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Functional Composites and Structures

PAPER

Electrochemical and structural performances of carbon and glass fiber-reinforced structural supercapacitor composite at elevated temperatures

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Keywords: structural energy storage, structural supercapacitor composite, electrochemical performance, structural properties, elevated temperatures

Supplementary material for this article is available online

OPEN ACCESS

RECEIVED
28 February 2024

REVISED
26 April 2024

ACCEPTED FOR PUBLICATION
28 June 2024

PUBLISHED
11 July 2024

Abstract

The structural supercapacitor can store electrical energy and withstand structural loads while saving substantial weight in many structural applications. This study investigated the development of a structural supercapacitor with a fiber-reinforced polymer composite system and explored the operating temperature's influence on its performance. The electrochemical and mechanical properties of structural supercapacitors beyond the ambient temperature have not yet been studied; hence, evaluating parameters such as specific capacitance, energy density, cycle life, and structural performance at elevated temperatures are highly desired. We have designed and manufactured single and parallelly connected multilayer structural supercapacitor composites in this research. Carbon fibers were used as a bifunctional component, acting both as a current collector while acting as a mechanical reinforcement. In addition, glass fibers were added as the separator which is also acting as an integral reinforcement. The electrochemical and mechanical behavior of structural supercapacitors at elevated temperatures up to 85 °C were experimentally investigated. The test results revealed that at room temperature, the developed double-cell structural supercapacitor, which demonstrated an area-specific capacitance of 1.16 mF cm^{-2} and energy density of 0.36 mWh cm^{-2} at 0.24 mA cm^{-2}, which are comparable to current achievements in structural supercapacitor research. The structural supercapacitor's tensile, flexural, and compression strengths were measured as 109.5 MPa, 47.0 MPa, and 50.4 MPa, respectively. The specific capacitance and energy density reached 2.58 mF cm^{-2} and 0.81 mWh cm^{-2}, while tensile, flexural, and compression strengths were reduced to 70.9 MPa, 14.2 MPa, and 8.8 MPa, respectively, at 85 °C. These findings provide new comprehensive knowledge on structural supercapacitor devices suitable for applications operating within a temperature range from ambient conditions to 85 °C.

1. Introduction

Fiber-reinforced polymer composite is a widely accepted alternative to metal-based engineering materials. It plays a vital role in many engineering fields, especially in civil and aviation industries, where lightweight design is a stringent requirement. Recently, the development of functional materials such as multifunctional fiber-reinforced composites has increased to realize lightweight and novel device structures [1–3].

Multifunctional composite can perform a variety of non-structural functions, such as energy generation, energy storage, self-healing capability, sensing, and actuating, apart from the primary structural functions [4]. With this development, energy-storable composites such as structural supercapacitor composite (SSC) have attracted significant attention from researchers, as this device can be designed to serve as load-bearing critical components of buildings and many engineering applications [5]. Therefore, the entire structure becomes an energy storage device, increasing the overall performance as the payload from battery packs is decreased. In addition, this type of structure can be prefabricated and pre-assembled at a plant, thus reducing the construction completion period to a few days.

The most common type of supercapacitor is the electric double-layer capacitor (also known as EDLC), the base for structural supercapacitor development. A structural EDLC embodiment (single-cell configuration) comprises two carbon fiber electrodes that sandwich an electrically insulating separator with a structural electrolyte. The separator plays a critical role in determining the electrochemical breaking voltage of the supercapacitor where micro short circuits may occur. Numerous studies have demonstrated that glass fiber (GF) fabric is an optimal separator for structural supercapacitors [6–8]. In addition, the structural electrolyte, which acts as both electrolyte and structural matrix, is a critical component in a structural supercapacitor, which determines the electrical conductivity of the supercapacitor. Despite the advancements in SSCs, realizing an effective structural supercapacitor remains a substantial challenge. Thus, exploration of this field is still in its early stage, making it a highly novel study area [6].

The lack of processable structural electrolytes is a significant hurdle in structural supercapacitor development [9]. Typically, the electrolyte defines the performance parameters such as ionic conductivity, electrochemical voltage window, and operating temperature [9, 10]. Notably, the low ionic conductivity and low voltage window of structural electrolytes significantly reduce the capacitance and, ultimately, the energy density of the structural supercapacitor. Therefore, it is essential to improve these two parameters to enhance the device's energy density. However, there is a trade-off between the electrical and structural performances of the structural electrolytes. The electrolyte with relatively high ionic conductivity comes with insufficient structural performance. Therefore, improving the energy density without compromising the structural performance is essential to increase the device's overall performance.

Solid polymer electrolytes based on bi-continuous ionic liquid structural matrix systems have been extensively explored when developing structural electrolytes [8, 11]. This approach enhances the ionic conductivity while maintaining structural integrity. The 15–30 wt% structural matrix has been recognized as the optimum composition that ensures a good balance between mechanical and electrochemical properties [11, 12], mainly because the low epoxy content makes the paths of ion mobility, leading to the increased high ionic conductivity [13]. Diglycidyl ether of bisphenol A (DGEBA) is a commonly used epoxy monomer worldwide for fabricating carbon fiber composites with high structural properties. Therefore, DGEBA is a suitable epoxy for developing structural electrolytes. However, the ability to ionic transport of the electrolyte decreases during the curing process due to increased crosslinks. Mixing nanoparticles (TiO_2, Al_2O_3, $BaTiO_3$) with structural electrolytes is a viable solution to minimize this problem [3].

Besides, the fabrication of a structural supercapacitor that combines the three major parts (electrodes, separator, and structural electrolyte) is critical for achieving the optimal multifunctional properties of the SSC. In particular, the fabrication process should retain the stiffness, strength, and toughness of the composite while maximizing the proportion of electrochemically active regions. The structural supercapacitors' fabrication process, consistent with conventional composite manufacturing, minimizes the design, manufacturing, and scale-up issues. It will further facilitate evaluating its mechanical performance following the test standards for composite materials.

SSCs are easily integrated into recent rapid construction and compacted/modular buildings, and it can be used as parts of smart building bodies (wall bricks and roof tiles). In addition, it is suitable for many applications such as body parts of electric and hybrid vehicles (the door panels, roof, chassis, and bonnet), body parts of electric rails, and body parts of energy generation units such as wind turbines and photovoltaic panels. However, for successful integration, the entire structure should be able to tolerate the harsh in-service conditions such as high temperatures. Temperature is an important parameter determining supercapacitor performance, cycle life, and safety. High temperatures promote electrochemical reactions but degrade the performance of supercapacitors with time [14, 15]. Nevertheless, the residual strength of fiber-reinforced composites drastically reduces at high temperatures [16, 17]. Therefore, SSC applications require in-depth knowledge of the materials' thermo-mechanical properties. Many applications of civil, infrastructure, and automotive industries are often exposed to extreme temperatures, especially above 60 °C. It has found that, the maximum temperature rise of body surfaces fully exposed to sunlight will be about 34–50 (°C) during a sunny day [18], and the average temperature of an equatorial country is around 34 °C [19]. Consequently, the maximum temperature of many structural applications exposed to sunlight can reach up to 84 °C.

Therefore, for SSCs to be viable candidates for such applications, they should withstand the temperature up to that level. To the best of the authors' knowledge, no studies have done so far to evaluate the electro-mechanical performance of SSCs at elevated temperatures [1].

On the other hand, from the perspective of structural composites, the thickness and strength should be easily controllable during the fabrication process to match the end-use requirement. Therefore, for industrial applications, the provision for varying the thickness of structural supercapacitors during the fabrication process is vital. The multilayer approach, achieved through the mutual stacking of supercapacitor functional layers, allows the fabricating of thicker and stronger devices [20]. Increasing the number of supercapacitor functional layers enables the strength and thickness to be easily customized while expanding the energy storage capacity. Therefore, the multilayer concept proposed by Anurangi *et al* [1] was adapted for the first time to evaluate electro-mechanical performance at two different thicknesses.

The aim of this study is to investigate the electrical and mechanical performances of structural supercapacitors at three different temperature levels (25 °C, 65 °C, and 85 °C) for the first time. The authors consider the electro-mechanical behavior of structural supercapacitor at elevated temperatures is essential for the maturation of this field. In addition, single-cell and double-cell SSCs were designed, and electrochemical and structural performances at elevated temperatures were compared. Thus, this study is highlighted as the first investigation of the comprehensive electro-mechanical performance of the SSC at elevated temperatures.

