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## DESCRIPTION WO2021261775A1

11 Verification method for monitoring charge - storage in self - charging supercapacitors including piezoelectric fibers and method for manufacturing the supercapacitor

## [0001]

16 The present invention relates to a self - charging supercapacitor and a method for manufacturing the same, and more particularly, to a method for manufacturing a self charging supercapacitor based on siloxane including piezoelectric fibers and a verification method for monitoring charge - storage in a self - charging supercapacitor.

## [0002]

23 The increasing energy demands of everyday life and the declining fossil fuel resources worldwide have driven the demand for the development of advanced energy collection, conversion and storage devices.

## [0003]

29 Energy devices operate through independent mechanisms for collection (nanogenerators, solar cells), conversion (photovoltaics, optoelectronics, electrochemical converters), and storage (batteries and supercapacitors) applications.

## [0004]

<sup>35</sup> To solve the energy crisis, combinations of solar cells, nanogenerators, and fuel cells with supercapacitors or batteries through external and/or proprietary integrated systems have been recently studied by various research groups.

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## [0005]

- 41 Native integration has advantages over external integration, as external integration requires complex power management systems that incur additional manufacturing costs.
- <sup>44</sup> To date, inherently integrated energy devices that can collect, convert, and store electrical energy in a single device have attracted great attention in basic scientific research and product development due to their multifunctional device design and concept.

## [0006]

51 Among the various types of intrinsically integrated energy devices reported so far, self - charging power cells (SCPCs) and self - charging supercapacitor power cells (SCSPCs) utilizing the piezoelectric concept are of major interest, but have the problem of low self - charging efficiency or index.

## [0007]

58 The present invention has been made to solve the problems of the prior art, and provides a self - charging supercapacitor with improved self - charging efficiency and a method for manufacturing the same.

## [0008]

64 In order to solve the above problems, the present invention provides a method for manufacturing a self - charging supercapacitor, including a step of manufacturing a siloxene sheet electrode; and a step of manufacturing a siloxene - PVDF piezoelectric fiber.

## [0009]

In addition, the siloxene sheet electrode manufacturing step includes a step of obtaining siloxene by immersing a precursor containing calcium silicide in an acid to dissolve calcium; a siloxene drying step of drying the siloxene; a coating solution manufacturing step of dispersing the siloxene and PVDF (Polyvinylidene Fluoride) powder in an N - methyl - 2 - pyrrolidone (NMP) solvent; and a coating step of coating the coating solution on the surface of a carbon fabric, thereby providing a method for manufacturing a self - charging supercapacitor.

## [0010]

*<sup>80</sup>* In addition, a method for manufacturing a self - charging supercapacitor is provided, characterized in that the acid is a strong acid having a temperature of 4 ° C or lower.

## [0011]

86 In addition, the method for manufacturing a self - charging supercapacitor is provided, characterized in that the coating solution manufacturing step comprises mixing siloxene and the PVDF powder in amounts of 80 to 99 wt% and 1 to 20 wt%, respectively, and dispersing them in an N - methyl - 2 - pyrrolidone (NMP) solvent.

## [0012]

93 In addition, the method for manufacturing a self - charging supercapacitor is provided, characterized in that the siloxene - PVDF piezoelectric fiber manufacturing step includes a step of obtaining siloxene by immersing a precursor containing calcium silicide in an acid to dissolve calcium; a siloxene drying step of drying the siloxene; a dispersion manufacturing step of dispersing the siloxene in a PVDF solution to produce a dispersion; and a piezoelectric fiber manufacturing step of electrospinning the dispersion to produce siloxene - PVDF piezoelectric fibers.

## [0013]

103 In addition, the method for manufacturing a self - charging supercapacitor further includes an electrolyte injection step after the siloxene - PVDF piezoelectric fiber manufacturing step, and the method for manufacturing a self - charging supercapacitor is characterized in that the electrolyte is a gelled electrolyte containing TEABF<sub>4</sub>.

## [0014]

In order to solve the above other problems, the present invention provides a self charging supercapacitor including a positive electrode and a negative electrode made of siloxene sheet electrodes, a siloxene - PVDF piezoelectric fiber positioned between the positive electrode and the negative electrode, and an electrolyte.

## [0015]

118 The present invention relates to a supercapacitor and a method for manufacturing the same, and can provide a supercapacitor having improved self - charging efficiency and a method for manufacturing the same by including a siloxene sheet electrode and a siloxene - PVDF piezoelectric fiber.

## [0016]

FIG. 1 is a schematic diagram showing the steps involved in the fabrication of a siloxene SCSPC, where a represents the fabrication of siloxene sheets via topochemical deintercalation of calcium from CaSi<sub>2</sub> in the presence of ice - cold HCI solution, b represents the fabrication process involving electrospinning of siloxene/PVDF piezoelectric fibers, and c represents the fabrication of a siloxene SCSPC device using siloxene sheet - coated carbon fabric as two symmetrical electrodes and electrospun siloxene - PVDF piezoelectric fibers impregnated with ionogel electrolyte as a separator.

## [0017]

136 FIG. 2 is a drawing showing the physicochemical properties of a siloxene sheet, where a is an X - ray diffraction spectrum of a siloxene sheet, b is a laser Raman spectrum of a siloxene sheet, c is a Fourier transform infrared spectrum of a siloxene sheet, d is an XPS measurement spectrum of a siloxene sheet, e is a Si 2p spectrum, and f is an O1s core - level spectrum of a siloxene sheet.

## [0018]

144 Figure 3 is a drawing showing the X - ray diffraction pattern of CaSi < sub > 2 < /sub > .

#### [0019]

148 Figure 4 is a diagram showing the structure of a siloxene sheet prepared through topochemical de - insertion of calcium from CaSi<sub>2</sub>.

## [0020]

FIG. 5 is a drawing showing the morphology and elemental analysis of siloxene sheets, where a - c are field emission - scanning electron microscope images of siloxene sheets, d is an elemental mapping analysis showing an overlay map, e - f are EDS mappings of Si and O present in the siloxene sheets, g is an EDS spectrum of Si and O present in the siloxene sheets, h is a high - resolution transmission electron microscope image of an individual siloxene sheet, i - j are EDS mappings of Si elements and O present in the siloxene sheets, and k is an elemental composition ratio spectrum of Si and O present in the siloxene sheets.

Figure 6 a - b are field - emission scanning electron microscopy images of siloxene -PVDF piezoelectric fibers at low (a) and high (b) magnifications, c is an overlay field - emission microscopy image of the siloxene - PVDF piezoelectric fiber, d - g are EDX mappings of carbon (d), fluorine (e), silicon (f), and oxygen (g) atoms present in the siloxene - PVDF piezoelectric fiber, and h is an EDX mapping of the siloxene -PVDF piezoelectric fiber.

