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Carbothermal conversion of siloxene sheets into silicon-oxy-carbide lamellae for high-performance supercapacitors

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ABSTRACT:

This work describes the carbothermal preparation of silicon-oxy-carbide (SiOC) lamellae using two-dimensional siloxene sheets and alginic acid as precursors. X-ray photoelectron spectra, Fourier-transform infrared spectra, high-resolution transmission electron micrographs, and Raman spectra revealed the formation of lamella-like SiOC nanostructures. Symmetric supercapacitors (SSCs) were fabricated using SiOC nanostructures as electrodes and evaluated in aqueous (1 M Li₂SO₄) and organic liquid (1 M TEABF₄) electrolytes. SiOC SSC fabricated with Li₂SO₄ electrolyte operated over a voltage window of 2.0 V, with an energy density of 14.2 Wh Kg⁻¹ and a power density of 6,666 W Kg⁻¹. SiOC SSC fabricated using TEABF₄ electrolyte operates over a voltage window of 3.0 V and delivered a device capacitance of about 16.71 F g⁻¹, energy density of 20.89 Wh Kg⁻¹, with excellent cyclic stability and superior rate capability. Strikingly, the high-power density of the TEABF₄-based SiOC SSC (15,000 W Kg⁻¹) reached the required power target for next-generation electric vehicles and is suitable for high-performance supercapacitor devices.

KEYWORDS: Silicon-oxy-carbide, carbothermal reaction, siloxene sheets, symmetric supercapacitor, power density.

1. Introduction

The rapid growth of renewable energy sources (solar, wind, and mechanical energy harvesting devices) has increased the demand for sustainable energy storage technologies in dayto-day life [1]. Among the available energy storage devices, including lithium- and sodium-ion batteries (LIBs and SIBs, respectively), supercapacitors (SCs) are of prime interest (over LIBs and SIBs) due to their high power density, moderate energy density, and long life cycle [2]. Synergetic relationships between electrode materials and electrolytes play a vital role in the energy/power performance of SCs [3–5]. Independent research over the last decade has sought to improve the energy/power performance of electrochemical energy storage (EES) through the development of novel separators with high ionic conductivity, elucidating the roles of electrolytes with different solvents, and developing new nanostructured materials for highcapacitance electrodes [6-8]. Among these strategies, the development of new electrode materials with high capacitance, temperature tolerance, high conductivity, high surface area, and excellent electrochemical stability is a promising approach to increasing SC performance [9,10]. The advent of two-dimensional (2D) materials beyond graphene, such as 2D transition metal dichalcogenides (TMDCs), transition metal carbides/nitrides/carbonitrides (MXenes), siloxenes, metal-organic frameworks, and 2D polymers, has resulted in new insights into novel electrodes for EES devices [11–15]. The high electrical conductivity and lightweight nature of these materials make them suitable for SC electrodes with high areal and volumetric capacitance [16,17]. Derivatives of these 2D materials, prepared via novel synthetic pathways, have exhibited exceptional electrochemical properties.

Among the various electrode materials used for SCs, silicon-based electrodes are used widely in microcapacitor applications with high power density. Silicon-based ceramics, such as

silicon carbide (SiC) and silicon oxy-carbide (SiO_x C_y), are promising electrode materials offering relatively good energy densities [18,19]. Furthermore, SC electrodes composed of silicon-based ceramics are thermally stable over wide temperature range, which is a major determinant of the utility of SCs at various temperatures [20,21]. Previous studies have demonstrated that the EES properties of SiOCs are highly dependent on the presence of (i) oxygen functional groups, (ii) a free-carbon phase, and (iii) the amorphous/crystalline phase ratio. However, the precise role of each of these factors is not completely understood [22,23]. Recently, electrodes based on silicon oxycarbide (SiOC) were suggested for use in SCs, LIBs, and SIBs. These materials feature a glassy SiO_xC_y phase and a free-carbon phase embedded uniformly throughout the SiOC matrix, which minimizes changes in volume over prolonged cycling [23,24]. SiOC glass-ceramics can be prepared using sol-gel methods, carbo-thermal reactions, or the pyrolysis of siloxane-based polymers[25,26]. Each of these strategies results in the formation of particles or irregularly shaped powders with specific morphologies and compositions [25,26]. It is well known that size, structure, surface area, chemical composition, and porosity play vital roles in the supercapacitive properties of an electrode material. To date, few studies have examined the preparation of SiOCs with controlled morphologies. In this work, siloxene sheets were carbothermally converted into oxygen-enriched SiOC lamellae for the first time. This novel material was then used as the electrode material in SC employing both aqueous and organic electrolyte.