2. Experiments

2.1. Materials

This research employed carbon fiber fabric (200 gsm, twill weave, purchased from ALT Composites Australia) without any activation or other surface modifications as the electrodes and E-GF fabric (120 gsm, plain weave, purchased from ALT Composites Australia) as the separator of the structural supercapacitor. The resin matrix was diglycidylether of bisphenol A (DGEBA) (Araldite GY 191) with Triethylenetetramine hardener (TETA, 97%, purchased from Sigma Aldrich). 1-Ethyl-3-methylimidazolium bis(trifluoro methylsulfonyl) imide (EMITFSI, 98%, purchased from Sigma Aldrich) acted as the ionic liquid. Bis(trifluoromethane) sulfonamide lithium salt (LiTFSI, purchased from Sigma Aldrich), propylene carbonate (PC, 99.7%, purchased from Sigma Aldrich), and TiO_2 (particle size 20–40 nm, XFNANO China) were mixed with the ionic liquid of EMITFSI in the liquid electrolyte formulation. Figure S1 presents the chemical structures of DGEBA, EMIMTFSI, LITFSI, and TETA. All chemical reagents were used without further purification.

2.2. Preparing carbon fiber electrodes

Initially, carbon fiber fabrics were dipped in acetone for 24 h to remove sizing agents and dried in an oven before further use. The CF fabric was cut into a rectangular of 50 mm × 80 mm with ±45 fiber orientation, and a copper sheet was attached to the surface to provide electrical contacts for subsequent electrochemical testing.

2.2.1. Preparing structural electrolyte

As suggested in previous work [20], 11.8 g EMIMTFSI, 0.1 g PC, and 1 g LiTFSI were thoroughly mixed by magnetic stirring for 30 min to obtain the liquid electrolyte (LE). The prepared LE was mixed with 3.65 g DGEBA for another 30 min until converted to a homogeneous solution. After adding 0.5 g of TiO_2 particles to the solution and stirring for 30 min, TETA was included in a mass ratio of DGEBA to TETA 7.81: 1. The mixtures were stirred for 5 min at room temperature to form the structural electrolyte (SE) solution. The prepared SE solution contains 75% LE (i.e. 25% structural resin matrix). TiO_2 content is 5% of the total weight of SE, and it was optimized in a previous study [21]. The developed structural electrolyte was characterized by scanning electron microscope (SEM) and thermogravimetric analysis (TGA) to understand its morphology and thermal stability better.

2.2.2. Assembling symmetric structural supercapacitor

Two GF layers were sandwiched between two carbon fiber (CF) layers, and the structural supercapacitor was fabricated by hand lay-up in a fully open environment. The structural electrolyte mixture is evenly coated on CF and GF, and the CF-GF-GF-CF configuration was adapted for single-cell structural supercapacitor fabrication. The structural supercapacitor was cured at room temperature (25 °C) for 48 h under pressure. Finally, it was subjected to a post-curing at 85 °C for three hours, prior to the electrochemical and mechanical testing.

When preparing the multilayer structural supercapacitor, the CF-GF-GF-CF-GF-GF-CF-GF-GF-CF configuration was adapted for a double-cell structural supercapacitor. Two basic structures, single-cell and

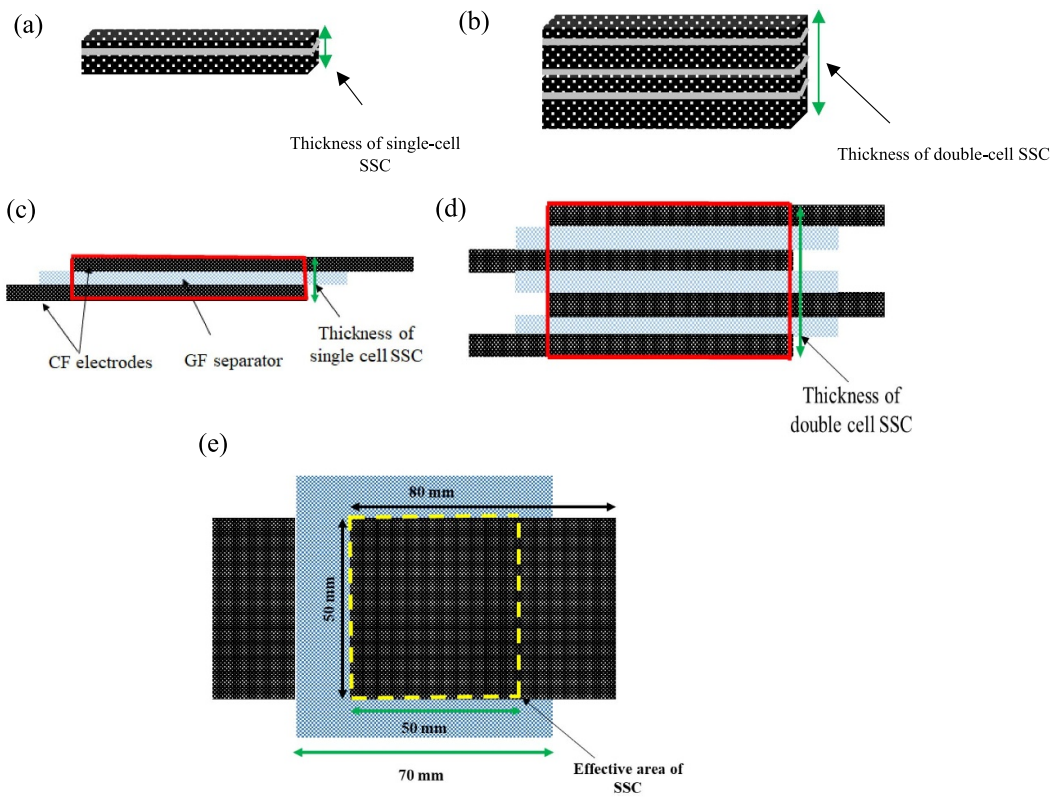

Figure 1. (a), (b) Configuration of single-cell and parallelly connected double-cell SSC; (c), (d), (e) experimental arrangement, CF electrodes are leading in two sides for connecting to the potentiostat and GF separator (70 mm × 70 mm) was laid out with a balanced lay-up on each side to prevent the direct contact of electrodes, (c) (d) side view of single-cell and double-cell SSC (layer thickness has been exaggerated for clarity), (e) Top view of single-cell and double-cell SSC.

Table 1. Summary of manufacturing condition and sample codes.

Manufacturing Conditions	Sample Code
Single-cell structural supercapacitor	SSC-1
Double-cell structural supercapacitor	SSC-2
Single-cell monofunctional composite	MC-1
Double-cell monofunctional composite	MC-2

parallelly connected double-cell SSCs, were fabricated as shown in figure S2. Figure 1 illustrates the top and side views of the supercapacitor and the effective surface area of the CF electrodes in the fabricated supercapacitor is 5 cm × 5 cm (i.e. the supercapacitor area is 25 cm^2). The electrochemical tests were performed on fabricated supercapacitors. The main advantage of this configuration, when making parallel connections in multilayer supercapacitor structure, is its wireless connection, which will reduce external damage. In addition, the overall structure remains functional even if one supercapacitor layer gets damaged.

Connecting these composite sheets in series provides the flexibility of varying the voltage to the expected level. Then, structural supercapacitor (SSC) panels (both single- and double-cell) were fabricated so that test coupons could be cut to estimate the mechanical properties. Finally, the monofunctional composite (MC) with the same configuration (single-cell and double-cell) but with pure structural resin matrix was fabricated to compare the structural performance with SSC. This research comprehensively studied the electrochemical and mechanical performance of both single- and double-cell SSCs under different conditions. Table 1 summarizes the four codes according to the manufacturing condition of composites.

2.3. Electrochemical testing

All electrochemical measurements were made using an *Autolab* electrochemical interface instrument (*PGSTAT 302N*). A series of cyclic voltammetry (CV) tests at different voltage windows, starting from 0 V and ending at 2 V, were conducted at a scan rate of 50 mVs^{-1}. The cell degradation at different voltage windows was analyzed to determine the optimum voltage window. The cycle life at different voltage windows

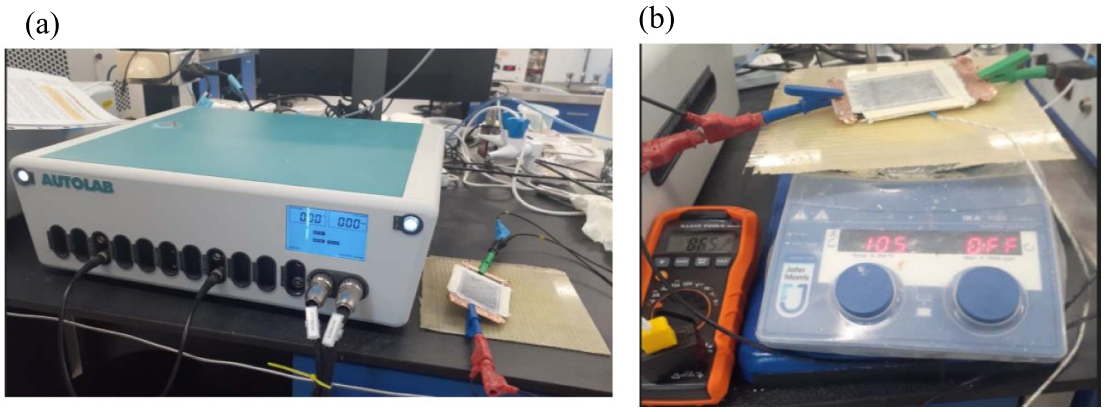

Figure 2. Experimental setup for electrochemical testing: (a) Room temperature, (b) High temperatures.