#### [0022]

<sup>173</sup> Figure 7 is a diagram showing the mechanical energy harvesting characteristics of siloxene - PVDF piezoelectric fibers, where a shows the voltage output of bare PVDF and siloxene - PVDF piezoelectric fibers subjected to an applied compressive force of 5 N, and b shows the effect of the applied compressive force on the voltage output characteristics of siloxene - PVDF piezoelectric fibers subjected to various levels of applied compressive force.

## [0023]

182 Figure 8 shows the laser Raman spectra of exposed PVDF and siloxene - PVDF electrospun piezoelectric fibers.

## [0024]

187 Figure 9a shows the mechanical energy harvesting characteristics of siloxene - PVDF piezoelectric fibers obtained using various levels of compressive force, and b shows the charging of a commercial capacitor (0.22 mF) using electrospun siloxene - PVDF piezoelectric fibers.

## [0025]

<sup>194</sup> Fig. 10 is a diagram showing the electrochemical energy storage characteristics of siloxene SCSPC, where a represents cyclic voltammetry characteristics of siloxene SCSPC recorded at different applied scan rates of 5 to 500 mVs<sup> - 1</sup>, b represents the effect of the applied scan rate on the device specific capacitance of siloxene SCSPC, c is electrochemical impedance spectroscopy of siloxene SCSPC in the form of a Nyquist plot, the inset of Fig. 10c represents an enlarged portion of the high frequency region, d is a galvanostatic charge - discharge profile of siloxene SCSPC, and f is a Ragone plot of siloxene SCSPC. Energy - power performance indicators, and the details provided in the inset of Fig. 10f are provided in Table 1.

## [0026]

209 Figure 11 is a diagram showing a board phase angle plot of a siloxene SCSPC device.

## [0027]

213 Figure 12 is a drawing showing the study of the mechanical flexibility of siloxene SCSPC tested through device bending, where a shows digital photographs of siloxene SCSPC in normal and bent states, respectively, and b shows CV profiles of siloxene SCSPC obtained in normal and bent states recorded using a scan rate of 100 mVs<sup> - 1</sup>.

## [0028]

221 Figure 13 shows the long - term cyclic stability of the SCSPC device over 5,000 consecutive charge - discharge cycles using an applied current of 10 mA.

## [0029]

FIG. 14 is a diagram showing the mechanically driven self - charge characteristics of siloxene SCSPC, where a - c represent the self - charge characteristics of siloxene SCSPC subjected to various levels of mechanical force of 10, 15, and 20 N, d represents the effect of the applied compressive force on the self - charge performance of siloxene SCSPC, e represents the stability of the self - charge characteristics of siloxene SCSPC subjected to a continuous compressive force of 15 N, and f represents the practical application of siloxene SCSPC which can supply power to a multi - functional electronic display.

## [0030]

237 Figure 15a shows the self - charge and discharge characteristics of siloxene SCSPC fabricated using bare electrospun PVDF fibers under a compressive force of 20 N, and b is a drawing comparing the self - charge performances of siloxene SCSPC fabricated using bare PVDF and siloxene - PVDF piezoelectric fibers.

#### [0031]

244 Figure 16 shows the self - charge and discharge characteristics of siloxene SCSPC under different frequencies [a 2 Hz, b 1 Hz, c 0.5 Hz] at a force of 20 N, where the discharge currents are 20, 10, and 10 mA for SCSPC at 2, 1, and 0.5 Hz, respectively.

#### [0032]

252 FIG. 17 is a schematic diagram showing the operating mechanism of a siloxene SCSPC device, where a represents the initial state of the siloxene SCSPC device when no compressive force is applied, b represents that when a compressive force is applied to the siloxene SCSPC device, siloxene/PVDF generates a piezoelectric potential that induces electrolyte ions to the electrode surface, c represents that an equilibrium state is reached between the generated piezoelectric potential and the electrochemical reaction of the siloxene SCSPC device, d represents the state of the siloxene SCSPC when the compressive force is stopped, that is, when the piezoelectric potential disappears and an equilibrium state is reached, and e represents the state of the siloxene SCSPC after one self - charge cycle is completed.

#### [0033]

266 Figure 18 is a diagram showing piezoelectric chemical spectroscopy measurements of a siloxene SCSPC device when a compressive force of 20 N is applied to the siloxene SCSPC device during the PECS measurement, where a represents a PECS measurement using cyclic voltammetry recorded at a scan rate of 100 mVs<sup> -1</sup>, b is a partial enlargement of a portion near the PZC region of Figure 8a, c represents a PECS measurement recorded using a scan of 50 mVs<sup> - 1</sup>, and d is a partial enlargement of Figure 8c.

## [0034]

276 Figure 19 shows the piezochemical spectroscopy of siloxene SCSPC recorded using chronoamperometry with different applied potentials such as a 0.0 V, b 0.25 V, c 1.5 V, and d 1.8 V, respectively.

## [0035]

282 Figure 20 is a diagram showing piezochemical spectroscopy of a siloxene SCSPC recorded using chronoamperometric techniques with an applied potential of 1.8 V, where a compressive force of 20 to 5 N was applied to the siloxene SCSPC device for 100 to 340 and 380 to 600 seconds.

## [0036]

- 289 Hereinafter, preferred embodiments of the present invention will be described in detail.
- 291 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.

293 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.

#### [0038]

301 The present inventors have applied for patents for a conventional self - charging supercapacitor (Korean Patent No. 10 - 1567693) and a supercapacitor including siloxene (Korean Patent No. 10 - 2053782), and the contents described in the above prior documents can all be referenced in the present invention.

## [0039]

308 In addition, the inventors of the present invention have conducted repeated studies to improve the self - charging efficiency of self - charging supercapacitors, and as a result, have discovered that self - charging supercapacitors can exhibit self - charging efficiency by including siloxene sheet electrodes and siloxene - PVDF piezoelectric fibers, leading to the present invention.

## [0040]

316 Figure 1 is a schematic diagram showing a method for manufacturing a self - charging supercapacitor according to the present invention.

## [0041]

*321* Referring to FIG. 1, the present invention discloses a method for manufacturing a self - charging supercapacitor, including a step of manufacturing a siloxene sheet electrode; and a step of manufacturing a siloxene - PVDF piezoelectric fiber.

## [0042]

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

## [0043]

332 The above - described method for manufacturing a siloxene sheet electrode is a step for manufacturing a siloxene sheet electrode utilized as an electrode in a self charging supercapacitor, and may include a step of obtaining siloxene by immersing

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a precursor containing calcium silicide in an acid to dissolve calcium; a siloxene drying step of drying the siloxene; a coating solution preparation step of dispersing the siloxene and PVDF (Polyvinylidene Fluoride) powder in an N - methyl - 2 - pyrrolidone (NMP) solvent; and a coating step of coating the coating solution on the surface of a carbon fabric.