2. Experimental section

2.1 Preparation of silicon-oxy-carbide (SiOC) via carbothermal reaction

A carbothermal reaction was used to prepare silicon-oxy-carbide (SiOC). Briefly, 0.4 g of siloxene sheets (synthesized by the topochemical reaction of CaSi₂ in ice-cold HCl [13,27]) and

5 g of sodium alginate were ground to a fine powder and annealed at 200 °C for 2 h at a heating rate of 2 °C. The temperature was then increased to 900 °C at a rate of 10 °C and held for 6 h in an Ar atmosphere followed by cooling to room temperature. The thermal treatment results in the removal of the functional groups attached to the edges of the siloxene sheets and carbonization of the biopolymer which finally lead to the formation of SiOC material. The resulting black colored SiOC powder was washed and characterized as described below. For the preparation of alginate-derived carbon, the above procedure was repeated in the absence of siloxene sheets.

2.2 Preparation of SiOC working electrodes

Initially, working electrodes were prepared from a homogeneous slurry made by grinding the active material (90 wt%) with 5 wt% carbon black and 5 wt% polyvinylidene fluoride (PVDF) binder dispersed in N-methyl-2-pyrrolidone (NMP). The slurry was spread onto aluminum (Al) foil via doctor blade to ensure uniform electrode thickness. The spread slurry was then dried at 80 °C in a vacuum oven to evaporate the solvent. After drying, the SiOC electrode-coated Al 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 coin cell fabrication. The fabrication of SiOC electrodes on stainless steel substrates (1×1 cm²) for three-electrode tests and SSC using 1M Li₂SO₄ were similar to the method reported in our earlier work[28].

2.3 Fabrication of coin-cell type symmetric supercapacitor devices

Symmetric supercapacitor (SSC) devices based on SiOC electrode were fabricated in a CR2032 coin cell configuration with an electroactive area of 1.54 cm², separated by a Celgard membrane. A solution of 1 M TEABF₄ was used as the electrolyte. The fabricated SSC device was crimped using an electric coin cell crimping and disassembling machine (MTI, Korea). Electrolyte handling and device fabrication were carried out in a glove box with less than 1 ppm

of moisture and oxygen. All electrochemical measurements of SiOC SSCs were performed using an Autolab PGSTAT302N electrochemical workstation via cyclic voltammetry (CV) at various scan rates, electrochemical impedance spectroscopy (EIS) analysis from 0.01 Hz to 100 kHz at an amplitude of 10 mV, and galvanostatic charge-discharge (CD) measurements over different currents.

3. Results and discussion

Figure 1 shows the preparation of SiOC lamellae using a carbothermal reaction at high temperature. Siloxene sheets (prepared via topochemical de-intercalation of calcium from CaSi₂ [29,30]) and alginic acid were used as the silicon and carbon precursors for the preparation of SiOC/carbon ceramics. The siloxene sheets and alginic acid were mixed at an appropriate ratio and heated at 900 °C, resulting in a black SiOC ceramic. To understand the formation mechanism of the SiOC, thermogravimetric analysis (TGA) was performed on siloxene, alginate, and mixtures of siloxene and alginate powders, as shown in Figure S1 of the Supporting Information (SI). The TGA thermogram of siloxene (Figure S1) indicated high thermal stability up to 900 °C. In contrast, the thermogram of alginate features three distinct stages: (i) removal of OH- and CO- groups at 220 °C, (ii) carbonization starting at 270 °C and, (iii) complete conversion of alginate into carbon at 900 °C [31,32]. Thermograms of powders containing a mixture of siloxene and alginate were similar to those of neat alginate, except that the residual weight percent was higher. The prepared SiOC powder was thermally stable up to 900 °C (see Figure S2 in the SI). Carbothermally prepared SiOC powders were characterized using X-ray photoelectron spectroscopy, X-ray diffraction, Fourier transformed infrared spectroscopy, Raman spectroscopy, and high-resolution transmission electron microscopy with elemental mapping analyses.

