical states, namely, SiO₃C, SiO₂C₂, SiOC₃, and SiO_x, indicated by peaks at 102.7, 101.8, 101.05, and 103.45 eV, respectively.

857 The O(1s) spectra of exposed siloxene, pristine carbon, and silicon oxycarbide thin film layers were examined in detail to evaluate the changes in oxygen bonding levels in the silicon oxycarbide thin film layers.

865 The O(1s) spectrum of the siloxene sheet (Fig. 4C, bottom) contains two peaks at 532.5 and 533.5 eV, corresponding to the Si-O₂ and Si-O_x states, respectively.

868 The peaks at 532.7 and 533.8 eV in the O(1s) spectrum of alginate-derived carbon (Fig. 2C, middle) indicated the presence of C-OH and C=O groups, respectively.

870 The O(1s) spectrum of the silicon oxycarbide thin film layer in Figure 4C (top) shows that significant changes occurred during the carbothermal reaction.

872 532.5, 533.7 The peaks at and 534.85 eV indicate the formation of C=O, Si-O₂, and Si-O_x groups, respectively, suggesting the conversion of siloxene to a silicon oxycarbide thin film layer.

875 The C(1s) spectrum of raw carbon (Fig. 4D, bottom) contains peaks corresponding to C–C, C=C, and C–O bonds at 284.5, 285.2, and 290.5 eV, respectively.

877 In contrast, the C(1s) spectrum of silicon oxycarbide (Fig. 4(D), top) contains peaks at 283.76, 284.47, 285.06, and 288.74 eV, indicating the presence of C-Si, C-C, C=C, and C-O groups.

880 This analysis also confirmed the formation of a silicon oxycarbide thin film layer through the carbothermal reaction between siloxene and alginate powder.

882 The atomic composition of silicon oxycarbide produced by carbon heating is 22.85:29.22:47.93 (Si:O:C).

[0112]

887 Figure 5A shows an X-ray diffractogram of a silicon oxycarbide thin film layer manufactured by carbon heating.

889 The presence of a broad diffraction peak of about 20 to 30° indicates the formation of amorphous silicon oxycarbide powder.

891 The amorphous nature of the silicon oxycarbide powder originates from the disordered carbon phase of silicon oxycarbide; the diffraction pattern is almost identical to that of silicon oxycarbide prepared by thermal decomposition of polyphenylsesquisiloxane and calcination of tetraethyl orthosilicate.

895 Figure 5B compares the Fourier-transform infrared spectroscopy (FT-IR) spectra of exposed siloxene, alginate-derived carbon, and silicon oxycarbide.

897 The spectrum of exposed siloxene has peaks at 452, 867, 1,034, 1,639, and 2,140 cm⁻¹, corresponding to (Si-Si), (Si-H), (Si-O-Si), (Si-OH), and

(OSi₂≡Si - H) vibrations, respectively.

These functionalities indicate the formation of Kautsky - type siloxenes via topochemical removal of calcium from CaSi₂.

The FT - IR spectrum of raw carbon (derived from pyrolysis of alginate) contains a weak band at 1,014 cm^{- 1}, which can be attributed to the presence of carbonyl groups (C - O).

The FT - IR spectrum of silicon oxycarbide is significantly different from those of siloxene and carbon. (i) The vibrational bands corresponding to Si - H, Si - OH, and OSi₂≡Si - H groups of siloxene were absent in the FT - IR spectrum of silicon oxycarbide. (ii) The intensity of the Si - Si band of silicon oxycarbide was significantly lower than that of bare siloxane. (iii) The spectrum of silicon oxycarbide contained two new bands at 1,409 and 1,655 cm^{- 1} corresponding to (Si - O - C) and (C=O) groups of silicon oxycarbide.

These changes further confirm the formation of silicon oxycarbide via carbon - thermal reaction.

[0113]

The Raman spectrum of silicon oxycarbide powder in Fig. 5C has peaks at 376, 590, 962, 1,345, and 1,568 cm^{- 1}.

376 And the band observed at 590 cm^{- 1} originates from the Si - O_x bond of silicon oxycarbide. The band at 962 cm^{- 1} is associated with the LO mode of Si - O.