was studied to evaluate the degradation with time. Afterward, all other tests were performed at the optimum voltage range for single- and double-cell structural supercapacitors. CV tests at scan rate of 100 mVs^{-1} and galvanostatic charge-discharge (GCD) tests at different current densities were conducted to evaluate the specific gravimetric capacitance at room temperature (RT, 25 °C). The electrochemical impedance spectroscopy (EIS) was performed at an amplitude of 10 mV in a frequency range of 0.01–10k Hz. All experiments were conducted in two electrode configurations, as shown in figure 2, to evaluate the performance in the symmetric configuration. In addition, CV tests were performed at elevated temperatures to evaluate the performance of the developed device when using elevated temperature applications. Before conducting tests at elevated temperatures, samples were conditioned for two hours in the oven at the relevant temperature. The measurements were taken while maintaining the corresponding temperature, as shown in figure 2(b). Subsequently, all other tests were performed up to optimum elevated temperature for single- and double-cell structural supercapacitors.

2.4. Dynamic mechanical analysis (DMA)

DMA was performed to determine the developed structural electrolyte's viscoelastic behavior and thermo-mechanical properties. Here, 8 mm × 45 mm sized structural supercapacitor specimens were tested using TA instruments HR-2 Discovery Hybrid Rheometer using the dual cantilever fixture. The temperature cycle comprised an oscillation (temperature ramp) mode, applying a displacement of 25 μm at a frequency of 1 Hz. Three samples were heated from 25 °C to 160 °C at a rate of 5 °C min^{-1}, and average results were presented.

2.5. Mechanical testing

The mechanical properties of two types of structural supercapacitors (SSC-1 and SSC-2) were evaluated by conducting tensile, flexural, compression, and shear tests according to the ASTM D3039 [22], ASTM D790 [23], ASTM D6641 [24], and ASTM D5379 [25] standards, respectively. A water jet cutter cut all specimens, and three specimens were examined for each test at room temperature (25 °C). The mechanical properties of the corresponding MC were studied for comparison purposes. Since mechanical properties are highly influenced by fiber mass fraction, it was measured for SSC and MC according to the standard ASTM D3171 [26] Method I. In addition, all mechanical tests were conducted at two elevated temperatures (65 °C and 85 °C) to evaluate the suitability of the developed device for elevated temperature applications. For high-temperature tests, each specimen was conditioned at the corresponding temperature for more than 15 min before mechanical testing and three samples were tested.

3. Results and discussion

3.1. Characterization of synthesized structural electrolyte

3.1.1. Microstructural characterization

Combining polymers with ionic liquid caused a significant change in the final material morphology and properties. Therefore, the microphase behavior of structural electrolytes was studied and compared with pure structural resin matrix by conducting SEM (figures 3(a) and (b)). Before SEM observation, ionic liquid in structural electrolytes was removed by acetone extraction to avoid image distortion [27]. According to the

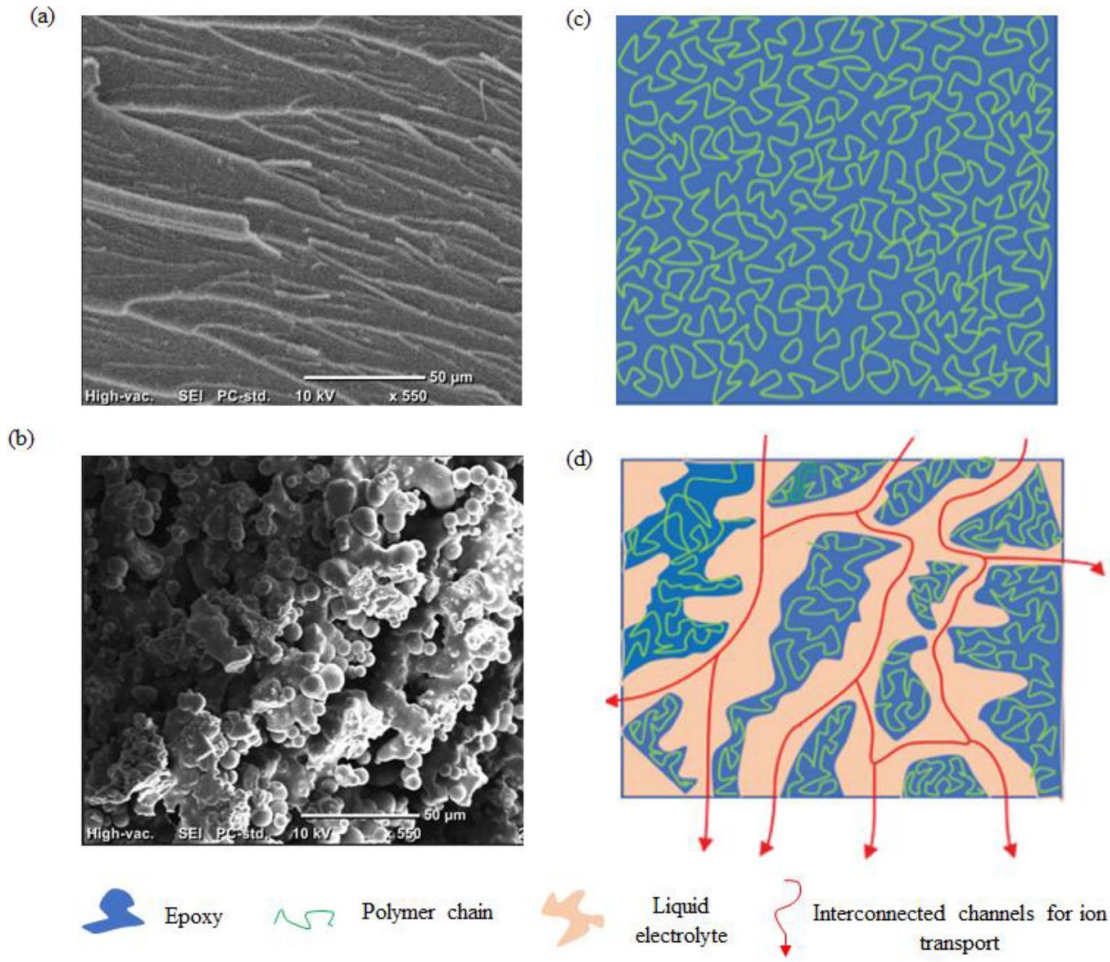

Figure 3. SEM micrographs: (a) structural resin matrix, (b) structural electrolyte (after ionic liquid extraction by acetone), (c) schematic representations of the crosslinks formation in the structural resin matrix, and (d) bi-continuous structure in resin matrix after liquid electrolyte is mixed which facilitates ion transport. Reproduced from [1]. CC BY 4.0.

SEM analysis, the structural electrolyte forms a porous or bi-continuous structure (as explained in figures 3(c) and (d)), in which the liquid electrolyte creates a separated phase inside the structural resin matrix. The crosslinked epoxy has enclosed and confined the liquid electrolyte [28]. The enclosed liquid electrolyte forms a separate phase inside the structural matrix, imbuing new functions to the final epoxy mixture [28]. Notably, the separate liquid electrolyte phase facilitates ionic conductivity through the interconnected channels formed within [1].

3.1.2. Optimum voltage window for SSC

The CV tests at different potential windows at the scan rate of 50 mV s^{-1} in a two-electrode system were recorded to evaluate the optimum voltage window for characterizing the SSC. As given in figure 4(a), no significant distortions were observed in the curve shape until the voltage window was 1.5 V. Thus, 1.5 V was selected for further characterizations of SSC. The redox peak (marked on the CV curve) slightly appeared at the corner when the voltage reached 1.5 V and was progressively significant when extending the potential beyond 1.5 V. This might be due to contamination with moisture from the ambient atmosphere during the structural electrolyte preparation and assembling the supercapacitor. This behavior indicates the involvement of non-capacitive processes due to the redox instability of structural electrolytes. As a result, the electrolyte will progressively degrade when the voltage window is beyond 1.5 V. It was confirmed by the cycle stability tests conducted at different voltage windows (figure S3), showing a lower cycle life for higher voltages.