Figure 2A shows X-ray photoelectron spectroscopy (XPS) survey spectra of siloxene, alginate-derived carbon, and SiOC lamellae. The presence of peaks corresponding to Si, O and C, at 103, 530 and 284 eV, respectively, in the XPS spectrum of SiOC indicate the carbothermal conversion of siloxene and alginate into SiOC nanostructures. To elucidate the chemical states of the elements in prepared SiOCs, core-level spectra of Si, O, and C were compared to those obtained from pristine siloxene and alginate-derived carbon, as shown in Figure 2(B-D). A comparison of the Si (2p) states of bare siloxene sheets and SiOC lamellae in Figure 2B shows that the chemical state of Si changed after the carbothermal reaction. The Si (2p) spectrum of siloxene sheets (Figure 2B, bottom) contains two peaks at 99 and 103 eV, which correspond to Si-Si bonds and oxygenated/hydrogenated functionalities in the siloxene sheets, respectively [13,33]. Interestingly, the carbothermal reaction and conversion of siloxene to SiOC lamellae has been shown to significantly change the bonding environment of Si. The occurrence of new bonds between Si, O, and C in SiOC lamellae results in Si (2p) states similar to those found in SiOC [19]. The disappearance of Si-Si bonds, indicated by an XPS peak at 99 eV, after the carbothermal reaction indicates the transformation of the silicene-intercalated groups in siloxene into O-Si-O-C groups in SiOC. The Si (2p) spectrum of carbothermally prepared SiOC lamellae (shown in Figure 2B, top) indicates the presence of four different chemical states: SiO_3C , SiO_2C_2 , SiOC₃, and SiO_x, indicated by peaks at 102.7, 101.8, 101.05 and 103.45 eV, respectively [19,23]. The O (1s) spectra of bare siloxene sheets, pristine carbon, and SiOC lamellae were examined in detail to assess changes in the oxygen bonding levels of SiOC lamellae. The O (1s) spectrum of siloxene sheets (Figure 2C, bottom) contained two peaks, at 532.5 and 533.5 eV, corresponding to Si-O₂ and Si-O_x states, respectively [30,33]. Peaks at 532.7 and 533.8 eV in the O (1s) spectrum of alginate-derived carbon (Figure 2C, middle) indicated the presence of C-OH and

C=O groups, respectively [34]. The O (1s) spectrum of SiOC lamellae in Figure 2C (top) shows that significant changes occurred during the carbothermal reaction. Peaks at 532.5, 533.7 and 534.85 eV indicate the formation of C=O, Si-O₂, and Si-O_x groups, respectively, suggesting the conversion of siloxene into SiOC lamellae [19,23]. The C (1s) spectrum of pristine carbon (Figure 2D, bottom) contains peaks corresponding to C-C, C=C, and C-O bonds at 284.5, 285.2, and 290.5 eV, respectively [34,35]. In contrast, the C (1s) spectrum of SiOC (Figure 2(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, respectively [19,23]. This analysis further confirms the formation of SiOC lamellae via a carbothermal reaction between siloxene and alginate powder. The atomic composition of carbothermally prepared SiOC was 22.85:29.22:47.93 (Si:O:C), which agrees with previous results obtained with SiOC [19].

