Article

Aligned $\text{Ti}_3\text{C}_2\text{T}_x$ Aerogel with High Rate Performance, Power Density and Sub-Zero-Temperature Stability

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Abstract: $\text{Ti}_3\text{C}_2\text{T}_x$ -based aerogels have attracted widespread attention for three-dimensional porous structures, which are promising to realize high-rate energy storage. However, disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels with highly tortuous porosity fabricated by conventional unidirectional freeze-casting substantially increase ion diffusion lengths and hinder electrolyte ions transport. Herein we demonstrate a new bidirectional ice-templated approach to synthesize porous ordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel with straight and aligned channels, straight and short ion diffusion pathways, leading to better ion accessibility. The aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel exhibits the high specific capacitance of 345 F g^{-1} at 20 mV s^{-1} and rate capability of 52.2% from 10 to 5000 mV s^{-1} . The specific capacitance is insensitive of mass loadings even at 10 mg cm^{-2} and an excellent power density of 137.3 mW cm^{-2} is obtained in symmetric supercapacitors. The electrochemical properties of $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel supercapacitors at sub-zero (to -30°C) temperatures are reported for the first time. The aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel delivers temperature-independent rate performance and high capacitance retention (73% at 50 mV s^{-1} from 25 to -30°C) due to the unique structure with metallic conductivity.

Keywords: supercapacitor; aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel; rate performance; power density; sub-zero-temperature stability

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1. Introduction

MXenes, a burgeoning family of two-dimensional nanomaterials, have attracted widespread interest for outstanding electrochemical properties [1]. Generally, MXenes can be expressed as $\text{M}_{n+1}\text{X}_n\text{T}_x$ ($n = 1, 2$, or 3), where M, X, T_x represents transition metals, C or N, and functional groups, respectively [1,2]. Titanium carbide ($\text{Ti}_3\text{C}_2\text{T}_x$) is the most commonly studied MXene with hydrophilic surfaces, abundant redox-active sites and outstanding metallic conductivity (approx. $10,000 \text{ S cm}^{-1}$) [3,4]. To exploit its full potential for electrochemical devices, a variety of approaches were reported to fabricate $\text{Ti}_3\text{C}_2\text{T}_x$ -based electrodes into film, fiber and aerogel structures [5,6]. Among these, $\text{Ti}_3\text{C}_2\text{T}_x$ -based aerogels possess promising electrochemical performance due to the three-dimensional (3D) porous morphology, larger specific surface areas and abundant ion transport channels [7].

Generally, $\text{Ti}_3\text{C}_2\text{T}_x$ -based aerogels are fabricated by hydrothermal method and freeze-casting technique to achieve high porosity [6,8]. On one hand, the $\text{Ti}_3\text{C}_2\text{T}_x$ gelation process in the hydrothermal strategy requires the use of cross-linkers (mostly graphene oxide), which will deteriorate the intrinsic properties of $\text{Ti}_3\text{C}_2\text{T}_x$ due to their low conductivity and limited capacitance [8–10]. Moreover, the heat treatment through the hydrothermal

process will inevitably accelerate the oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$, limiting its capacity and rate capability [11–13]. On the other hand, the traditional unidirectional freeze-casting technique yields an intrinsically disordered aerogel structure with high pore tortuosity, leading to longer ion diffusion pathways and sluggish ion transport [14,15]. Therefore, it is crucial to develop an effective assembly and fabrication technique for $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels to optimize ion transport and diffusion kinetics without sacrificing its inherent metallic conductivity, thereby improving the overall electrochemical performance.

Realistically, considering that a large fraction of global population usually experiences sub-zero temperatures (even $-30\text{ }^\circ\text{C}$) in winter, thus energy storage devices are expected to operate under such cold conditions [16]. Improving sub-zero-temperature electrochemical performance is crucial and challenging for supercapacitors, especially for pseudocapacitors [17]. Although pseudocapacitors exhibit higher specific capacitance over electric double-layer capacitors, a more significant capacitance decay (25–45% from near 25 to $0\text{ }^\circ\text{C}$ [18–21]) occurs in pseudocapacitive energy storage due to the sluggish redox reaction process, poor electrical conductivity and decelerated ion transport [22,23]. $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels appear as a solution due to their metallic conductivity and rapid ion redox kinetics. However, the electrochemical properties of $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels under such temperatures remain unexplored to date.