#### [0044]

<sup>346</sup> In the step of obtaining the above siloxene, the acid may be a strong acid having a temperature of 4 ° C or lower, and preferably may be hydrochloric acid.

<sup>348</sup> In addition, maintaining a temperature of 0 to 2 ° C. while vigorously mixing the precursor containing the calcium silicide with the hydrochloric acid allows the reaction to proceed efficiently, which is advantageous in obtaining a siloxene of a desired form.

## [0045]

<sup>355</sup> The step of obtaining 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 manufacture the desired siloxene.

## [0046]

362 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 powder can be washed with water and acetone, and the manufactured siloxene powder can be recovered by washing it with water and ultrasonic waves, separating it from the water, and then drying it (siloxene drying step).

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

## [0047]

372 In addition, the siloxene drying step can be performed at a drying temperature of 60 to 90 ° C. for 6 to 20 hours, in which case drying can be performed efficiently without damaging the siloxene and removing reaction residues.

#### [0048]

378 The above coating solution preparation step is a step of preparing a coating solution in which siloxene is dispersed in order to coat siloxene on carbon fabric. The coating solution may be prepared by mixing siloxene and PVDF (Polyvinylidene Fluoride) powder in amounts of 80 to 99 wt% and 1 to 20 wt% and dispersing them in an N - methyl - 2 - pyrrolidone (NMP) solvent, preferably by mixing siloxene and PVDF powder in amounts of 93 to 98 wt% and 2 to 7 wt% and dispersing them in an N - methyl - 2 - pyrrolidone (NMP) solvent, and most preferably by mixing siloxene and PVDF powder in amounts of 95 wt% and 5 wt% and dispersing them in an N - methyl - 2 - pyrrolidone (NMP) solvent.

382 The above dispersion can be performed using ultrasound, which can be performed at15 to 25 kHz.

#### [0049]

<sup>394</sup> The above coating step is a step of coating the coating solution on the surface of carbon fabric. The coating solution can be coated on the surface of carbon fabric through drop - casting, and after coating, the surface can be dried at a drying temperature of 60 to 90 ° C. for 6 to 20 hours to manufacture a siloxene sheet electrode.

## [0050]

402 In this way, the manufactured siloxene sheet electrodes can be used as positive and negative electrodes of self - charging supercapacitors.

## [0051]

407 In the present invention, the siloxene - PVDF piezoelectric fiber manufacturing step is a step for manufacturing siloxene - PVDF piezoelectric fibers used as a separator of a self - charging supercapacitor, and may include a step of obtaining siloxene by immersing a precursor containing calcium silicide in an acid to dissolve calcium; a siloxene drying step of drying the siloxene; a dispersion manufacturing step of dispersing the siloxene in a PVDF solution to manufacture a dispersion; and a piezoelectric fiber manufacturing step of electrospinning the dispersion to manufacture siloxene - PVDF piezoelectric fibers.

#### [0052]

418 The step of obtaining the above siloxene and the step of drying the siloxene can be performed in the same manner as the step of manufacturing the siloxene sheet electrode.

## [0053]

424 The above dispersion preparation step is a step of preparing a dispersion so that siloxene and PVDF can be electrospun, and can be performed by dispersing siloxene in a PVDF solution.

#### [0054]

430 Specifically, the PVDF solution can be prepared by dispersing PVDF powder in a mixed solution of acetone and dimethylacetamide at 5 to 20 wt%, and preferably, by dispersing PVDF powder in a mixed solution of acetone and dimethylacetamide at 8 to 12 wt%, and if the content of the PVDF powder is outside the range of 5 to 20 wt%, formation of piezoelectric fibers may not be easy.

## [0055]

438 The above acetone and dimethylacetamide mixed solution can be prepared by mixing 20 to 40 volume % of acetone and 60 to 80 volume % of dimethylacetamide. If the volume % range is exceeded, the PVDF powder can be easily dispersed in the mixed solution, but the efficiency of the piezoelectric fiber can be reduced.

#### [0056]

- <sup>445</sup> Thereafter, a dispersion can be prepared by dispersing 5 to 20 wt% of the siloxene in the PVDF solution, and preferably, a dispersion can be prepared by dispersing 8 to 12 wt% of the siloxene.
- <sup>448</sup> When dispersing the siloxene in the PVDF solution, the siloxene may be in powder form, and the dispersion may be performed for 1 to 3 hours using ultrasonic waves, and the ultrasonic waves may be performed at 15 to 25 kHz.

## [0057]

454 Once the above dispersion is prepared, a piezoelectric fiber preparation step of preparing a siloxene - PVDF piezoelectric fiber by electrospinning the dispersion can be performed.

#### [0058]

460 Specifically, after the dispersion is filled into a syringe using a stainless steel nozzle, electrospinning can be performed at a constant flow rate of 400 to 600 uLh<sup> - 1</sup> under a constant DC voltage of 10 to 20 kV, and the distance between the tip and the collector can be maintained at a constant distance of 5 to 20 cm.
464 After electrospinning, siloxene - PVDF piezoelectric fibers were manufactured by

drying at a temperature of 50 - 70 ° C for 10 - 14 hours.

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## [0059]

<sup>469</sup> Thus, the formed siloxene - PVDF piezoelectric fibers can be used as separators in self - charging supercapacitors.

## [0060]

474 The above method for manufacturing a self - charging supercapacitor may further include an electrolyte injection step after the process of manufacturing the siloxene - PVDF piezoelectric fiber, and the electrolyte may be a gel electrolyte containing TEABF<sub>4</sub>, and preferably may be an ionogel.

## [0061]

481 The above ionogel can be manufactured, for example, by adding 1 g of PVDF - co -HFP (Poly(vinylidene fluoride - co - hexafluoropropylene)) to 10 ml of a solution containing dimethylacetamide (70 vol%) and acetone (30 vol%), stirring to form a homogeneous solution, then adding 1 g of TEABF<sub>4</sub> and stirring until a transparent ionogel is formed.

## [0062]

489 According to another aspect of the present invention, a self - charging supercapacitor is disclosed, comprising a positive electrode and a negative electrode made of siloxene sheet electrodes, a siloxene - PVDF piezoelectric fiber positioned between the positive electrode and the negative electrode, and an electrolyte.

## [0063]

<sup>496</sup> In the present invention, the self - charging efficiency can be improved by using the siloxene sheet electrodes as positive and negative electrodes and the siloxene -PVDF piezoelectric fibers as a separator, and the electrolyte can be a gel electrolyte containing TEABF<sub>4</sub>, and preferably can be an ionogel.

#### [0064]

503 In addition, the self - charging super capacitor can maintain a device capacitance of about 85% or more of the initial capacitance after 5,000 repeated cycles, thereby ensuring excellent stability.