Figure 3A shows an X-ray diffractogram of carbothermally prepared SiOC lamellae. The presence of a broad diffraction peak around 20 to 30° indicates the formation of an amorphous SiOC powder [36]. The amorphous nature of the SiOC powder originates from the disordered carbon phase of SiOC; the diffractogram closely matches those of SiOCs prepared via the pyrolysis of polyphenylsesquisiloxane and calcination of tetraethyl orthosilicate [36–38]. Figure 3B compares the Fourier-transform infrared spectroscopy (FT-IR) spectra of bare siloxene, alginate-derived carbon, and SiOC. The spectrum of bare siloxene contains peaks at 452, 867, 1,034, 1,639, and 2,140 cm⁻¹, corresponding to v(Si–Si), v(Si–H), v(Si–O–Si), v(Si–OH), and v(OSi₂ = Si–H) vibrations, respectively. These functional groups indicate the formation of Kautsky-type siloxene via the topochemical removal of calcium from CaSi₂ [39]. The FT-IR spectrum of pristine carbon (derived from the pyrolysis of alginate) contains a weak band at 1,014 cm⁻¹ that can be attributed to the presence of a carbonyl (C–O) group [40]. The FT-IR

spectrum of SiOC was significantly different than those of siloxene and carbon. (i) The vibrational bands corresponding to the Si-H, Si–OH, and $OSi_2 \equiv Si$ –H groups of siloxene were absent from the FT-IR spectrum of SiOC. (ii) The intensity of the Si-Si band of SiOC was significantly lower than that of bare siloxane. (iii) The spectrum of SiOC contained two new bands at 1,409 and 1,655 cm⁻¹, corresponding to v(Si-OC), and v(C=O) in SiOC [30,41,42]. The vibrational bands in the FT-IR spectrum of SiOC were consistent with previously published reports[30,41,42]. These changes further confirm the formation of SiOC via a carbothermal reaction.

The Raman spectra of SiOC powders in Figure 3C contain peaks at 376, 590, 962, 1,345, and 1,568 cm⁻¹. The bands observed at 376 and 590 cm⁻¹ originate from Si-O_x bonds in SiOC. The band at 962 cm⁻¹ is related to the LO modes of Si-O [19,43]. The bands at 1,345 and 1,570 cm⁻¹ correspond to the D and G bands of carbon in the SiOC, respectively [19,43,44]. Raman spectra of SiOC, siloxene sheets, and alginate-derived carbon are compared in Figure S3. Figure 3(D-H) presents high-resolution transmission electron spectroscopy (HR-TEM) micrographs of SiOC powders, showing the presence of lamella-like structures with irregular lateral dimensions. The micrograph in Figure 3G shows the crumpled edges of SiOC, which may be a side effect of the high-temperature reaction. The inset of Figure 3G depicts the selected area electron diffraction (SAED) pattern of SiOC, which shows the characteristic halo pattern indicating of the amorphous nature of SiOC lamellae [45]. To understand the distributions of Si, O, and C atoms in the SiOC, elemental mapping was performed during acquisition of the HR-TEM micrograph (Figure 3H); these maps are shown in Figure 3(I-K), respectively. C, O, and Si atoms were homogeneously distributed throughout the lamella-like sheets, suggesting a molecular-level transformation of siloxene into SiOC. Figure S4 shows that the N2 adsorption-desorption

isotherm of SiOC closely approximates a typical Type II isotherm [46], indicating monolayer formation on a macroporous surface at low pressure. The Brunauer–Emmett–Teller (BET) surface area of our prepared SiOC samples was 5.64 m² g⁻¹, which is comparable to those of previously reported SiOCs derived from pyrolyzed poly(methylphenyl silsesquioxane (1.8 and 4.3 m² g⁻¹, respectively) [46,47].

To investigate the charge storage capabilities of an individual SiOC electrode, three electrode analysis were performed using Li₂SO₄ electrolyte and provided in Figure 4. Figure 4A shows cyclic voltammograms acquired for SiOC electrodes at various scan rates (5 to 100 mV s⁻¹) from -1.0 to +1.0 V. The rectangular shape of the resulting voltammograms is consistent with Type A behavior, indicative of a capacitive or pseudocapacitive nature of SiOC electrode [48]. Therefore, the mechanism of charge storage at the SiOC electrode is likely due to a combination of double layer capacitance from the carbon component of the SiOC and intercalation capacitance from the Si-Si and/or Si-O components. Also, note that no redox peaks were observed in any of the voltammograms, indicating the absence of any Faradaic processes in the SiOC electrode. Figure 4(B and C) illustrates the ideal polarization nature of SiOC electrodes in the positive and negative voltage regimes, respectively, both of which delivered a typical rectangular voltammogram. The cyclic voltammograms provided in Figure 4D indicates that SiOC electrodes can function as both positrodes and negatrodes in an EES device [49]. The EIS measurements were performed with the SiOC electrode to elucidate the capacitive nature and fundamental modes of charge transfer at the electrode surface. Figure 4E shows the Nyquist plot obtained with SiOC electrode and indicates the presence of solution resistance (R_s of 2.488 Ω) and charge-transfer resistance (R_{ct} of 1.19 Ω) with additional Warburg impedance. The Warburg line, observed in the low-frequency regime, is closer to the imaginary axis of the impedance and