For calculating the capacitance retention, the capacitance of the structural supercapacitor was calculated by applying equation S1. Capacitance retention after completing 5000 cycles showed 71% under 1.5 V while 41% under 2 V. The capacitance retention increased by 15% when the supercapacitor discharged to 50% (discharge from 1.5 V to 0.75 V) without discharging to 0 V (figure S3(d)). After that, a series of CV tests (figures 4(b) and (c)) was conducted for both single- and double-cell SSCs at different scan rates at optimum

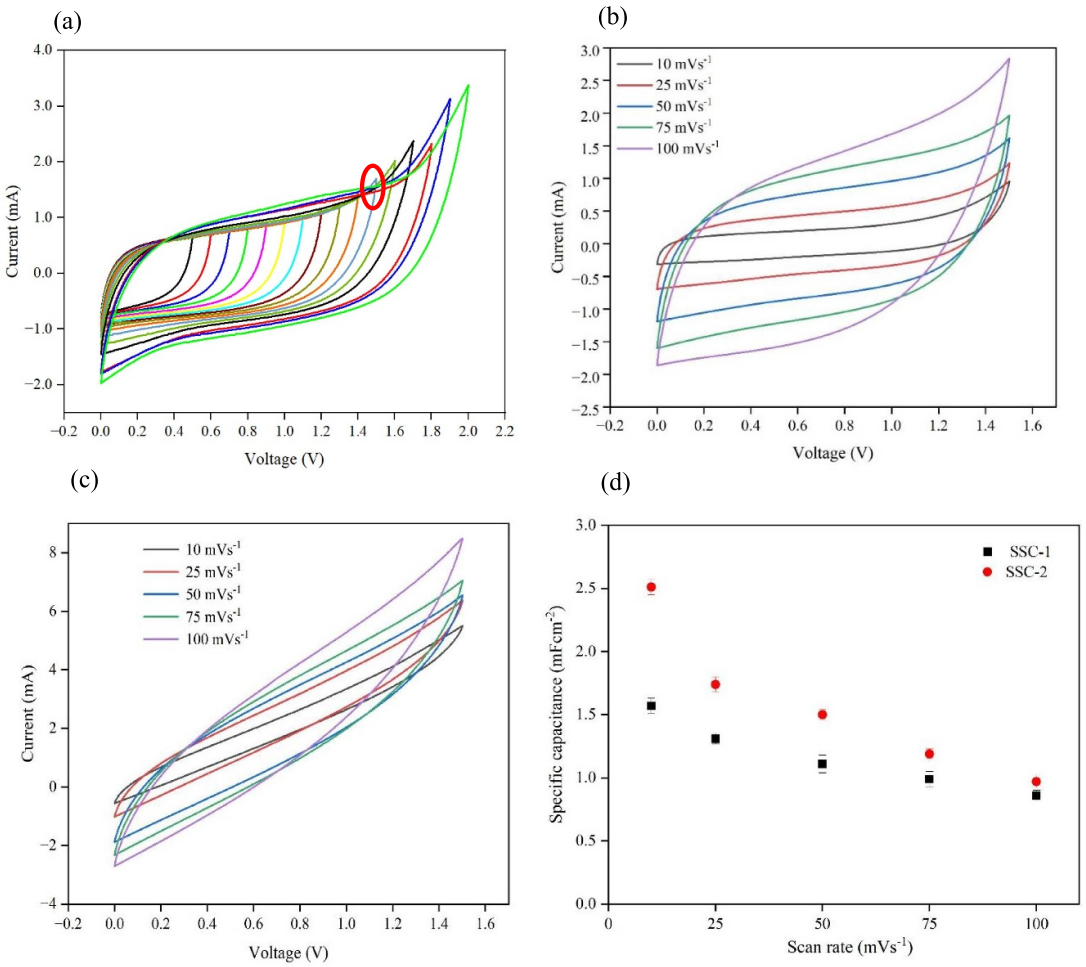

Figure 4. (a) CV curves of the SSC-1 at various operating voltage windows at the scan rate of 50 mV s^{-1}. CV test at different scan rates, (b) single-cell, (c) double-cell, (d) area specific capacitance vs scan rates.

voltage (1.5 V). The capacitances of the supercapacitor were calculated at the corresponding scan rate using equation S2 and presented in table S1. The plot (figure 4(d)) showed that the capacitance decreased with the increased scan rates. For a double-cell supercapacitor, the specific capacitance is reduced to 24.28 mF at a scan rate of 100 mVs^{-1}, which is around 39% of the capacitance at 10 mVs^{-1}. This common effect can be explained by decreasing ion diffusion coefficients at higher scan rates. Electrolyte ions have sufficient time at a lower scan rate to intercalate and de-intercalate on the surface of the electrodes, resulting in a higher capacitance value. However, electrolyte ions have a limited time at higher scan rates, which subsequently reduces the capacitance value of the device [29].

3.1.3. Thermal degradation of structural electrolyte

TGA assessed the thermal stability of the structural electrolyte under a continuous flow of N_2 gas (80 ml min^{-1}). Figure 5 illustrates the thermal degradation temperatures of the structural electrolyte and structural resin matrix. The thermograms indicated a single-step decomposition for the structural resin matrix, starting at around 345 °C.

However, structural electrolytes showed a two-stage decomposition similar to those reported by Shirshova and co-workers [12]. The first region had a temperature range between 325 °C and 369 °C, followed by the second region with a temperature range of 369 °C–500 °C. The onset temperatures of structural electrolytes were measured as 330 °C. The slight reduction of thermal stability of the structural electrolyte compared to the resin matrix was primarily due to the LiTFSI's low lattice energy, which was dissolved in the structural electrolyte [30]. The structural electrolyte loses less weight during the first stage and more during the second stage. The overall weight loss was 88% during the total decomposition process.

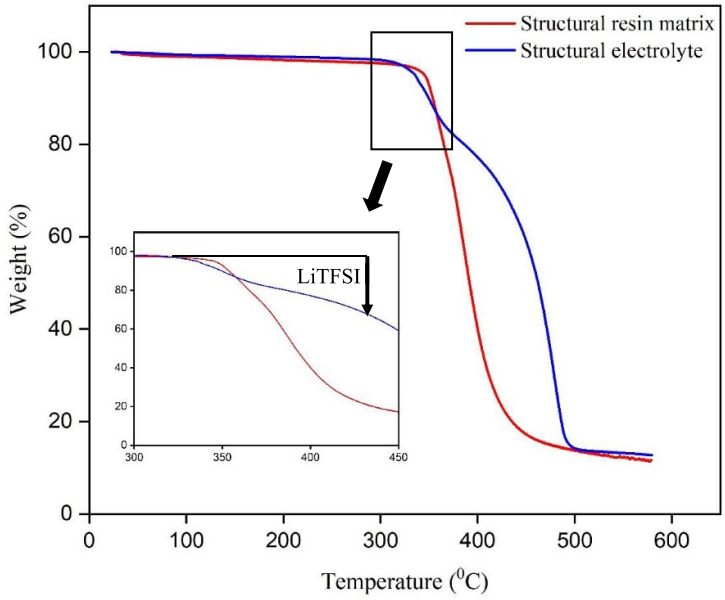

Figure 5. TGA curves for structural resin matrix and structural electrolyte.

However, the weight loss from RT (25 °C) to maximum temperature (85 °C) is less than 1% when the electrolyte is heated.

3.2. Electrochemical characterization at different temperatures

The CV, GCD, and EIS tests evaluated the electrochemical performance of single-cell and double-cell SSCs at various temperature levels. It revealed that the integral area of the double-cell device is always higher than the single-cell device due to the higher capacitance value of the double-cell device (figure S4). Therefore, the energy storage of the developed structural supercapacitor can increase by raising the number of parallelly connected supercapacitor layers.

Further, the energy storage of SSC gradually increases with increased temperature (figure S5), however, high temperature is one of the factors that cause electrolyte decomposition. During prolonged cycling, the cycle life of the supercapacitor gradually reduces at elevated temperatures [31]. As shown in figures 6(a) and (b), the shape of all CV curves remains quasi-rectangular up to temperature 85 °C, proving that the developed device can be used in the temperature range tested without redox reactions inside the material [32]. Therefore, the capacitance retentions of the assembled SSC at elevated temperatures of 65 °C and 85 °C as a function of the number of charge–discharge cycles (figure S6) were assessed to evaluate the device's lifespan. At high operating temperatures, the capacitance decreases quickly compared to RT, i.e. reaching 52% and 41% of the initial capacitance at 65 °C and 85 °C, respectively, after 1000 cycles. Evidently, the lifespan gradually decreases with increasing temperature, and using extended cycles at elevated temperatures may lead to device failure.