## [0066]

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

## [0068]

513 Materials and Experimental Methods

## [0069]

- 517 Calcium silicide (CaSi<sub>2</sub>) powder was purchased from Kojundo Chemicals Laboratory Co., Ltd., Japan.
- 519 ) was purchased from.
- 520 Polyvinylidene fluoride (PVDF) is manufactured by Sigma Aldrich Ltd. of Korea.
- 521 ) was purchased from.
- 522 Carbon fiber was purchased from a fuel cell store in South Korea.
- 523 Hydrochloric acid (HCI), acetone, dimethylacetamide, and N methyl 2 pyrrolidone (NMP) were purchased from Daejung Chemical Co., Ltd., Republic of Korea.
- 525 Tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) electrolyte was purchased from Alfa Aesar Chemicals, Korea.
- 527 Ultrasonic investigations were performed on a VCX 750 ultrasonicator (Sonics and Materials, Inc, USA, 20 kHz, 750 W) using a direct immersion titanium horn.

## [0070]

- 532 The electrospinning process for the fabrication of siloxene/PVDF piezoelectric fibers was performed on a NanoNC electrospinning machine (Model: ESR200R2, Korea).
- 534 X ray diffractograms of siloxene sheets were recorded using an Empyrean X ray diffractometer (Malvern Panalytical, UK) with Cu K radiation ( =1.54184 Å).
- 536 Fourier transform infrared (FT IR) spectra were measured using a "Thermo Scientific Nicolet - 6700 FT - IR" spectrometer.
- 538 Laser Raman spectra were obtained using a "Lab Ram HR Evolution" Raman spectrometer (laser excitation source at wavelength 514 nm, Horiba Jobin - Yvon, France).
- 541 The chemical states of the elements present in the siloxene sheets were determined by X - ray photoelectron spectrometry (ESCA - 2000, VG Microtech Ltd.).
- 543) was analyzed.
- 544 The surface morphology of siloxene powder and electrospun fibers was examined using a field emission scanning electron microscope (TESCAN, MIRA3) at different magnifications with energy dispersive X - ray spectroscopy (EDS) and HR - TEM (JEM - 2011, JEOL) with a CCD 4k x 4k camera (Ultra Scan 400SP, Gatan).

## [0071]

- 550 The energy harvesting characteristics were measured under different levels of applied compressive force using a linear motor "LinMot E1100".
- 553 The output voltage was recorded with a Keithley electrometer (model number: 6514).
- 555 The energy storage and self charge characteristics of the self charging supercapacitor were measured on an "Autolab PGSTAT302N" electrochemical workstation.
- 558 Cyclic voltammetry (CV) recorded using different levels of applied scan rates, galvanostatic charge - discharge (CD) recorded using various applied current ranges, electrochemical impedance spectroscopy (EIS), and long - term cycling stability tests were used to understand the charge storage performance of the self - charging supercapacitors.
- 563 The mechanical flexibility of the self charging supercapacitor was studied by measuring the CV profiles under bending conditions using a bending tester (JUNIL -JIBT - 200).
- 566 The self charge characteristics of the self charging supercapacitor were determined by measuring the voltage (using an electrochemical workstation) while applying a continuous compressive force to the device.
- 569 After the self charging process, a constant discharge current is applied to the self charging supercapacitor to discharge it.
- 571 The device specific capacitance, energy (E) and power (P) densities of the self charging supercapacitor device were determined from the CD profile using the following mathematical equations 1 to 3.

[0072] 577 [Mathematical Formula 1]

[0073] 581 C<sub>A</sub> = (I T<sub>d</sub>) / (A V)

[0074] 585 [Mathematical formula 2]

[0075] 589 E = [C<sub>A</sub> V<sup>2</sup>]/2 [0076] 592 [Mathematical Formula 3]

[0077] 597 P = E / T<sub>d</sub>

## [0078]

601 In the above mathematical expressions 1 to 3, "C<sub>A</sub>" represents the device specific capacitance (Fcm<sup> - 2</sup>), "I" is the discharge current, "Td" is the time required for discharge, "A" is the electroactive region of the device, and "V" is the operating voltage window.

#### [0800]

608 Example

## [0081]

612 1. Siloxene manufacturing

## [0082]

- 616 Siloxene sheets were prepared via a topochemical route involving de insertion of calcium from CaSi<sub>2</sub> in the presence of ice cold HCl.
- 618 Briefly, CaSi<sub>2</sub>powder (1 g) was slowly added to a 0 solution containing concentrated HCL and stirred vigorously using a magnetic stirrer for 4 days.
- 621 The color change from gray white (CaSi<sub>2</sub>) to green (siloxene sheets) indicates the dissolution of calcium in the HCL solution, which resulted in the formation of siloxene sheets.
- 624 After the reaction was completed, the green siloxene powder was washed with water and acetone.
- 626 Additionally, the manufactured siloxene powder was redispersed in water (100 mL) and irradiated with ultrasound for 1 hour, after which a similar washing process was performed.
- 629 Finally, the manufactured siloxene was dried at 80 ° C for 12 hours.

#### [0084]

633 2. Manufacturing of siloxene sheet electrodes

## [0085]

- 637 A coating solution was prepared by mixing 95 wt% of siloxene and 5 wt% of PVDF powder and dispersing them through ultrasonic treatment for 30 minutes in an NMP solvent.
- 640 The above coating solution was coated on the surface of carbon fabric through drop casting and dried at 80 ° C for 12 hours.

## [0087]

645 3. Manufacturing of siloxene - PVDF piezoelectric fibers

## [0088]

- 649 PVDF powder (10 wt%) was dissolved in a mixed solution of acetone and dimethylacetamide (30:70 vol%), thereby obtaining a PVDF solution.
- 651 Thereafter, the previously prepared siloxene (10 wt%) was added to the PVDF solution for 2 hours in the presence of an ultrasonic irradiation process to disperse the siloxene in the PVDF solution, thereby preparing a dispersion.
- <sup>654</sup> The prepared dispersion (viscous solution containing siloxene and PVDF) was filled into a syringe (15 mL) with a stainless steel nozzle (21G).
- <sup>656</sup> Next, the electrospinning process was performed at a constant flow rate of 500  $\mu$  Lh<sup> 1</sup> under a constant DC voltage of 15 kV.
- 658 Here, the distance between the tip and the collector was maintained at 10 cm to manufacture siloxene - PVDF piezoelectric fibers, and the manufactured siloxene -PVDF piezoelectric fibers were dried at 60 ° C for 12 hours.