indicates the capacitive nature of the SiOC electrode [50]. Figure 4F gives CD profiles of SiOC electrode from -1.0 to +1.0 V, recorded at various current ranges from 1.0 to 25.0 mA. The shape of the CD profiles is quasi-triangular, with no plateau region which is in good agreement with Figure 4A and indicates that the observed capacitance is due to the combination of double layer formation and pseudocapacitance [51].

In general, electrochemical studies employing a two-electrode configuration are wellsuited for the performance evaluation of supercapacitor and to distinguish the electrode property to that of a device property [52,53]. Herein, SSC devices employing two ideal SiOC electrodes were fabricated using two electrolytes: (i) aqueous Li₂SO₄ (beaker-type cell) or (ii) organic TEABF₄ (CR2032 coin cell-type cell). Based on the above three-electrode analyses, these SiOC SSC devices were deemed capable of operating within an operation voltage window (OVW) of 2.0 V in Li_2SO_4 electrolyte, while the TEABF₄ electrolyte extended the OVW to 3.0 V. Figure 5(A-D) shows the electrochemical characterization of of SiOC SSCs obtained in Li₂SO₄ electrolyte. The cyclic voltammograms in Figure 5A show that the SiOC SSC can operate within an OVW of 2.0 V without any sign of gas evolution, largely due to the neutral nature of Li₂SO₄ (since acidic and basic electrolytes tend to have limited OVWs) [3,54]. Figures 5B and 5C show the cyclic voltammograms obtained in Li₂SO₄ electrolyte at various scan rates (5 to 500 mV s⁻¹), respectively. The rectangular shape of the voltammetric curves indicate the ideal capacitive nature of the electrodes [55]. Figure 5D shows the effects of scan rate on the specific capacitance of single SiOC electrode (obtained using $C_{electrode} = 4 \times C_{device}$) and SiOC SSC device. At a low scan rate of 5 mV s⁻¹, the SiOC device exhibits a high specific device capacitance of 35.26 F g⁻¹, from which the capacitance of a single electrode can be calculated as 141.07 F g^{-1} .

To determine the OVW of the SiOC SSC in TEABF₄ electrolyte, cyclic voltammograms were acquired at different OVWs (from 0.0 to 3.0) at a scan rate of 200 mV s⁻¹, as shown in Figure 5E. The cyclic voltammograms evidence the presence of rectangular-shaped curve even at an OVW of 3.0 V, thus indicating better capacitive properties of the SiOC SSC in TEABF₄ electrolyte with a stable and large OVW compared to aqueous electrolyte [56]. The specific capacitance of the SiOC SSC in TEABF₄ (in Figure S5) increased from 2.51 to 7.02 F g⁻¹ with increasing OVW from 0.5 to 3.0 V. Figures 5F and 5G show rectangular voltammograms obtained with SiOC SSC at various scan rates ranges from 5 to 1000 mV s⁻¹, indicative of an ideal capacitor [20]. The effect of scan rate on the specific capacitance of SiOC SSC is summarized in Figure 5H. A specific device capacitance of about 28.82 F g⁻¹ was obtained from the CV recorded at a scan rate of 5 mV s⁻¹; the corresponding capacitance of a single SiOC electrode was 115.30 F g⁻¹.