Further, according to figure 6(a), the largest area under the CV curve corresponded with the structural supercapacitor at around 85 °C, suggesting that elevated temperature improves its energy storage capacity, and that the device can perform well within the tested temperature (table S2). The area-specific capacitance values of single-cell and double-cell SSC reached 1.15 mF cm^{-2} and 2.86 mF cm^{-2} at scan rate 100 mV s^{-1}, respectively. According to the analysis, this behavior is mainly due to the higher ionic conductivity of the electrolyte due to faster reaction kinetics and higher ionic mobility [33].

Figures 6(c) and (d) illustrate that in a GCD test, the discharging times prolong with the temperature increase from RT to 85 °C at the same current density. The capacitive performance of the devices at different temperatures was calculated according to the GCD profile. As per figure 6(e), it shows a gradual increase with increasing temperature. Next, the energy density was calculated using equation S3 (figure 6(f)). SSC-1 and SSC-2 have the highest capacitance values at 85 °C, and the area-specific capacitance and energy density reached 2.58 mF cm^{-2} and 0.81 mWh cm^{-2}, respectively, for the double-cell device. These results confirmed the energy storage is increased and developed SSC is suitable for elevated temperature applications. However, in case of exposing to high temperatures, it is recommended to adapt suitable strategies to mitigate

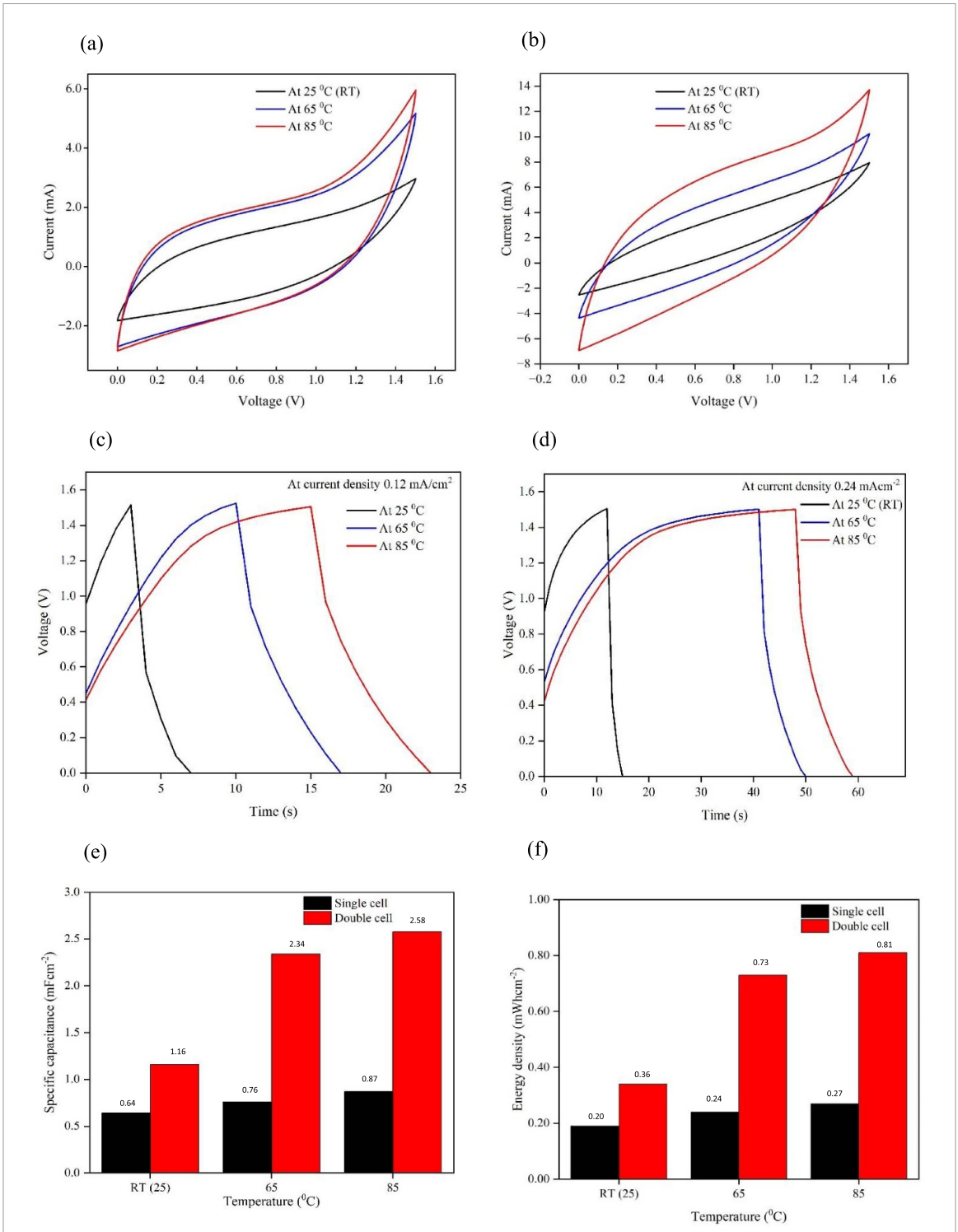

Figure 6. CV test at different temperatures (RT, 65 °C, 85 °C, and 100 °C) at 100 mV s^{-1} scan rate: (a) single-cell, (b) double-cell; GCD test at different temperatures (RT (25 °C), 65 °C, 85 °C, and 100 °C)): (c) single-cell, (d) double-cell, (e) specific capacitance vs temperature, (f) energy density vs temperature.

performance decay due to the direct exposure of the device to high temperatures. When exposed to elevated temperatures, a skin heat barrier to encapsulate the developed structural supercapacitor can be considered as an appropriate strategy to minimize the potential deterioration.

The electrochemical impedance spectra can also conform to the higher ionic conductivity at elevated temperatures. Figure 7 illustrates a comprehensive plot depicting the impedance data for both single- and double-cell configurations at three different temperatures. The smallest high-frequency semicircle is at 85 °C for both single- and double-cells. Therefore, increasing temperature reduces the charge transfer resistance.

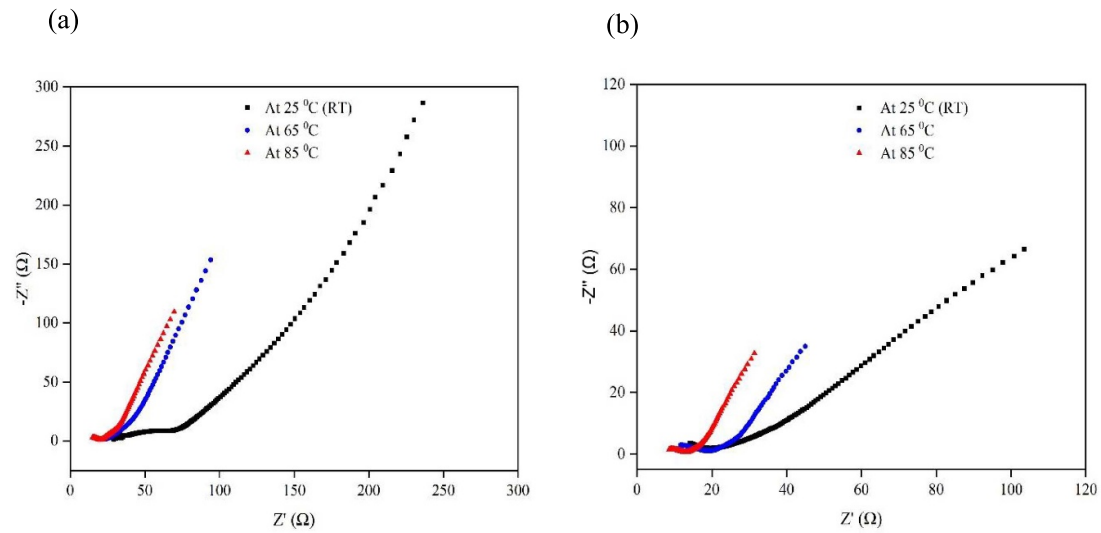

Figure 7. Nyquist plots in three different temperature levels (RT- 25 °C), 65 °C, and 85 °C): (a) single-cell, (b) double-cell.