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,345 and the bands at 1,570 cm^{- 1} correspond to the D and G bands of carbon in silicon oxycarbide, respectively.

[0114]

Raman spectra of silicon oxycarbide, siloxene sheets, and alginate - derived carbon are compared in Fig. 6.

Figure 5(D - H) shows high - resolution transmission electron spectroscopy (HR - TEM) micrographs of silicon oxycarbide powder, showing the presence of a thin - film layer - like structure with irregular lateral dimensions.

Micrographs of the 5G show crumpled edges of silicon oxycarbide, which may be a side effect of the high - temperature reaction.

The inset in Figure 5G depicts a selected area electron diffraction (SAED) pattern of silicon oxycarbide, which shows a characteristic halo pattern indicating the amorphous nature of the silicon oxycarbide thin film layer.

To understand the distribution of Si, O, and C atoms in silicon oxycarbide, elemental distribution measurements were performed while obtaining HR-TEM micrographs (Fig. 5H), and these distribution measurements are shown in Fig. 5(I-K), respectively.

C, O, and Si atoms are homogeneously distributed throughout the thin-film-like sheets, suggesting a molecular-level transformation of siloxene into silicon oxycarbide.

Figure 7 shows that the N₂ adsorption-desorption isotherm of silicon oxycarbide is very close to a typical type II isotherm, indicating the formation of a monolayer on a macroporous surface at low pressure.

The Brunauer-Emmett-Teller (BET) surface area of the fabricated silicon oxycarbide sample was 5.64 m²g⁻¹, which is comparable to those of silicon oxycarbides derived from pyrolyzed polymethylphenyl silsesquioxane (1.8 and 4.3 m²g⁻¹, respectively).

[0115]

To investigate the charge storage capacity of individual silicon oxycarbide electrodes, three electrode analyses were performed using Li₂SO₄electrolytes and are presented in Fig. 8.

Figure 8A shows cyclic voltammograms obtained for the silicon oxycarbide electrode at various scan rates (5–100 mVs⁻¹) from -1.0 to +1.0 V.

The rectangular shape of the generated voltage curves is consistent with type A behavior, which indicates capacitive or pseudocapacitive characteristics of silicon oxycarbide electrodes.

Therefore, the charge storage mechanism in the silicon oxycarbide electrode may be attributed to the combination of double layer capacitance from the carbon component of silicon oxycarbide and intercalation capacitance from the Si-Si and/or Si-O components.

Additionally, no redox peak was observed in any voltage curve, indicating no faradaic process at the silicon oxycarbide electrode.

Figures 8(B and C) show the ideal polarization characteristics of the silicon oxycarbide electrode in the positive and negative voltage regions, respectively, and both electrodes provide typical rectangular voltage curves.

The cyclic voltammograms provided in Figure 8D demonstrate that the silicon oxycarbide electrode can function as both positrode and negatrode in electrochemical energy storage (EES) devices.

Electrochemical impedance spectroscopy (EIS) measurements were performed with silicon oxycarbide electrodes to elucidate the capacitive characteristics and fundamental charge transfer modes at the electrode surface.

Figure 8E shows the Nyquist plot obtained with a silicon oxycarbide electrode, indicating the presence of solution resistance (Rs 2.488Ω) and charge transfer resistance (Rct 1.19Ω) with additional Warburg impedance.

The Warburg lines observed in the low - frequency region are closer to the imaginary axis of impedance and represent the capacitive characteristics of the silicon oxycarbide electrode.

Figure 8F provides galvanostatic charge and discharge (CD) profiles of the silicon oxycarbide electrode from - 1.0 to +1.0 V recorded over various current ranges from 1.0 to 25.0 mA.

The shape of the CD profile is quasi - triangular without a plateau region, which matches well with Fig. 8A, indicating that the observed capacitance is due to a combination of double layer formation and pseudocapacitance.

[0116]

In general, electrochemical studies utilizing a two - electrode configuration are well suited for evaluating the performance of supercapacitors and distinguishing electrode characteristics from device characteristics.