## [0090]

664 4. Manufacturing self - charging supercapacitors

## [0091]

- 668 Symmetric supercapacitors (SSCs) were fabricated by sandwiching siloxene PVDF piezoelectric fiber separators (gelled with TEAFB<sub>4</sub>ionogel) between siloxene coated carbon fabrics and sealed in moisture resistant pouches using a "GBC Fusion 3000L" laminator.
- 672 The preparation of the ionogel electrolyte and the fabrication of the self charging supercapacitor device were performed in an argon filled glove box.

#### [0093] 676 result

## [0094]

681 1. Description of the manufacturing process of self - charging supercapacitors

## [0095]

- 685 Figure 1 graphically illustrates the overall process involved in manufacturing a self charging supercapacitor.
- 687 Referring to Figure 1, siloxene is synthesized through a topochemical reaction of ice - cold HCl and CaSi<sub>2</sub> (Figure 1a), which leads to deintercalation of calcium ions by partial oxidation of Si sheets, thereby forming siloxene.
- 690 Fine dispersion of siloxene sheets in a PVDF solution is performed through an ultrasonic irradiation process, and siloxene - PVDF piezoelectric fibers are manufactured through an electrospinning process (Fig. 1b).
- 693 Figure 1c illustrates the structure of the self charging supercapacitor, where siloxene - coated carbon fabric (siloxene sheet electrode) is used as two symmetrical electrodes separated by ionogel - coated electrospun siloxene - PVDF piezoelectric fibers.

## [0097]

700 2. Characteristics of manufactured siloxene sheets

## [0098]

704 Figure 2 illustrates the physicochemical characterization of the manufactured 2D siloxene sheets.

## [0099]

- 709 The X ray diffraction pattern of the siloxene sheets (Fig. 2a) shows broad diffraction peaks at 13.5 ° and 27 °, indicating the removal of calcium from CaSi<sub>2</sub> and the formation of siloxene sheets (see Fig. 3, XRD pattern of CaSi<sub>2</sub>).
- 713 The laser Raman spectrum of the siloxene sheets (Fig. 2b) shows major bands at 497 and 521 cm<sup> - 1</sup>, which correspond to the Si - O - Si and Si - Si vibrations of the oxygen - interconnected Si<sub>6</sub> rings present in the hexagonal silicon skeleton of the siloxene sheets. The band located at 375 cm<sup> - 1</sup> arises from the vibration of the Si - Si band, whereas the other

bands located at 641 and 731 cm<sup> - 1</sup> correspond to the Si - H vibrations of the siloxene sheets.

- The FT IR spectrum of the siloxene sheet (see Fig. 2c) shows different bands at 1,050 cm<sup> - 1</sup> (Si - O - Si network) and 2,150 cm<sup> - 1</sup> (O -Si<sub>2 </sub>Si - H), and the prepared siloxene is of Kautsky type (Si<sub>6</sub> rings interconnected via Si - O - Si bridges in the Si plane, see Fig. 4).
- 730 525, 880 And the bands centered at 1,632 cm<sup> 1</sup> arise from the vibrations of Si - Si, Si - H, and Si - OH groups present in the siloxene sheet, respectively.
- 733 X ray photoelectron survey scans of the siloxene sheets (shown in Figure 2d) reveal the presence of Si2p states (100 eV) and O1s states (530 eV).
- 735 The core level spectrum of the Si 2p state (Fig. 2e) can be divided into two peaks as follows:

## [0100]

740 (i) The peak at 99 eV corresponds to the Si - Si state, and (ii) the peak at 102.5 eV is attributed to the Si - O - Si state present in the siloxene sheets.

## [0101]

- 745 Figure 2f shows the O1s spectrum of the siloxene sheet derived from the oxygenated groups present in the siloxene sheet.
- 747 The determined O/Si atomic ratio of the siloxene sheets from XPS analysis is about 1.25.

## [0102]

752 Figure 5 shows the morphology and elemental composition analysis of siloxene sheets using field - emission scanning electron microscopy (FE - SEM) and high resolution transmission electron microscopy (HR - TEM) along with elemental mapping analysis.

## [0103]

759 Figures 5a - c provide FE - SEM micrographs (recorded at different magnifications) of siloxene sheets, clearly showing the formation of sheet - like nanostructures of siloxene via topochemical reaction. The lateral dimensions of the siloxene sheets are not uniform (varying from 1 to 2  $\mu$  m), which may be due to the irregular size of the CaSi<sub>2</sub> precursor used in the production of siloxene.

#### [0105]

- <sup>771</sup> Figures 5d f show the overlay map and Si and O element maps of the siloxene sheet, which show the uniform distribution of Si and O atoms in the siloxene sheet.
- 773 The EDS spectrum given in Fig. 5g shows that the O/Si ratio of the siloxene sheets is about 0.93.
- <sup>775</sup> Figures 5h k show HR TEM micrographs of individual siloxene sheets with lateral dimensions of 1.2  $\times$  1.2  $\mu$ m.
- 777 Elemental maps (Fig. 3i j) show that Si and O atoms are homogeneously distributed over the entire surface of the siloxene sheet, and the corresponding O/Si atomic ratio is about 1.47 (analyzed using the Clip - Lorimer ratio method).
- 780 From this, it can be seen that 2D siloxene sheets are formed from the topochemical reaction.

#### [0107]

785 **3**.

786 Characterization of electrospun siloxene - PVDF piezoelectric fibers

## [0108]

- 790 FE SEM micrographs of the electrospun siloxene PVDF piezoelectric fibers obtained at low and high magnifications are shown in Fig. 6 a b.
- 792 Referring to Figure 6 a b, the presence of siloxene PVDF fibers with a width of 50 nm having a porous structure is shown, which is an essential design consideration for ion transport channels in supercapacitors.

## [0109]

798 Elemental mapping and EDS spectra of the siloxene - PVDF piezoelectric fibers (Fig. 6c-h) reveal a uniform distribution of silicon atoms (from siloxene sheets) in the PVDF matrix of the fibers.

## [0110]

804 Figure 7a summarizes the mechanical energy harvesting characteristics of electrospun siloxene - PVDF piezoelectric fibers compared to bare PVDF fibers obtained at a compressive force of about 5 N, and the energy harvesting mechanism from bare PVDF fibers (output voltage 3 V) is due to the piezoelectric properties of PVDF.

## [0111]

- 815 When siloxene sheets are incorporated into the PVDF matrix, the output voltage is 7 V, which is higher than that of bare PVDF, indicating improved mechanical energy harvesting characteristics.
- 818 The improved energy harvesting properties of the siloxene PVDF piezoelectric fibers are due to the enhanced dipole alignment in the PVDF by the incorporation of siloxene sheets (as shown in the laser Raman spectra presented in Figure 8).