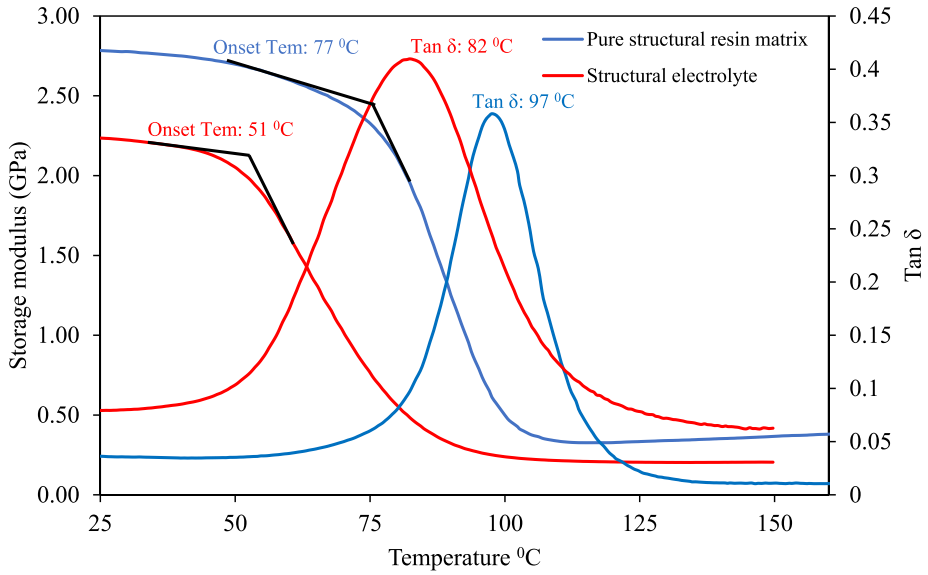

Figure 8. DMA results.

The SSC at elevated temperatures gives the smallest high-frequency semicircle, indicating the smallest electrode-electrolyte charge transfer resistance and a fast charge-transport rate [34]. In addition, the straight line reflects the conduction and diffusion rate of ions in the electrolyte. The slopes of the straight lines increase with the temperature, indicating a faster ion transfer rate between electrolyte and electrode material. This agrees with its higher capacitance and energy storage at higher temperatures [35].

3.3. Analysis of thermo-mechanical properties

The structural performance of fiber-reinforced composites becomes unpredictable at elevated temperatures. Therefore, studying material behavior under thermal stress at various temperatures is essential, especially when the material is utilized in practical applications subjected to elevated temperatures.

Thermostable matrices can maintain their elastic and fracture properties up to temperatures close to their glass transition temperature (Tg). Therefore, the Tg of the structural electrolyte is a critical parameter that indicates the service condition of a structural supercapacitor. According to the DMA analysis (figure 8),

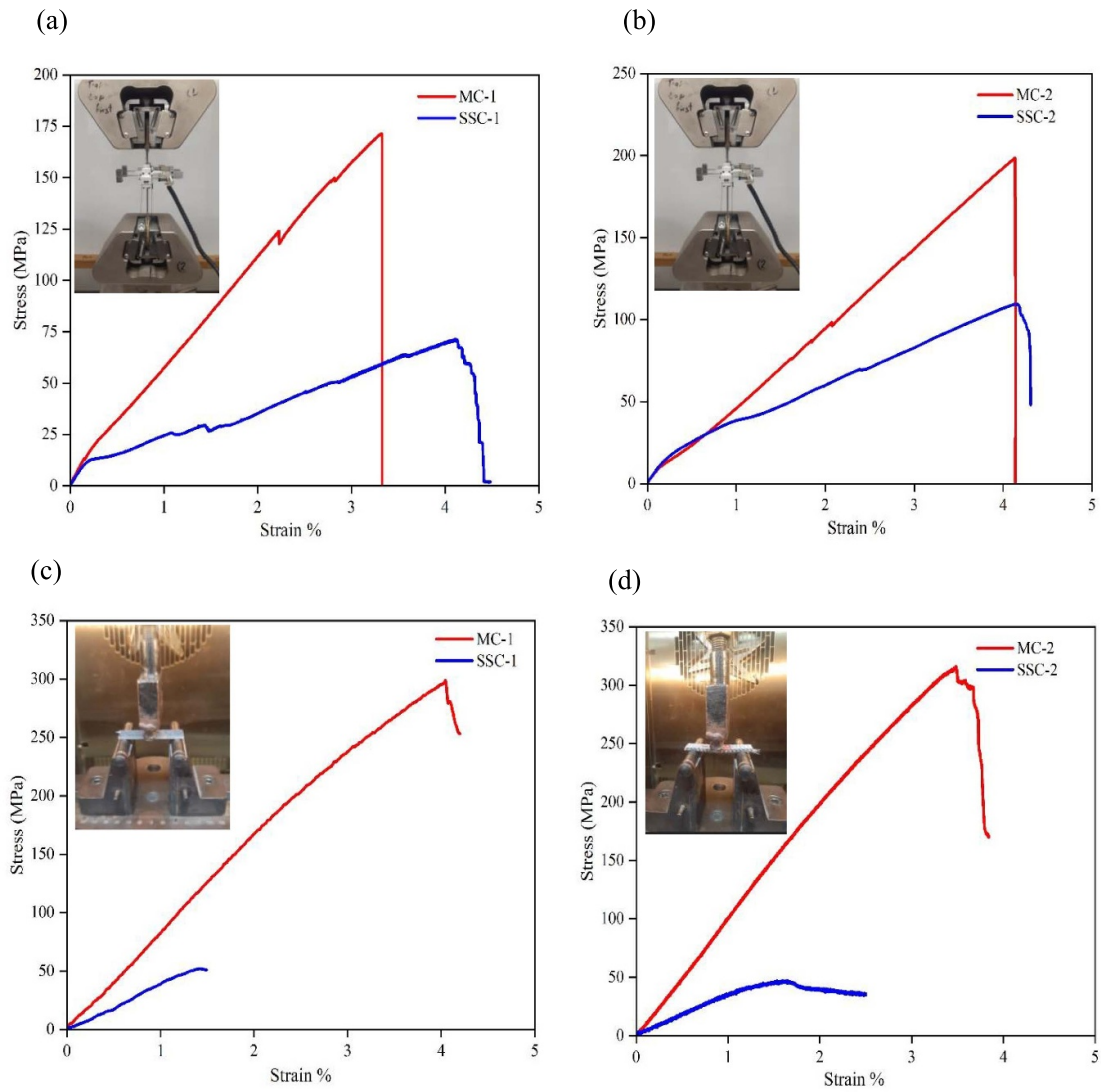

Figure 9. Tensile test profile of SSC and MC (a) single-cell, (b) double-cell; flexural test profile of SSC and MC (c) single-cell, (d) double-cell; compression test profile of SSC and MC (e) single-cell (f) double-cell; V notch shear test profile of SSC and MC (g) single-cell, (h) double-cell.

the peak tan δ and onset temperature of the developed structural electrolyte were 82 °C and 51 °C, respectively, proving its suitability for elevated-temperature applications up to around 82 °C.

3.4. Mechanical testing

The mass fiber fractions of developed structural supercapacitor and MC were experimentally evaluated as 53% and 50%, respectively, and therefore no significant difference in reinforced fiber mass fractions between SSC and MC. It was evident that the primary factor influencing the alteration of mechanical properties of structural supercapacitors is the modification of the resin matrix due to added ionic liquid.

When developing structural electrolytes, it has been observed that the addition of ionic liquid leads to improved electrochemical performance and reduces the mechanical performance of the structural resin matrix. The ionic liquid and lithium salt in the epoxy matrix create a separate phase within the matrix and reduce continuous crosslinks formation. Thus, the crosslinking density of the matrix decreased after adding LE. The DSC test confirmed this by an energy reduction for crosslinking (figure S7). The DSC graph shows that the curing enthalpy of the structural electrolyte is lower than the structural resin matrix. On the other hand, introducing the ionic liquid may cause plasticization of the epoxy matrix and further reduce the mechanical performance of the final device [20].