Herein, symmetric supercapacitor devices using two ideal silicon oxycarbide electrodes were fabricated using the following two electrodes: (i) aqueous Li₂SO₄ (beaker - type cell) or (ii) organic TEABF₄ (CR2032 coin - type cell).

[0117]

Based on the above three - electrode analysis, these silicon oxycarbide symmetric supercapacitor devices are considered to be able to operate within the operating voltage window (OVW) of 2.0 V in Li₂SO₄electrolyte, while the TEABF₄electrolyte extends the OVW to 3.0 V.

[0118]

Figure 9(A - D) shows the electrochemical characteristics of silicon oxycarbide symmetric supercapacitors obtained from Li₂SO₄electrolyte.

The cyclic voltammograms in Fig. 9A show that the silicon oxycarbide symmetric supercapacitor can operate within an OVW of 2.0 V without any sign of gas evolution due to the neutral nature of Li₂SO₄ (acidic and basic electrolytes tend to have limited OVW).

[0119]

Figures 9B and 9C show the cyclic voltammograms obtained in Li₂SO₄electrolytes at various scan rates (5 to 500 mVs^{- 1}), respectively.

1028 Figures 9B and 9C show cyclic voltammograms obtained in Li₂SO₄electrolytes at various scan rates (5 to 500 mVs⁻¹), respectively.

1028 The rectangular shape of the voltage curve represents the ideal capacitance characteristics of the electrode.

1033 Figure 9D shows the effect of scan rate on the specific capacitance of a single silicon oxycarbide electrode (obtained using C_{전극} = 4 x C_{장치}) and the silicon oxycarbide symmetric supercapacitor device. At a low scan rate of 5 mV s⁻¹, the silicon oxycarbide device exhibits a high device specific capacitance of 35.26 Fg⁻¹, from which the capacitance of the single electrode can be calculated to be 141.07 Fg⁻¹.

[0120]

1043 To determine the OVW of silicon oxycarbide symmetric supercapacitors in TEABF₄ electrolyte, periodic voltage curves were acquired at different OVWs (0.0 to 3.0) at a scan rate of 200 mVs⁻¹, as shown in Fig. 9E.

1047 The cyclic voltammetry curves show the presence of a rectangular curve even at an OVW of 3.0 V, indicating better capacity characteristics of silicon oxycarbide symmetric supercapacitors in TEABF₄ electrolyte with stable and large OVW compared to aqueous electrolyte.

[0121]

1054 The specific capacitance of the silicon oxycarbide symmetric supercapacitor in TEABF₄ (Fig. 10) increased from 2.51 to 7.02 Fg⁻¹ as the OVW increased from 0.5 V to 3.0 V.

1057 Figures 9F and 9G show rectangular voltage curves obtained with silicon oxycarbide symmetric supercapacitors at various scan rates from 5 to 1,000 mVs⁻¹, which represents an ideal capacitor.

1060 The effect of scan rate on the specific capacitance of silicon oxycarbide symmetric supercapacitors is summarized in Fig. 9H. A device specific capacitance of about 28.82 Fg⁻¹ was obtained from the CV recorded at a scan rate of 5 mVs⁻¹.

1064 The corresponding capacitance of a single silicon oxycarbide electrode was 115.30 Fg⁻¹.

[0122]

1069 The Nyquist plots obtained for silicon oxycarbide symmetric supercapacitors using

Li₂SO₄ and TEABF₄ electrolytes are shown in Figures 9I and 9J, respectively.

1071 The Nyquist plot clearly shows three distinct regions corresponding to (i) high frequency, (ii) medium frequency, and (iii) low frequency regions of impedance.

1075 The solution resistances of silicon oxycarbide symmetric supercapacitors using Li₂SO₄ and TEABF₄ electrolytes were 1.36 and 2.5 Ω, respectively, as measured from the high-frequency region of the Nyquist plot.

1079 The charge transfer resistance of the silicon oxycarbide symmetric supercapacitor was about 3.89Ω for the Li₂SO₄electrolyte and 16.10Ω for the TEABF₄electrolyte.