Nyquist plots obtained for the SiOC SSCs using Li_2SO_4 and TEABF₄ electrolytes are shown in Figures 5I and 5J, respectively. Three distinct regions are evident in the Nyquist plot which corresponds to the (i) high-, (ii) mid-, and (iii) low-frequency regimes of the impedance [13]. The solution resistance of SiOC SSCs using Li_2SO_4 and TEABF₄ electrolyte was 1.36 and 2.5 Ω , respectively, as determined from the high-frequency regime of the Nyquist plot. The charge-transfer resistance of SiOC SSCs was about 3.89 Ω for the Li_2SO_4 electrolyte and 16.10 Ω for the TEABF₄ electrolyte. The higher solution and charge-transfer resistances for SiOC SSCs employing TEABF₄ electrolyte are due to the low ionic conductivity and higher ionic radii of TEABF₄ compared to Li_2SO_4 electrolyte [3,57,58]. Furthermore, the low-frequency region indicates the presence of Warburg diffusion, which is closely related to the diffusion-mediated capacitance of the SSC. Noticeably, the magnitude of the Warburg line is lower for Li₂SO₄ than

that for the TEABF₄, which is due to the differential ion diffusion kinetics of these electrolytes. Figure 5K shows Bode phase angle plots of SiOC SSCs with Li₂SO₄ and TEABF₄ electrolytes as a representation of the change in phase angle as a function of the applied frequency [59]. At 0.01 Hz, the phase angles of the SiOC were -85.04° and -64.61° for Li₂SO₄ and TEABF₄ electrolytes, respectively. The capacitor response frequencies (f_o) at a phase angle of -45°, determined from the Bode phase angle plot shown in Figure 5K, were 0.83 and 0.43 Hz for the Li₂SO₄ and TEABF₄ systems, respectively, resulting in relaxation times of 1.20 and 2.27 s. Figure 5L shows the specific device capacitances of SiOC SSCs using Li₂SO₄ and TEABF₄ electrolytes with respect to applied frequency. In both cases, specific device capacitance decreased with increasing frequency and a high device capacitance of 21.2 and 9.01 F g⁻¹ for SiOC SSCs with Li₂SO₄ and TEABF₄ electrolytes were obtained at 0.01 Hz.

Figures 6A and 6B show galvanostatic CD profiles of SiOC SSC devices fabricated using Li_2SO_4 (OVW of 2.0 V) and TEABF₄ (OVW of 3.0 V) electrolytes at different levels of applied current. Note that the CD profiles obtained at high currents are more symmetric than those obtained over low currents with sloppy symmetric profiles. These data demonstrate the roles of surface and intercalation capacitances at the SiOC electrode [27,60]. The effects of the applied current range on specific device capacitance are shown in Figure 6C. SiOC SSCs delivered specific device capacitances of 25.58 and 16.71 F g⁻¹ for devices containing Li₂SO₄ and TEABF₄, respectively, as determined from the discharge profile recorded at a current of 0.5 mA. The specific device 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 of Li⁺ ion (about 0.06 nm). Note that the ionic radius of TEA⁺ ion is approximately 0.343 nm, but remains functional over a relatively wide OVW of 3.0 V [3]. Figures 6D and 6E illustrate the cyclic

stability of SiOC devices over 5,000 continuous CD cycles. Interestingly, the device containing the TEABF₄ electrolyte exhibited a greater capacitance retention (~92.8%) compared to the Li₂SO₄-based SSCs (86.2%). FE-SEM and elemental mapping of SiOC electrodes are shown before (Figure S6) and after electrochemical testing in 1 M Li₂SO₄ (Figure S7) and 1 M TEABF₄ (Figure S8). No structural changes were evident in either system at the SiOC electrode after 5,000 continuous CD cycles. Elemental mapping of the as-fabricated SiOC electrode (Figure S6(B-F)) indicated the presence of Si, O, C, and F atoms arise from the SiOC active material and PVDF binder. SiOC electrodes cycles with Li₂SO₄ (Figure S7(B-G)) contained S atoms originated from sulphate anions in the electrolyte. SiOC electrodes cycles with TEABF₄ showed the presence of N, F, and B atoms uniformly dispersed over their surface, as shown in Figure S8(B-H). These data show the structural stability of SiOC electrodes even after uninterrupted CD cycles in both aqueous and organic electrolytes. To examine the rate capability of SiOC SSCs in TEABF₄ electrolyte, continuous CD profiles were recorded at various levels, from low to high currents and vice-versa, as shown in Figure 6F. The electrodes exhibited excellent capacitance retention over the different applied currents and highlight the rate capability of SiOC SSCs [13,61].