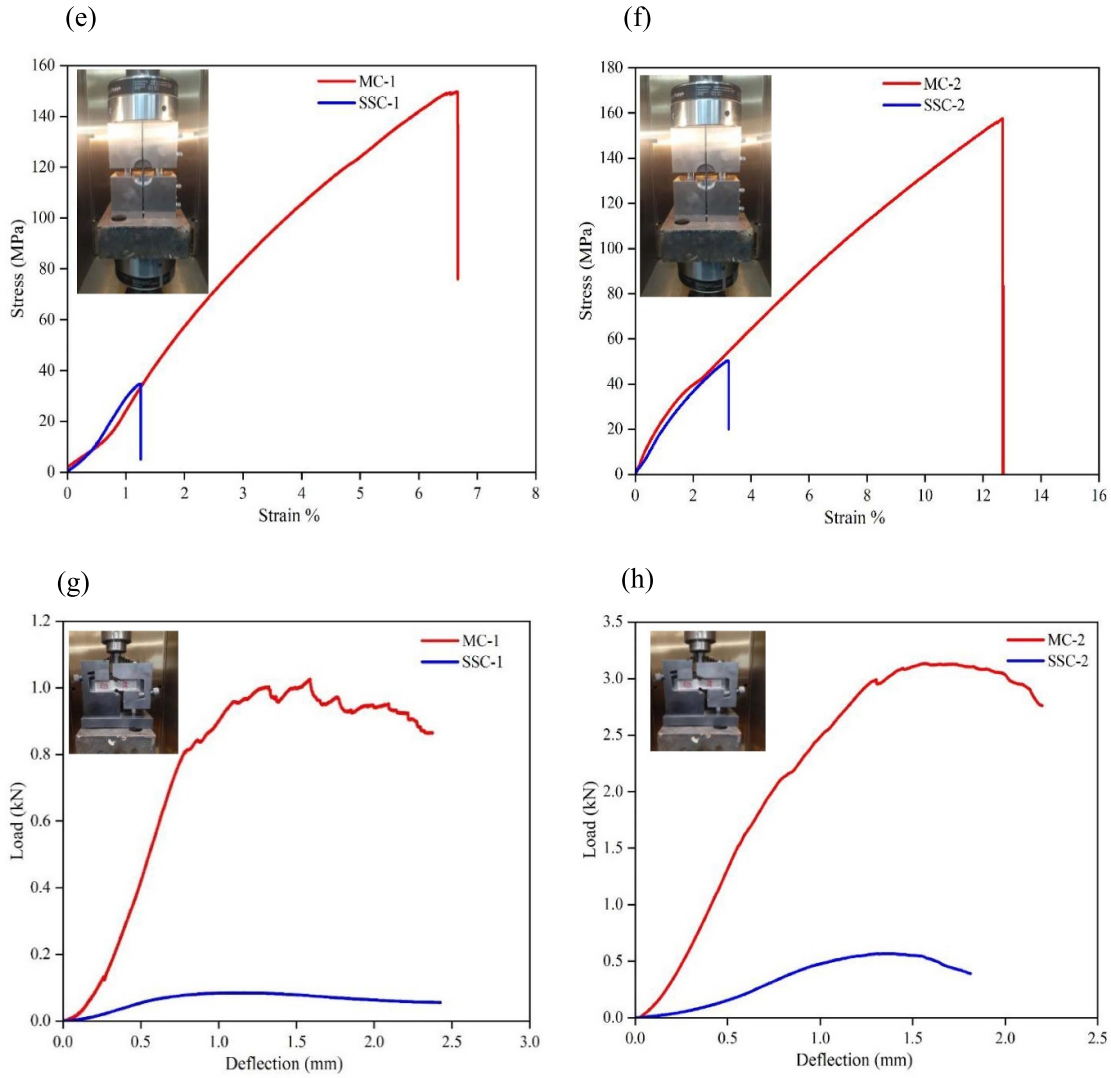

Figure 9. (Continued.)

3.4.1. Mechanical properties of structural supercapacitor vs MC

The tensile, flexural, compression, and shear test data were analyzed to evaluate the mechanical performance of SSCs. Figures 9(a)–(d) illustrates the tensile and flexural test profiles of SSC and corresponding MC, and figures 9(e)–(h) shows the compression test and V-notch shear test results. The single-cell SSC showed a tensile strength of 71.4 MPa and modulus of 8.3 GPa, while flexural strength was 52.1 MPa. To provide a comparison for this study, summary of the performance of various structural supercapacitors (at room temperature) from the literature is presented in table 2.

Fabricating the double-cell SSC increased the tensile strength and modulus to 109.5 MPa and 9.7 GPa, respectively, showing a 54% strength increase compared to single-cell SSC. At the point of tensile failure, each structural supercapacitor exhibits a delamination failure (figure S8) while having a higher elongation compared to the corresponding MC (figures 9(a) and (b)).

The MC has demonstrated a sharp, brittle failure (figure S8) with less deformation at the breaking point. The flexural and compression strengths of the SSC-2 were 47.0 MPa and 50.4 MPa, respectively. Figures 9(g) and (h) shows the shear response process given by the axial load-displacement curves. The reduction of maximum loads can be observed in SSCs compared to MCs. The reason could be the weak interfacial bonding between the fiber and the matrix.

According to the results, the mechanical properties of SSCs were consistently lower than that of MCs. This proves that adding ionic liquid and lithium salt into the structural resin matrix reduces the load transfer

Table 2. Summary of the literature on structural supercapacitors, focusing on devices for which tensile strength, modulus and flexural strength have been reported.

Electrode	Separator	Electrolyte	Capacitance	Tensile		Flexural strength (MPa)	Compression strength (MPa)	Reference
				Strength (MPa)	Modulus (GPa)			
CF	GF	DGEBA (Araldite GY 191) + IL (EMITFSI) + LiTFSI-single cell	0.63 mFcm^{-2}	71.4	8.3	52.1	34.6	This work
CF	GF	DGEBA (Araldite GY 191) + IL (EMITFSI) + LiTFSI-double cell	1.15 mFc m^{-2}	109.5	9.7	47.0	50.4	This work
CuO-CF	GF	PES + IL (EMIMBF4) + LiTf	6.75 F g^{-1}*	259.82	20.18	—	—	[36]
CF	GF	PEGDGE + IL (EMITFSI)	4.02 mF g^{-1}	160	23.3	—	—	[37]
Urea activated graphene nanoflakes -CF	GF	PEGDGE + IL (EMITFSI)	47.98 m g^{-1}	90	20.7	—	—	[37]
Activated CF	CP	Epoxy + 1 M TEABF4 in PC	25.4 mFg^{-1}	—	—	29.1	—	[38]
CF	GF	Epoxy + PVDF + LiTf	0.128 mFcm^{-2}	—	—	47.5	—	[39]
CF	GF	PEGDGE + IL	3.07 mFg^{-1}	340	—	—	—	[32]
CAG-CF	GF	DGEBA + IL (EMITFSI)	18.5 mFcm^{-2}	110	32.9	—	—	[40]
Silane treated MnO2-CF	GF	Epoxy + IL (EMITFSI)	5.68 mFcm^{-2}	397	14	103	40.6	[41]
CF	GF	Epoxy + IL (EMITFSI) + LiTFSI + PC	32.4 mFcm^{-2}	—	—	—	160	[20]

Note: *Normalized to weight of active material; CuO: copper oxide; PES: polyester resin; LiTf: lithium trifluoromethanesulfonate; PEGDGE: poly(ethylene glycol) diglycidylether; TEABF4: tetraethylammonium tetrafluoroborate; PC: propylene carbonate, PVDF: poly(vinylidene fluoride); CP: cellulose paper, VG: vertical graphene, MnO2: manganese dioxide; CAG: carbon aerogel.

from matrix to fiber, thus reducing the mechanical properties. Modifying the structural matrix with liquid electrolyte forms a porous or bicontinuous structure, as explained in section 3.1.1, which reduces the mechanical strength of SSC compared to MC.

3.4.2. The effect of temperature on mechanical properties

The tensile, flexural, compression, and shear behavior were studied at elevated temperatures and illustrated in figure 10. All curves confirm that the ultimate strength values gradually decrease with increasing temperatures, as anticipated. As per figure 10(a), a 22% and 35% tensile strength loss (SSC-2) was observed at 65 °C and 85 °C, respectively. When the temperature was increased to 85 °C, the compressive and flexural strengths of SSC-2 were reduced by 82% and 70%, respectively. The mechanical performance losses at 85 °C are mainly due to the resin softening after passing the glass transition region, as explained in section 3.3. This can be minimized by using structural electrolytes with a high Tg value.

The test results and trends in the data indicate that the mechanical properties might drastically reduce at extremely harsh environmental conditions such as extreme temperatures and fire conditions. The skin thermal barrier suggested in section 3.2 will be a good solution here to prevent mechanical degradation due to harsh environmental conditions. Herein, the fabricated structural supercapacitor serves as the core layer, and the whole structure becomes a sandwich composite comprising two thermal barrier skin layers.