1082 The higher solution and charge-transfer resistance for silicon oxycarbide symmetric supercapacitors using TEABF₄electrolyte is attributed to the lower ionic conductivity and higher ionic radius of TEABF₄ compared to Li₂SO₄electrolyte.

[0123]

1089 Additionally, the low-frequency region indicates the presence of Warburg diffusion, which is closely related to the diffusion-mediated capacitance of symmetric supercapacitors.

1092 Notably, the magnitude of the Warburg line is lower for Li₂SO₄ than for TEABF₄, which is due to the differential ion diffusion kinetics of these electrolytes.

1095 Figure 9K shows the Bode phase angle plot of silicon oxycarbide symmetric supercapacitors with Li₂SO₄ and TEABF₄ electrolytes showing the variation of phase angle as a function of applied frequency.

1099 0.01 At Hz, the phase angles of silicon oxycarbide were -85.04° and -64.61° for Li₂SO₄ and TEABF₄ electrolytes, respectively.

1102 The capacitor response frequency (f_o) at a phase angle of -45° determined from the Bode phase angle plots shown in Fig. 9K was 0.83 and 0.43 Hz for the Li₂SO₄ and TEABF₄ systems, respectively, and the relaxation times were 1.20 and 2.27 s.

1106 Figure 9L shows the device specific capacitance of silicon oxycarbide symmetric supercapacitors using Li₂SO₄ and TEABF₄ electrolytes with respect to the applied frequency.

1109 In both cases, the device specific capacitance decreases with increasing frequency and high device capacitances of 21.2 and 9.01 Fg⁻¹ were obtained at 0.01 Hz for silicon oxycarbide symmetric supercapacitors with Li₂SO₄ and TEABF₄ electrolytes.

[0124]

Figures 11A and 11B show the galvanostatic CD profiles of the fabricated silicon oxycarbide symmetric supercapacitor devices at different levels of utilized current using Li₂SO₄ (OVW 2.0 V) and TEABF₄ (OVW 3.0 V) electrolytes.

[0125]

The CD profile obtained at high current is a coarse symmetric profile and is more symmetric than the CD profile obtained at low current. These data demonstrate the role of surface and insertion capacitance in silicon oxycarbide electrodes. The effect of the applied current range on the device specific capacitance is shown in Figure 11C. The silicon oxycarbide symmetric supercapacitors delivered device specific capacitances of 25.58 and 16.71 Fg⁻¹, respectively, determined from discharge profiles recorded at a current of 0.5 mA for devices including Li₂SO₄ and TEABF₄. The device specific capacitance obtained with Li₂SO₄ was higher than that obtained with TEABF₄ due to the higher ionic conductivity of aqueous Li₂SO₄ and the lower ionic radius (about 0.06 nm) of Li⁺ ions. The ionic radius of TEA_NER210 ion is about 0.343 nm, but it remains functional over a relatively wide OVW of 3.0 V. Figures 11D and 11E illustrate the cyclic stability of silicon oxycarbide devices over 5,000 consecutive CD cycles. Interestingly, the device containing TEABF₄electrolyte exhibited higher capacitance retention (about 92.8%) compared to the Li₂SO₄based symmetric supercapacitor (86.2%).

[0126]

FE-SEM and elemental distribution measurements of silicon oxycarbide electrodes are shown before (Fig. 12) and after electrochemical testing in 1 M Li₂SO₄ (Fig. 13) and 1 M TEABF₄ (Fig. 14). 5,000 No structural changes were observed in any of the silicon oxycarbide electrode systems after continuous CD cycling. Elemental distribution measurements of the as-fabricated silicon oxycarbide electrodes (Fig. 12(B-F)) indicated that the presence of Si, O, C, and F atoms originated from the silicon oxycarbide active material and PVDF binder. The silicon oxycarbide electrode cycle using Li₂SO₄ (Fig. 13(B-G)) contained S atoms derived from the sulfate anion of the electrolyte. The silicon oxycarbide electrode cycling using TEABF₄ showed the presence of N, F, and B atoms uniformly distributed on the surface, as shown in Fig. 14(B-H).