#### [0112]

- 824 Figure 8 shows the laser Raman spectra of exposed electrospun PVDF and siloxene -PVDF piezoelectric fibers over the 780-900 cm<sup> - 1</sup> region.
- 826 The Raman spectrum of bare electrospun PVDF exhibits three main bands at 796 and 838 cm<sup> - 1</sup> corresponding to the and phases of PVDF, respectively. The band observed at 878 cm<sup> - 1</sup> is due to the combination of the vibration of CF<sub>2</sub> groups and the carbon - carbon backbone of PVDF.
- Raman spectra of siloxene PVDF fibers show the presence of vibrational bands at 802, 814, 839, and 879 cm<sup> 1</sup>, respectively. The presence of the band at 802 cm<sup> 1</sup> is due to the phase of PVDF, and the small shift observed in the band position is due to the interaction between the siloxene sheets and PVDF.
- 836 The band observed at 814 cm<sup> 1</sup> in electrospun siloxene PVDF may originate from the Si - O - Si present in the siloxene sheets or the phase of PVDF.
- 838 Additionally, the characteristic bands of PVDF, such as CF<sub>2</sub> and the phase and vibration of carbon - carbon chains, were preserved in the spectra of siloxene - PVDF fibers.

#### [0113]

The mechanical energy harvesting characteristics of siloxene - PVDF piezoelectric fibers subjected to various applied compressive forces are provided in Fig. 9a.

#### [0114]

849 Figure 7b shows the effect of various levels of compressive force on the energy harvesting characteristics of the siloxene - PVDF piezoelectric fiber. The output voltage of the siloxene - PVDF piezoelectric fiber increases from 7 V to 15.4 V with a linear increase in the applied compressive force from 5 N to 20 N, exhibiting ideal mechanical energy harvesting characteristics.

- 855 The ability of siloxene PVDF piezoelectric fibers as efficient piezoelectric nanogenerators to charge commercial capacitors is provided in Fig. 9b.
- 859 This demonstrates the importance of electrospun siloxene PVDF piezoelectric fibers for use as piezoelectric polymer separators in SCSPC.

#### [0116]

864 4. Energy storage performance of self - charging supercapacitors

## [0117]

868 The electrochemical energy storage properties of the fabricated self - charging supercapacitors were characterized using a series of experimental techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), galvanostatic charge - discharge (CD) analysis, and long - term stability tests.

## [0118]

875 Figure 10a shows the CV profiles of the self - charging supercapacitor recorded at an operating voltage window (OVW) of 1.8 V using differently applied scan rates (5 to 500 mV s<sup> - 1</sup>).

## [0119]

- <sup>881</sup> The presence of quasi rectangular CV profiles indicates that the charge storage mechanism in the siloxene electrode is due to ion insertion pseudocapacitance.
- 883 No redox peaks were observed in the CV profiles, indicating that there is no faradaic process involved in the charge - storage characteristics of the self - charging supercapacitor.

## [0120]

889 As the scan rate increases from 5 mVs<sup> - 1</sup> to 500 mVs<sup> - 1</sup>, the current range of the CV profile increases without any distortion of the

rectangular shape, showing excellent capacitance characteristics.

#### [0121]

895 Figure 10b shows the effect of applied scan rate on the device capacitance of a self charging supercapacitor with a high device capacitance of 27.58 mFcm<sup> - 2</sup> at a low scan rate of 5 mVs<sup> - 1</sup>.

## [0122]

- *gos* Figure 10c presents EIS data of the self charging supercapacitor device in the form of a Nyquist plot (a plot of the real versus imaginary components of impedance).
- 905 The Nyquist plot of the self charging supercapacitor device reveals the presence of three well - defined regions: low, medium and high frequency regions, which are directly related to the frequency - dependent synchronous, asynchronous and non synchronous charging behaviors of the self - charging supercapacitor.

## [0123]

912 From Fig. 10c, it can be confirmed that the equivalent series resistance (ESR) of the self - charging supercapacitor is 9.7 , which is relatively higher than that of the siloxene supercapacitor using liquid TEABF<sub>4</sub>electrolyte, because the ion conductivity of the ionogel is lower than that of the liquid electrolyte.

## [0124]

919 The observation of quasi - semicircles like arcs in the high - frequency region is attributed to the charge - transfer resistance (R<sub>ct</sub> of 4 ) of the self charging supercapacitor, and the high - frequency region shows evidence of a straight line (Warburg line) almost parallel to the y - axis, which represents the charging region of the self - charging supercapacitor as a result of the diffusion of electrolyte ions to the electrode surface.

## [0125]

928 The Bode phase angle plot of the self - charging supercapacitor (see Figure 11) shows that the phase angle at low frequency (0.01 Hz) is approximately - 69°, indicating pseudocapacitive behavior of the electrode.

#### [0126]

934 Figure 11 shows the Bode phase angle plot of the self - charging supercapacitor,
 which shows that the phase angle in the low frequency region is about - 69 °,
 demonstrating the pseudocapacitive characteristics of the siloxene electrode.

## [0127]

940 Figure 10d shows the CD profiles of the self - charging supercapacitor device

recorded using different applied current ranges over an OVW of 1.8 V, and the presence of a symmetrical triangular shaped CD profile of the self - charging supercapacitor indicates quasi - capacitive (insertion - type) charge storage characteristics.

## [0128]

949 The effect of applied current on the device capacitance of the self - charging supercapacitor is summarized in Fig. 10e, where the device capacitance increases linearly with decreasing applied current range, and a high device capacitance of about 28.98 mFcm<sup> - 2</sup> was obtained for the self - charging supercapacitor from the CD profile recorded using a current of 5 mA.

## [0129]

- 957 Figure 10f shows the energy power performance metrics of the self charging supercapacitor device in the form of a Ragone plot.
- <sup>959</sup> The self charging supercapacitor was shown to have a high energy density of 46.97
   mJ cm<sup> 2</sup> at a corresponding power density of 1.12 mW cm<sup> 2</sup> measured from the recorded CD profile using an applied current of 5 mA.
- 962 As the applied current range increases from 5 mA to 25 mA, the self charging supercapacitor device maintains an energy density of 12.03 mJcm<sup> - 2</sup>, while the power density increases to 5.62 mWcm<sup> - 2</sup>.

## [0131]

- 968 Referring to Table 1 above, it can be seen that the performance index (No. 10) of the self - charging supercapacitor according to the present invention is relatively superior to many reported silicon - based symmetric supercapacitors.
- 971 The mechanical flexibility of the self charging supercapacitor was confirmed using CV analysis recorded by applying bending conditions to the device as shown in Fig. 12a, and there was no significant change in the CV profile of the self charging supercapacitor recorded in the bending state compared to the normal state (Fig. 12b).
- 976 The retention ratio (C/C<sub>o</sub>) of the device capacitance obtained in the bending state (C) with respect to the normal state (C<sub>o</sub>) is approximately 1.07, which indicates the mechanical stability of the self - charging supercapacitor.