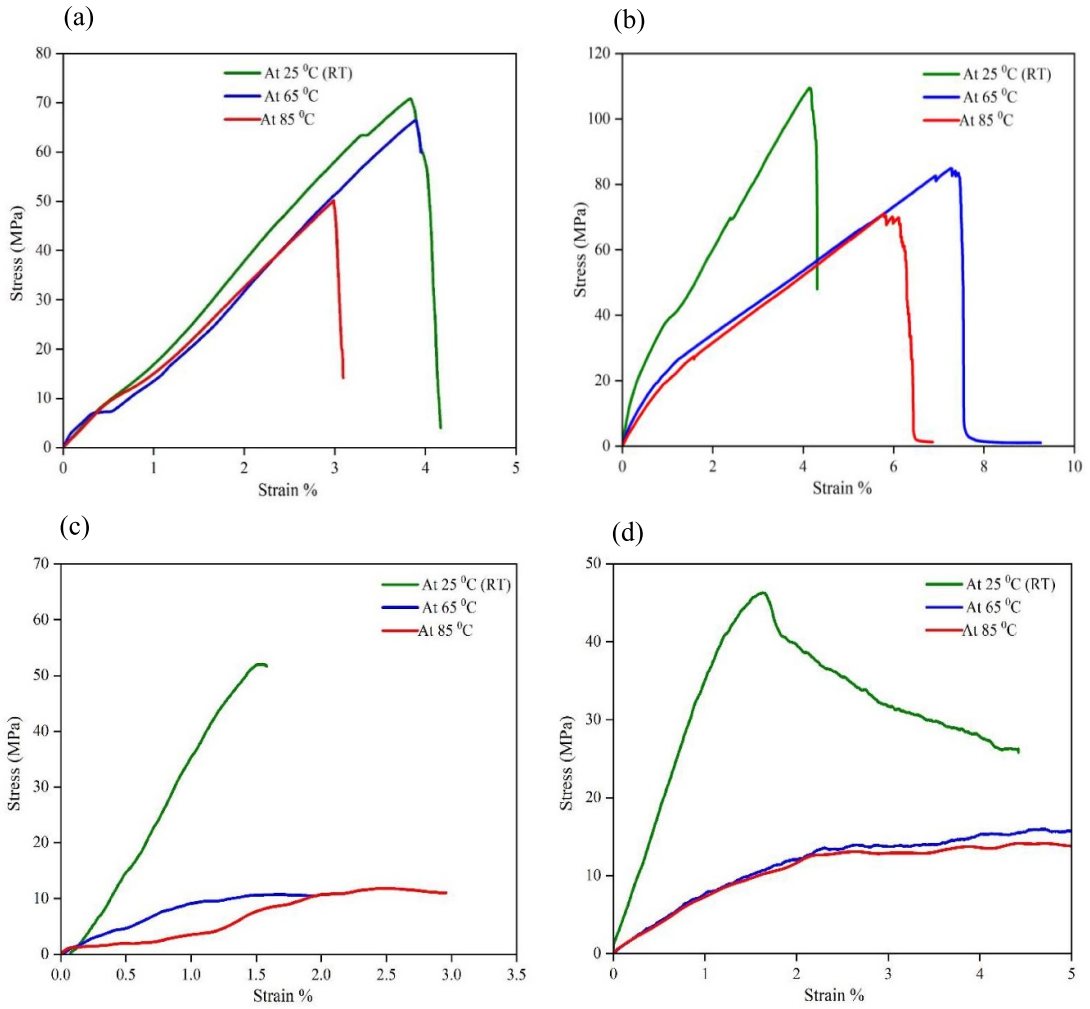

Figure 10. Tensile behavior at elevated temperatures (a) single-cell (b) double-cell; flexural behavior at elevated temperatures (c) single-cell (d) double-cell; compression behavior at elevated temperatures (e) single-cell (f) double-cell; shear behavior at elevated temperatures (g) single-cell (h) double-cell.

4. Conclusions

A structural supercapacitor with a fiber-reinforced polymer composite system was manufactured in this study to accomplish two functions together: (1) storing energy and (2) withstanding mechanical loads.

Two basic structures, single and parallelly connected double-cell structural supercapacitors, were devised, and the influence of operating temperature on their performance was evaluated. The developed double-cell SSC demonstrated high electrochemical and structural performance from room temperature (25 °C) to 85 °C, making it a promising candidate for structural applications such as building materials. It exhibited a specific capacitance of 1.16 mF cm^{-2} and energy density of 0.36 mWh cm^{-2} at 0.24 mA cm^{-2}, while tensile, flexural, and compression at room temperature were 109.5 MPa, 47.0 MPa, and 50.4 MPa, respectively. When increasing the temperature to 85 °C, the specific capacitance and energy density were increased to 2.58 mF cm^{-2} and 0.81 mWh cm^{-2}, while tensile, flexural, and compression were reduced to 70.9 MPa, 14.2 MPa, and 8.8 MPa, respectively.

The lifespan evaluated by charge-discharge cycles proved that the developed SSC has 41% capacitance retention after 5000 cycles at room temperature and 40% capacitance retention after 1000 cycles at 85 °C. The results prove that despite high electrochemical performance at elevated temperatures, the supercapacitors' performance degrades at elevated temperatures. Therefore, exploring some protection levels to ensure an extended lifespan to develop the proposed concept for extremely harsh environmental conditions is beneficial. In this context, we hope the skin thermal barrier will protect the developed structural supercapacitor while preventing thermal and electrical degradation.

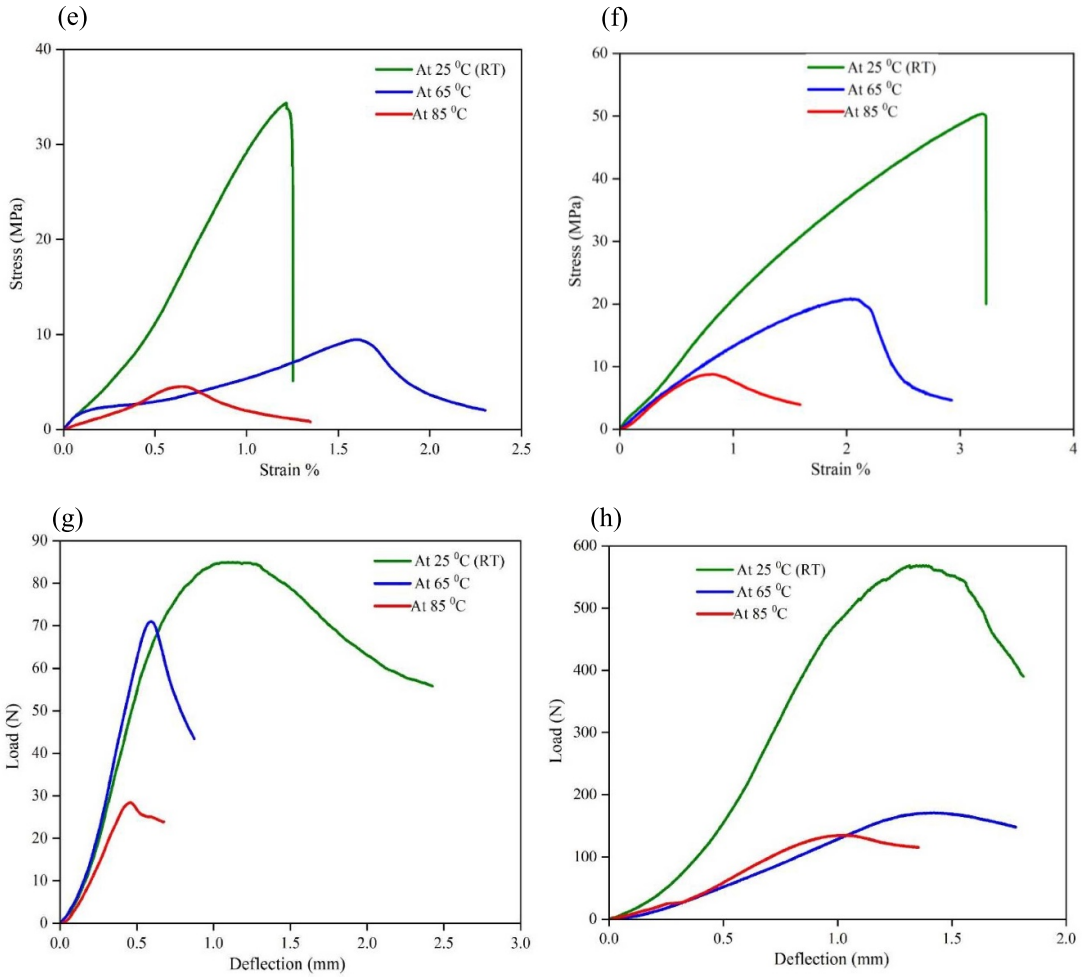

Figure 10. (Continued.)

Further studies are necessary to investigate in-situ mechano-electrochemical performance, scale-up issues, demonstrate the multilayer assemblies for complex geometry structural components. Solving these technical challenges would enable these emerging multifunctional materials to greatly impact smart building structures and beyond in the future.

Acknowledgments

The authors are thankful to Ms. Darshanie Prematilake for the support provided in proofreading. Moreover, authors express gratitude to the University of Southern Queensland, Australia and Uva Wellassa University, Sri Lanka for facilitation in conducting this project.

Author contribution

Jayani Anurangi: Conceptualization, methodology, investigation, formal analysis, and writing-original draft. **Thanuja Galhena:** Methodology, supervision. **Madhubhashitha Herath:** Formal analysis, supervision. **Jayantha Epaarachchi:** Conceptualization, formal analysis, and supervision.

Conflict of interest

The authors declare no competing financial interest.

Funding

This research was supported by the AHEAD operation (Accelerate Higher Education Expansion and Development), a World Bank funded project in Sri Lanka.

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