[0127]

These data demonstrate the structural stability of silicon oxycarbide electrodes after uninterrupted CD cycling in both aqueous and organic electrolytes. To investigate the rate capability of silicon oxycarbide symmetric supercapacitors in TEABF₄electrolyte, continuous CD profiles were recorded at various levels from low to high current and vice versa, as shown in Fig. 11F. The electrodes exhibited excellent capacitance retention for different applied currents, highlighting the rate performance of silicon oxycarbide symmetric supercapacitors.

[0128]

Energy/power density is often a critical parameter that determines the practical applications of symmetric supercapacitor devices. The energy/power performance metrics of TEABF₄based silicon oxycarbide symmetric supercapacitors were determined from CD analysis and are presented as Ragone plots in Fig. 16. Similar data for the Li₂SO₄based system are shown in Fig. 15. The Li₂SO₄based system yielded an energy density of 14.2 Wh kg⁻¹ with a corresponding power density of 333 Wkg⁻¹ at a constant current of 0.5 mA. As the current increased to 10 mA, the silicon oxycarbide symmetric supercapacitor exhibited a maximum power density of 333 Wkg⁻¹ at an energy density of 9.61 Wh kg⁻¹.

[0129]

In contrast, the energy density of the silicon oxycarbide symmetric supercapacitor fabricated with TEABF₄ was as high as 20.89 Wh kg⁻¹, and the corresponding power density at a constant current of 0.5 mA was 750 W kg⁻¹. Additionally, the silicon oxycarbide symmetric supercapacitor fabricated with TEABF₄ maintained an energy density of 3.79 Wh kg<sup>-

1</sup> at a current of 10 mA and a power density of 15,000 W kg⁻¹.

[0132]

Tables 1 and 2 above compare the gravimetric and areal measurements of state-of-the-art supercapacitors using organic/ionic liquid electrolytes with silicon oxycarbide symmetric supercapacitor devices. The energy density of silicon oxycarbide symmetric supercapacitors using TEABF₄ electrolyte is higher than that of recently reported symmetric supercapacitors fabricated with activated carbon (8 Wh kg⁻¹), porous carbon (11.4 Wh kg⁻¹), graphene (16.5 Wh kg⁻¹), reduced graphene oxide, (17.7 Wh kg⁻¹), rGO (9.4 Wh kg⁻¹), coPIL-RGO (14.7 Wh kg⁻¹), Ti₃C₂Tx/MWCNT (3 Wh kg⁻¹), siloxene (5 Wh kg⁻¹)), 2D-MoS₂ (18.43 Wh kg⁻¹), and commercial supercapacitors. It was high. In addition, the power density of silicon oxycarbide symmetric supercapacitors reached up to 15,000 W kg⁻¹, indicating their suitability as power sources for next-generation automobiles. The data in Table 1 above provide evidence for the superior power performance of silicon oxycarbide symmetric supercapacitors compared to other supercapacitor systems using electrodes such as graphene, rGO, coPIL-RGO, MoS₂, MXene, and siloxene.

[0133]

The data in Table 2 show that the areal energy-power performance index of silicon oxycarbide symmetric supercapacitors is higher than that of other silicon-based symmetric supercapacitors.

[0134]

Figure 16B shows a real-time application of silicon oxycarbide symmetric supercapacitors to power a multi-function electronic display that indicates ambient temperature and relative humidity. The silicon oxycarbide symmetric supercapacitors were initially charged to 3.0 V using an applied current of 1 mA. The stored energy is sufficient to power an electronic display for more than 12 minutes, demonstrating the potential applications of silicon oxycarbide symmetric supercapacitors.

[0136]

In this way, the supercapacitor according to the present invention and the manufacturing method thereof can provide a supercapacitor exhibiting excellent energy density and power density by including a silicon oxycarbide thin film layer and a manufacturing method thereof, and accordingly, it can be seen that the supercapacitor according to the present invention is useful for the development of a high - performance energy storage device.

[0138]

The preferred embodiments of the present invention have been described in detail above.

The description of the present invention is for illustrative purposes only, and those skilled in the art will appreciate that other specific modifications can be easily made without changing the technical spirit or essential characteristics of the present invention.

[0139]

Accordingly, the scope of the present invention 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 invention.