## [0132]

983 Figure 13 shows the long - term cycling stability of the self - charge supercapacitor

device for 5,000 continuous charge - discharge cycles recorded using an applied current of 10 mA. After 5,000 repeated cycles, the self - charge supercapacitor device retains about 85% of the initial capacitance, indicating excellent electrochemical stability, and the capacitance retention value is comparable to and higher than that of the state - of - the - art supercapacitors, such as conventional rGO SSCs (93% after 1,500 cycles), RGOCMK - 5 composite SSCs (90% after 2,000 cycles), and RGO - RuO2 SSCs (70% after 2,000 cycles).

## [0134]

995 5. Self - charging performance of self - charging supercapacitors

## [0135]

- <sup>999</sup> Figure 14 shows the self charging behavior of the self charging supercapacitor for various levels of applied compressive force.
- 1001 When a compressive force of 10 N is applied to the surface of the self charging supercapacitor, the voltage of the self - charging supercapacitor increases from 105 mV to 180 mV within 250 s, as shown in Fig. 14a, demonstrating self - charging characteristics through mechanical deformation.
- 1005 After this mechanically induced self charging process, the self charging supercapacitor is discharged to its initial state within 100 s using a discharge current of 10 A.

## [0136]

1011 Figures 14b - c show the self - charge characteristics of the self - charging supercapacitor under applied compressive forces of 15 and 20 N, followed by discharge using constant currents of 10 and 20 A, and it can be seen that the voltage of the self - charging supercapacitor increases from 101 to 237 mV and from 107 to 314 mV within 250 s when subjected to forces of 15 and 20 N, respectively.

## [0137]

- Figure 14d shows the self charging performance of the self charging supercapacitor, which shows that the device can be charged up to 75, 136, and 207 mV (within 250 s) for compressive forces of 10, 15, and 20 N, respectively.
- 1023 The increase in self charge voltage of the self charging supercapacitor with increasing applied force level is attributed to the piezoelectric effect of the electrospun siloxene - PVDF piezoelectric fibers, which generates larger electrical output as the mechanical force increases.

#### [0138]

1030 Figure 15 shows the self - charge characteristics of a self - charging supercapacitor fabricated using exposed electrospun PVDF piezoelectric fibers as a separator.

#### [0139]

- 1035 When subjected to an applied compressive force of 20 N, the device can self charge up to 141 mV (from 118 mV to 259 mV), which is lower than that of self charging supercapacitors with siloxene - PVDF piezoelectric fibers as separators (see Figure 14c).
- 1039 This is because the mechanical electrical energy conversion characteristics of the siloxene - PVDF piezoelectric fibers are superior to those of the exposed PVDF piezoelectric fibers, as shown in Fig. 7a.

#### [0140]

1045 Figure 16 shows the effect of the applied frequency of the compressive force (20 N) on the self - charging performance of the self - charging supercapacitor.

- 1047 It can be seen that the self charge performances of the self charging supercapacitor are 207, 102, and 59 mV, respectively, when the applied compressive force is 20 N and the frequencies are 2, 1, and 0.5 Hz.
- 1050 The self charge capacitance of the self charging supercapacitor is about 3.62 mF cm<sup> - 2</sup> (based on the calculation of the discharge curve) and was obtained under a compressive force of 20 N.
- 1053 Figure 14e shows the repetitive self charging process of the self charging supercapacitor over six consecutive cycles, which demonstrates that the output of the self - charging supercapacitor is almost similar (130±5 mV) during different cycles, ensuring excellent electromechanical stability.

#### [0141]

The performance of self - charge supercapacitor (207 mV in 250 s) is higher than that of conventional MnO<sub>2</sub>SCSPC (110 mV in 300 s), carbon fabric SCSPC (100 mV in 40 s), CNT SCSPC (70 mV in 40 s) and asymmetric supercapacitor - based SCSPC (151 mV in 80 s) (in terms of voltage output), which may be due to the use of high - power siloxene electrodes, and the comparison results between self - charge supercapacitor and conventional SCSPC reveal that electrode materials, electrolyte, separator and cell design are some important parameters that affect the self - charge parameters of SCSPC.

#### [0142]

1072 Figure 14f shows a practical application of a fully charged self - charging supercapacitor to power a multifunction electronic display (MED) over 5 minutes.
 1074 Parameters such as temperature, time and relative humidity of the MEDs were visible for 5 minutes, demonstrating the practical applicability of the fabricated self - charging supercapacitor.

## [0144]

1080 6. Working mechanism of self - charging supercapacitor

## [0145]

- 1084 The working mechanism of the self charging supercapacitor can be explained through the piezochemical process occurring at the surface/interface between the siloxene electrode and the siloxene - PVDF piezoelectric fiber, as illustrated in Fig. 17.
- 1088 In the initial state, the self charging supercapacitor is discharged with two siloxene electrodes separated by ionogelated siloxene - PVDF piezoelectric fibers, in which electrolyte ions (TEA<sup> + </sup> and BF<sub>4</sub><sup> - </sup>) are homogeneously distributed throughout the space (see Fig. 17a).
- 1092 Since the ionogelated siloxene PVDF piezoelectric fibers are in close contact with the symmetric siloxene electrodes, they can easily access the piezoelectric potential generated from the piezoelectric fibers under compressive force.
- 1095 When subjected to an applied compressive force, the positive and negative piezoelectric potentials generated by the piezoelectric fiber will be approached by the two siloxene electrodes, i.e., the positrode and negatrode, as illustrated in Fig. 17b.
- This leads to piezoelectric potential driven electrolyte ion transport (i.e., movement of TEA<sup>+</sup> and BF<sub>4</sub><sup> </sup> ions toward the cathode and anode) toward the siloxene electrodes via a combination of (i) and (ii):
  (i) physical ion adsorption kinetics and (ii) ion transport via ionically conductive pathways via the ionogellated siloxene PVDF piezoelectric fibers (see Figure 17c).
- 1105 In particular, since PVDF membranes are well known ionic conductors for TEABF<sub>4</sub> ions, PVDF can be used as a matrix/base for ionogel (known for its mechanical and piezoelectric properties) and a binder for supercapacitor electrodes.

- 1112 As the concentration increases around the two siloxene electrodes, the distribution of cations and anions leads to the formation of a potential difference that allows the self - charging supercapacitor to self - charge (Fig. 17c).
- 1112 During the self charge process of the self charging supercapacitor, electrolyte ions are adsorbed and/or inserted into the siloxene electrode, and this process proceeds unhindered by the piezoelectric potential across the siloxene - PVDF piezoelectric fibers.
- 1119 In SCSPC, the potential of the 2 siloxene electrode increases in the opposite direction during the self - charge process (self - charge capacitance) and reaches a certain operating voltage until the siloxene electrode reaches a new chemical equilibrium.
- 1123 At this stage, the distribution of electrolyte ions equalizes the generated piezoelectric potential, thereby stopping the ion transport process through the interface between the electrolyte and the two siloxene electrodes in the SCSPC, thus terminating the self - charging process.
- 1127 When the applied compressive force is removed (Fig. 17d), the piezoelectric properties of the electrospun siloxene PVDF piezoelectric fibers disappear, and the equilibrium state is maintained due to the redistribution of electrolyte ions (Fig. 17e), and the self charging process is repeated when the compressive force is applied again to the self charging supercapacitor.