Herein, a 3D porous ordered $\text{Ti}_3\text{C}_2\text{T}_x$ architecture (i.e., aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel) is rationally devised via a simple bidirectional ice-templated strategy without any other additives. Such architecture can effectively shorten ion diffusion pathways, accelerate ion transport, and provide more electrochemically active sites, thereby improving the rate performance, power density, and low-temperature stability of the supercapacitor. Consequently, the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel exhibits a specific capacitance of 345 F g^{-1} at 20 mV s^{-1} and a high-rate capability of 52.2% from 10 to 5000 mV s^{-1} . Moreover, symmetric supercapacitors deliver a maximum power density of 137.3 mW cm^{-2} (at 0.076 mWh cm^{-2}) and exhibit remarkable capacitance stability of 85.5% over 20,000 cycles at 100 mA cm^{-2} . Furthermore, benefiting from fast ion diffusion kinetics in the 3D ordered conductive architecture, the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel exhibits temperature-independent rate performance (64.5% and 63.6% from 10 to 1000 mV s^{-1} at $25\text{ }^\circ\text{C}$ and $-30\text{ }^\circ\text{C}$, respectively) and high capacitance retention of 73% at 50 mV s^{-1} within the range of operating temperatures from 25 to $-30\text{ }^\circ\text{C}$.

2. Experimental Section

2.1. Materials Fabrication

$\text{Ti}_3\text{C}_2\text{T}_x$ dispersion was prepared by acid etching Ti_3AlC_2 powder (400 mesh, Jilin 11 Technology Co., Ltd, China) [24]. Specifically, 9 M HCl solution (40 mL) was poured into a PTFE bottle to completely dissolve 2 g of LiF power, then slowly adding 2 g of Ti_3AlC_2 powder in almost 15 min. The mixture was kept at $35\text{ }^\circ\text{C}$ under magnetic stirring for 24 h, followed by repeated washing with deionized water and centrifugation at 7500 rpm for 10 min until the pH returned to 6. Subsequently, $\text{Ti}_3\text{C}_2\text{T}_x$ suspension was sonicated for 30 min in an ice bath and then centrifuged for 1 h at 3500 rpm. The resultant colloidal dispersion with a maximum concentration of $\approx 80\text{ mg mL}^{-1}$ was collected for further fabrication.

The aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels with mass loadings from 0.8 to 10 mg cm^{-2} were synthesized by a bidirectional ice-templated approach. Briefly, about 2 mL $\text{Ti}_3\text{C}_2\text{T}_x$ dispersion with different concentrations was transferred into a $40\text{ mm} \times 40\text{ mm} \times 5\text{ mm}$ customized mold covered by a self-designed copper groove [22]. The appropriate amount of liquid nitrogen was placed under the mold for about 15–30 min, and then bidirectionally growing ice templates derived from horizontal and vertical temperature gradients on the copper surface assembled and rejected dispersed $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets [22,25]. After the complete freezing of $\text{Ti}_3\text{C}_2\text{T}_x$ suspension, the sample was freeze-dried for over 12 h at $-80\text{ }^\circ\text{C}$ and 10 Pa to obtain free-standing aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels. For comparison, the disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at 0.8 mg cm^{-2} was fabricated by conventional unidirectional freeze-casting methods [26]. Briefly, 2 mL $\text{Ti}_3\text{C}_2\text{T}_x$ dispersion at 6.4 mg mL^{-1} was firstly frozen at the

refrigerator and then freeze-dried at the same conditions to construct disordered aerogel structures.

2.2. Material Characterizations

The microstructures of samples were investigated by scanning electron microscope (SEM, Hitachi SU-70, Japan) and transmission electron microscope (TEM, JEOL JEM-2100, Japan). The crystal structures were characterized by X-ray diffraction (XRD) patterns (1.5425 Å, Shimadzu, Japan). N₂ adsorption/desorption measurements were conducted by Quantachrome instruments. The specific surface area and pore size distribution were calculated via Brunauer-Emmett-Teller (BET) and density functional theory (DFT) methods, respectively.

2.3. Electrochemical Measurements

Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were conducted through the electrochemical workstation (PGSTAT302N, Metrohm Autolab B.V., Switzerland). In three-electrode Swagelok configurations, Ti₃C₂T_x aerogel electrodes, activated carbon films and Ag/AgCl electrodes were employed as working, counter and reference electrodes, respectively. The CV and GCD tests were conducted within the potential window from −0.5 to 0.3 V. Symmetric supercapacitors were assembled with two pieces of aligned Ti₃C₂T_x aerogels separated by the porous polypropylene film in the two-electrode configuration. The low-temperature electrochemical tests were performed in the high/low-temperature test chamber (SARTEC SS-7123). EIS tests were conducted with a 5 mV amplitude in a frequency range from 0.01 to 10⁵ Hz. 3 M H₂SO₄ aqueous solution was utilized as an electrolyte in all electrochemical tests.