Energy/power density is an important parameter that often determines the practical application of an SSC device [62]. The energy/power performance metrics of our TEABF₄-based SiOC SSC were determined from CD analyses and are presented in the Ragone plot in Figure 7A. The analogous data are shown for the Li₂SO₄-based system in Figure S9. The Li₂SO₄-based system yielded an energy density of 14.2 Wh kg⁻¹, with a corresponding power density of 333 W kg⁻¹. In contrast, the energy density of SiOC SSC made with TEABF₄ was as high as 20.89 Wh kg⁻¹, with a corresponding power density of 750 W kg⁻¹. Furthermore, this system maintained an

energy density of 3.79 Wh kg⁻¹ at a power density of 15,000 W kg⁻¹. Tables S1 and S2 compare the gravimetric and areal metrics of SiOC SSC devices against those of state-of-the-art SCs using organic/ionic liquid electrolytes. The energy density of SiOC SSC using TEABF₄ electrolyte was higher than those of recently reported SSCs made with activated carbon (8 Wh kg⁻¹), porous carbon (11.4Wh 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 SCs [13,63–70]. Furthermore, the power density of SiOC SSCs reached up to 15,000 W kg⁻¹, which indicates their suitability as a power source for next-generation vehicles [71]. The data in Table S1 provide evidence for the superior power performance of SiOC SSCs over other SC systems employing electrodes such as graphene, rGO, coPIL-RGO, MoS₂, MXene, and siloxene [13,66,67,69,70,72]. The data in Table S2 show that the areal energy-power performance metrics of SiOC SSCs are higher than those of other siliconbased SSCs. Figure 7B shows the real-time application of a SiOC SSC to power a multifunctional electronic display showing atmospheric temperature and relative humidity. The SiOC SSC was initially charged to 3.0 V using an applied current of 1 mA. The stored energy was sufficient to power the electronic display for over 12 min, demonstrating the applicability of SiOC SSCs.

4. Conclusions

This study demonstrates the preparation of SiOC lamellae from 2D siloxene sheets and alginic acid. The formation of SiOC powders and the homogeneous distribution of their composite elements (Si, O, C) were confirmed via spectroscopic, morphological, and elemental analyses. Electrochemical studies of SiOC SSCs using aqueous Li_2SO_4 (OVW of 2.0 V) or organic TEABF₄ (OVW of 3.0 V) electrolytes indicated enhanced capacitance, improved cyclic

stability and rate capability, and specific energy densities of 14.2 and 20.89 Wh Kg⁻¹, respectively. Furthermore, the SiOC SSCs employing the TEABF₄ electrolyte yielded a maximum power density of 15,000 W Kg⁻¹, which is the minimum required power for next-generation electric vehicles. Collectively, this study demonstrates a new synthetic strategy for the preparation of SiOCs lamellae from 2D siloxene sheets, and the exceptional supercapacitive performance of SiOC lamellae. This work will be useful for the development of high-performance energy storage devices.

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Conflicts of interest

"There are no conflicts to declare."

Supporting information

The experimental section, supporting experimental results, tables for performance comparison of SiOC SSC with reported devices are provided in the supplementary information.

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Figure captions

Figure 1. Schematic showing the preparation of silicon-oxy-carbide (SiOC) lamellae via the carbothermal reaction between siloxene sheets and sodium alginate biopolymer at 900°C.

Figure 2. Physicochemical characterization of SiOC lamellae: (A) comparative X-ray photoelectron spectroscopy (XPS) survey spectra of bare siloxene, carbon, and SiOC, (B) comparative XPS spectra of the Si (2p) states in bare siloxene and SiOC, (C) comparative XPS spectra of the O (1s) states present in bare siloxene, carbon, and SiOC, and (D) comparative XPS spectra of the C (1s) states in carbon and SiOC.