## [0147]

- 1135 This mechanism is the overall mechanism for converting mechanical energy into electrochemical energy in self - charging supercapacitors via piezoelectric phenomenon, and overall, the piezoelectric effect induced by siloxene - PVDF piezoelectric fibers causes cations and anions to move toward the negative and positive electrodes (negatrode and positrode) in the self - charging supercapacitors, thereby inducing the self - charging process.
- 1141 The proposed self charging mechanism of the self charging supercapacitor can be explained using the Nernst theory, and the electrode potential and electrolyte ion concentration of the siloxene electrode can be calculated by the following mathematical equations 4 and 5.

[0148] 1148 In normal condition,

[0149] 1152 [Mathematical Formula 4]

#### [0151]

1157 When subjected to applied compressive force,

[0152] 1161 [Mathematical Formula 5]

## [0154]

1165 In the above equation, " <sub>(siloxene)</sub>" represents the actual electrode potential of the two siloxene electrodes in the SCSPC,

" <sup>o</sup><sub>(siloxene)</sub>," represents the standard electrode potential of the two siloxene electrodes used in the SCSPC, "R", "T" and "F" represent the gas constant, temperature and Faraday constant, respectively, "X" represents the active or occupied fraction of positively and negatively charged ions at the outer and/or inner surfaces of the cathode and the anode, respectively, "P" represents the insertion pressure due to the insertion of ions between the middle layers of siloxene sheets, and "X<sup>o</sup>" and "P<sup>o</sup>" represent the "X" and "P" when a compressive force is applied.

## [0155]

1178 When a compressive force is applied to the self - charging supercapacitor (i.e., in the piezoelectric region), cations (TEA<sup> + </sup>) and anions (BF<sub>4</sub><sup> - </sup>) migrate toward the negative and positive electrodes of the self - charging supercapacitor, which leads to a change in ion occupancy at the siloxene electrode (i.e., X<sup>o</sup> > X).

1183 This causes a net potential difference between the two siloxene (energy storage) electrodes in the SCSPC device, which drives the self - charging process.

## [0156]

- <sup>1188</sup> To understand the piezoelectric process in detail, the state of charge dependence of the self - charging supercapacitor under compressive stress was investigated using piezoelectric chemical spectroscopy (PECS).
- 1191 PECS measurements include characterization of the cyclic voltammetry profiles (Figure 18) of self - charging supercapacitors with and without compressive stress (mechanical strain).

- 1197 Figure 18a shows the PECS measurement results of the self charging supercapacitor recorded using CV measurements (scan rate of 100 mVs<sup> -1</sup>) at OVW from 0 to +1.8 V.
- 1197 Comparison of CV profiles with and without mechanical deformation provides significant variation in the current magnitude (induced by piezoelectric displacement) of the SCSPC with respect to the applied voltage.
- 1203 In the absence of compressive force, the CV profile of the self charging supercapacitor exhibits a quasi - rectangular curve, similar to the result shown in Fig. 7a.
- 1206 Here, the charge storage mechanism in self charging supercapacitors is attributed to direct electrochemical processes occurring at the electrolyte - electrode interface.
- 1209 The CV profiles of the self charging supercapacitor under continuously applied compressive force show the appearance of current spikes due to the additional current generated via the piezochemical process.
- 1212 When force is applied to the self charging supercapacitor device, the formation of a piezoelectric field in the surface separator causes electrolyte ions to float to the siloxene electrode surface.
- 1215 These excess charges, injected from the electrolyte to the electrode surface through the piezochemical process, are observed as current spikes in the CV profile of the self - charging supercapacitor (under compression).
- 1218 A zoomed in portion of the PECS results near the zero charge (PZC) region is provided in Fig. 18b, from which it is evident that the current spikes are observed with negative polarity below the PZC region, while the current spikes are observed with positive polarity above the PZC.
- 1222 Figures 18c,d show the PECS results of the self charging supercapacitor device recorded from the CV profile at a scan rate of 50 mVs<sup> - 1</sup>, which show similar results compared to Figure 18a.

## [0158]

- 1228 The voltage dependence of the magnitude of the piezochemically generated current can be related to the effect of the "state of charge" (SOC) of the self - charging supercapacitor.
- 1231 The increase in the current spike magnitude from the PZC region to high voltage is due to the different electrolyte ion concentrations at different applied voltages, which can be directly related to " (P<sup>o</sup>/X<sup>o</sup>) " (Mathematical Formula 5), as follows.

## [0159]

1238 The electrolyte ion concentration near the PZC region is lower than that over the

increased applied voltage range.

- 1240 When the self charging supercapacitor device is subjected to an applied compressive force, the size of the current spike is reduced at low applied potentials due to the low ion concentration at the siloxene electrode surface.
- 1244 At much higher applied potentials, a high concentration of ions surrounds the siloxene electrode, which results in greater surface - localized charge injection due to the applied compressive force, thus increasing the size of the current spike.
- 1247 To verify this, the chronoamperograms of the self charging supercapacitor were investigated at different applied potentials (0.0, 0.25, 1.5, and 1.8 V) under a compressive force similar to the conventional nanoimpact measurement, and the presence of spikes at the negative polarity for the applied potential values of 0.0 and 0.25 V are shown in Fig. 19a - b.
- 1252 As the applied potential value increased to 1.5 and 1.8 V, the polarity of the piezoelectric induced generated current was changed, as can be seen in Fig. 19c d.

## [0160]

1258 Additionally, the effect of the applied compressive force is presented in Fig. 20, indicating the important role of the piezochemical process on the current generated through excessive charge injection from the electrolyte into the siloxene electrode.

## [0161]

1264 Thus, PECS measurements directly confirm the "piezoelectric chemical effect" associated with the self - charging process of self - charging supercapacitors, which may help in understanding the energy conversion and storage mechanisms of SCSPCs.

## [0163]

1271 In this way, the self - charging supercapacitor and the manufacturing method thereof according to the present invention can provide a supercapacitor with improved self - charging efficiency and a manufacturing method thereof by including a siloxene sheet electrode and a siloxene - PVDF piezoelectric fiber.

## [0165]

- 1278 The preferred embodiments of the present invention have been described in detail above.
- 1280 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.

#### [0166]

1289 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.