The gravimetric capacitance C_m (F g^{−1}) and areal capacitance C_a (mF cm^{−2}) from CV curves are calculated by [27,28]:

$$C_m = \frac{1}{2mv\Delta V} \int i dV \quad (1)$$

$$C_a = \sigma C_m \quad (2)$$

where i refers to current (A), ΔV denotes potential window (V), v refers to scan rate (V s^{−1}), m is the mass of electrode material/device (g), σ is mass loading (mg cm^{−2}) based on the area of one electrode, respectively.

The capacitance $C_{m/a}$ (F g^{−1} or mF cm^{−2}) from GCD profiles are calculated by [29]:

$$C_{m/a} = \frac{I\Delta t}{\Delta V} \quad (3)$$

where I denotes current density (A g^{−1} or mA cm^{−2}), Δt refers to discharge time (s), ΔV denotes the potential window (V) excluding voltage drop, respectively.

The energy density E (mWh cm^{−2}) and power density P (mW cm^{−2}) derived from GCD tests in symmetric supercapacitors are given by [30,31]:

$$E = \frac{C_a \Delta V^2}{2 \times 3600} \quad (4)$$

$$P = \frac{3600E}{\Delta t} \quad (5)$$

where ΔV and Δt are the potential window (V) and discharge time (s), respectively. Dividing by 3600 converts the unit of E from mJ cm^{−2} to mWh cm^{−2}.

3. Results and Discussion

3.1. Fabrication and Characterization

To demonstrate the excellent electrochemical performance in the 3D porous ordered architecture, the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel is fabricated via a simple bidirectional ice-templated strategy, which could avoid the oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$ [14]. We have designed the customized dual-temperature gradients (i.e., vertical and horizontal directions) which turned to be the key factors to control the ordered structure. In contrast with the commonly used disordered growth of ice induced by random cold environments, our custom-designed dual-temperature gradients give rise to bidirectional growing ice crystals to assemble and expel dispersed $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets from solid/liquid interfaces. After the sublimation, 3D porous ordered aerogels with well-aligned lamellar structures are obtained as replicas of ice templates [32].

The cross-sectional (Figure 1a) and top-view (Figure 1b) SEM images of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at 1.25 mg cm^{-2} show porous highly-ordered lamellar architecture in both horizontal and vertical directions with the interlamellar spacing of $30\text{--}40 \text{ }\mu\text{m}$. Notably, with the increasing mass loading from 0.8 to 10 mg cm^{-2} , long-range (millimeter-scale) ordered architectures are successfully retained and the spacing between the lamellae decreases from $30\text{--}60 \text{ }\mu\text{m}$ to $10\text{--}20 \text{ }\mu\text{m}$ (Figure S1). Such an architecture can create abundant ion-accessible redox sites, enable fast ion transport and shorten ion diffusion pathways within the electrode [8,22]. Conversely, the disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel through unidirectional freeze-casting reveals a very disordered non-lamellar structure with highly tortuous ion pathways owing to the randomly growing ice crystals (Figure S2) [8,26].

Figure 1. (a) Cross-sectional and (b) Top-view SEM images of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at 1.25 mg cm^{-2} ; (c) XRD patterns of Ti_3AlC_2 powder, disordered and aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel; (d) The TEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

$\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are prepared by acid etching Al atoms from Ti_3AlC_2 . The XRD patterns of disordered and aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels exhibit a lower shift of (002) peak without residual peaks of Ti_3AlC_2 , thus proving the successful etching (Figure 1c) [24]. The TEM image of the as-prepared $\text{Ti}_3\text{C}_2\text{T}_x$ displays a typical two-dimensional sheet morphology with a lateral size of several micrometers (Figure 1d). In addition, aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel exhibits the higher specific surface area ($115.7 \text{ m}^2 \text{ g}^{-1}$) than the disordered counterpart ($33.4 \text{ m}^2 \text{ g}^{-1}$), suggesting more abundant porosity and easier access to electrolytes in the aligned architectures. The pore size distribution curves (Figure S3) indicate that both disordered and aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels possess micropores and mesopores. Furthermore, numerous macropores also exist in the aerogel structures as shown in previous SEM images.