Figure 3. Physicochemical characterization of SiOC lamellae: (A) X-ray diffractogram of SiOC, (B) Fourier-transformed infrared spectra of bare siloxene, carbon, and SiOC, (C) Raman spectra of SiOC lamellae, (D–H) high-resolution transmission electron micrographs of SiOC lamellae obtained at various magnifications. The inset in (H) shows the SAED pattern of SiOC lamellae. Elemental maps of SiOC: (I) overlay image, (J) Si atoms, (K) O atoms and (L) C atoms.

Figure 4. Electrochemical analyses of SiOC electrodes in 1 M Li_2SO_4 using a three-electrode cell. Cyclic voltammograms of SiOC electrodes were acquired at various scan rates over operating potential windows of (A) -1.0 to 1.0 V, (B) -1.0 to 0.0 V, and (C) 0.0 to 1.0 V. (D) Cyclic voltammograms were also acquired at a scan rate of 100 mV s⁻¹. A Nyquist plot of the SiOC electrode is shown in (E) and charge-discharge (CD) profiles of the SiOC electrode obtained using various applied currents from 1.0 to 25 mA are shown in (F).

Figure 5. Electrochemical analyses of SiOC symmetric supercapacitors (SSCs) using 1 M Li_2SO_4 and 1 M TEABF₄ electrolytes: (A) cyclic voltammograms in 1 M Li_2SO_4 were measured at different operating voltages of 0.0 to 2.0 V at a scan rate of 100 mV s⁻¹ and (B–C) at scan rates from 5 to 500 mV s⁻¹. (D) The effects of scan rate on the specific capacitance of a SiOC SSC in 1

M Li₂SO₄. (E) Cyclic voltammograms of SiOC SSCs were acquired in 1 M TEABF₄ at different operating voltages, of 0.0 to 3.0 V, using a scan rate of 200 mV s⁻¹ and (F–G) at scan rates from 5 to 1,000 mV s⁻¹. (H) The effects of scan rate on the specific capacitance of SiOC SSC in 1 M TEABF₄. (I–J) Nyquist plot of SiOC SSCs in 1 M Li₂SO₄ and 1 M TEABF₄, respectively. (K) Bode phase angle plots of SiOC SSCs in 1 M Li₂SO₄ and 1 M TEABF₄, respectively. (L) The specific capacitances of SiOC SSCs are given as a function of applied frequency in 1 M Li₂SO₄ and 1 M TEABF₄.

Figure 6 Electrochemical analyses of the SiOC SSCs in 1 M Li_2SO_4 and 1 M TEABF₄: (A–B) Galvanostatic CD profiles of SiOC SSCs were obtained at various applied currents from 0.5 to 10 mA in 1 M Li_2SO_4 and 1 M TEABF₄. (C) the effects of discharge current are shown on the specific capacitances of SiOC SSCs in 1 M Li_2SO_4 and 1 M TEABF₄, (D–E) the cycling stability of SiOC SSCs is shown over 5,000 continuous charge-discharge cycles in 1 M Li_2SO_4 or 1 M TEABF₄, and (F) the rate capability of SiOC SSC is shown using 1 M TEABF₄.

Figure 7. (A) A Ragone plot of SiOC SSC in TEABF_4 shows its superior energy/power characteristics over those of previously reported SSCs. (B) A fully charged SiOC in TEABF_4 was used to power a multifunctional electronic display for over 720 seconds.



Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5.



Figure 6.





Figure 7.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Graphical Abstract



Highlights

- Silicon-oxy-carbide (SiOC) was prepared via carbothermal conversion of 2D-siloxene.
- > SiOC symmetric supercapacitor (SSC) was fabricated using aqueous and organic electrolytes.
- > The charge-storage mechanism of SiOC electrode was discussed.
- The SiOC SSC in aqueous electrolyte delivers high energy of 14.2 Wh Kg⁻¹ with a power of 6666 W Kg⁻¹.
- The energy (20.89 Wh Kg⁻¹) and power (15 KW Kg⁻¹) densities of SiOC SSC was boosted using organic electrolyte.