3.2. High Rate Performance of Aligned $\text{Ti}_3\text{C}_2\text{T}_x$ Aerogel

To demonstrate the advantages of 3D porous ordered structures, disordered and aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel with the same mass loading of 0.8 mg cm^{-2} are measured for comparison in three-electrode configurations. Figure 2a displays CV curves of the two samples at 200 mV s^{-1} . Both CV curves reveal a similar shape with a pair of redox peaks due to the reversible intercalation/deintercalation of H^+ and the changes in the Ti oxidation state [33]. The slight redox potential difference between disordered and aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel is likely attributed to the difference of pore tortuosity and orientation. The aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel presents a larger CV integration area than disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel, indicating the higher specific capacitance [30]. With the increasing scan rates from 10 to 5000 mV s^{-1} , CV profiles of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel maintain the original shape without any obvious distortion until 1000 mV s^{-1} due to the short ion diffusion pathways and fast ion transports kinetics in the aligned structures (Figure 2b). Furthermore, the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ interlayer spaces could raise the accessibility and mobility of protons to the surface redox reaction sites, thus improving electrochemical performances. Conversely, more apparent distortion is found for the disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel within the same range of scan rates (Figure S4). In addition, GCD profiles of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel retain symmetric and nonlinear shapes from 1 to 250 A g^{-1} , in concert with CV results (Figure S5).

Figure 2. (a) CV curves of disordered and aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at 200 mV s^{-1} . (b) CV curves from 10 to 5000 mV s^{-1} for aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel. (c) Specific capacitance versus scan rate for disordered and aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel in comparison with previously reported $\text{Ti}_3\text{C}_2\text{T}_x$ film. (d) Rate capabilities of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel compared with $\text{Ti}_3\text{C}_2\text{T}_x$ -based electrodes in recently reported works. (The capacitance retention is estimated and calculated from the plots in the literature by the graph digitizer software Getdata). (e) The plot of peak current response against scan rates. (f) Nyquist plots.

As shown in Figure 2c, aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel exhibits a capacitance of 345 F g^{-1} at 20 mV s^{-1} , higher than that of disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel (307 F g^{-1}) and stacked $\text{Ti}_3\text{C}_2\text{T}_x$ films (approx. $222\text{--}253 \text{ F g}^{-1}$) [34,35]. Meanwhile, the rate capability is a significant parameter associated with the characteristic time scales of the charge/ionic motion, which affects the charging/discharging speed and power density of supercapacitors [36]. The capacitance retention of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel achieved 52.2% from 10 to 5000 mV s^{-1} , better than that of disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel (35.8%) and filtered $\text{Ti}_3\text{C}_2\text{T}_x$ films (approx. 18%) [34]. Notably, such high-rate performance also surpasses other reported $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel [37,38], $\text{Ti}_3\text{C}_2\text{T}_x$ hydrogel [39] and $\text{Ti}_3\text{C}_2\text{T}_x$ /holey graphene film [40] (Figure 2d). The superior electrochemical performance of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel over the $\text{Ti}_3\text{C}_2\text{T}_x$ -based materials mentioned above can be attributed to fully accessible redox surfaces,

unimpeded electrolyte ions transport channels along with reduced ion diffusion pathways in the porous ordered architecture.

To investigate the electrochemical kinetics in the unique structures, the power-law relationship between peak current (i_p) and scan rate (v) is analyzed by [39]:

$$i_p = av^b \quad (6)$$

where a and b are fitting parameters. The b -value near 0.5 and 1 indicate sluggish diffusion-dominant and rapid surface-dominant capacitive processes, respectively [39]. The aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel exhibits a higher b value (closer to 1) than that of disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel (0.89) (Figure 2e), suggesting better ion transport efficiency and rate performance.

Ion transport processes are further studied through the EIS tests and Nyquist plots are presented in Figure 2f. A steeper slope is observed for the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at the low frequency, indicative of better capacitive behavior [30]. In the mid-high-frequency region, the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel reveals an inappreciable semicircle and negligible Warburg region, thus demonstrating rapid ion transport and diffusion properties in the ordered structure [30]. The related impedance values are further fitted with equivalent circuits and detailed fitting results are presented in Figure S6. R_s , R_{ct} and R_w are the representatives of equivalent series resistance, charge transfer resistance and Warburg impedance [30,41], respectively. The R_{ct} (0.46 Ω) and R_w (1.74 Ω) of the disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel are much higher than that of the aligned counterpart (0.19 and 0.25 Ω , respectively) due to the prolonged ion diffusion pathways and highly tortuous porosity in the disordered structure.

Notably, mass loading or areal capacitance of the electrode is also a critical parameter to estimate supercapacitor devices, while drastic degradation of electrochemical performance with the increasing mass loading up to the application-relevant level (i.e., 10 mg cm^{-2}) is commonly reported due to the severely limited ion transport and diffusion [42]. To illustrate the merits of porous ordered structure in potential industrial applications, aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel with mass loadings ranging from 0.8 to 10 mg cm^{-2} are prepared for further electrochemical measurement in three-electrode configurations. All CV curves retain similar shapes with apparent redox peaks independent of mass loadings at 20 mV s^{-1} (Figure 3a), suggesting outstanding ion-transport properties [34]. Meanwhile, nearly symmetric and nonlinear shapes are observed in all GCD profiles at 5 mA cm^{-2} (Figure 3b), in great agreement with CV results. With the increased mass loadings, areal capacitances of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels significantly improved from 10 to 300 mV s^{-1} (Figure 3c). Furthermore, the areal capacitance of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels exhibits almost a linear relationship with mass loadings even at 100 mV s^{-1} , which is attributed to the short ion diffusion pathways and unobstructed ion transport in the aligned architecture (Figure 3d). It is worth noting that the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at 10 mg cm^{-2} achieves the maximum capacitance of 2.98 F cm^{-2} at 10 mV s^{-1} , surpassing other high-performance $\text{Ti}_3\text{C}_2\text{T}_x$ -based electrodes, e.g., 1.013 F cm^{-2} at 15 mg cm^{-2} for EDA-assisted $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel [43] and 1.173 F cm^{-2} at 15 mg cm^{-2} for $\text{Ti}_3\text{C}_2\text{T}_x/\text{Ag}$ film [44].

3.3. High Power Density Pseudocapacitor

To further demonstrate the suitability of ordered aerogel structures for practical applications, a symmetric supercapacitor is fabricated based on aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels at 10 mg cm^{-2} in two-electrode test configurations. Figure S7 exhibits CV curves of the pseudocapacitor at different voltages at 10 mV s^{-1} and an operating potential window of 0.8 V is obtained. All CV curves deliver quasi-rectangular shapes from 2 to 200 mV s^{-1} (Figure 4a), revealing the promising rate capability even at the applications-relevant level of mass loading. Meanwhile, all GCD curves exhibit symmetric quasi-triangular shapes from 1 to 200 mA cm^{-2} and areal capacitance of 1140 mF cm^{-2} is obtained at 1 mA cm^{-2} (Figure 4b,c). The long-term cycling tests are conducted at 100 mA cm^{-2} for 20,000 cycles. The pseudocapacitor exhibits 85.5% retention of the initial areal capacitance with 100% coulombic efficiency (Figure 4d) and a negligible change is detected in the GCD profiles during 20,000 test cycles (Figure 4e), signifying the outstanding cycling reversibility and

stability. On account of high mass loading and high ion transport efficiency in aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels, the as-prepared pseudocapacitor delivers the maximum power density of 137.3 mW cm^{-2} at an energy density of $0.076 \text{ mWh cm}^{-2}$, which maintains 0.401 mW cm^{-2} at a maximum energy density of $0.101 \text{ mWh cm}^{-2}$. The maximum power density is significantly larger compared to the recently reported $\text{Ti}_3\text{C}_2\text{T}_x$ -based supercapacitor, e.g., 26.1 mW cm^{-2} at $0.057 \text{ mWh cm}^{-2}$ for EDA-assisted $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel//CNF asymmetric supercapacitor [43], 6.12 mW cm^{-2} at $0.022 \text{ mWh cm}^{-2}$ for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene/rGO gels symmetric supercapacitor [45], etc [46–48] (Figure 4f). These results imply the great potential of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels for high power density supercapacitor applications.

Figure 3. (a) CV curves at 20 mV s^{-1} , (b) GCD profiles at 5 mA cm^{-2} and (c) Areal capacitance versus scan rate from 10 to 1000 mV s^{-1} for aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel with mass loadings ranging from 0.8 to 10 mg cm^{-2} . (d) The relationship between areal capacitance and mass loading from 10 to 100 mV s^{-1} .

Figure 4. Electrochemical performances of symmetric supercapacitor based on aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at 10 mg cm^{-2} . (a) CV curves from 2 to 200 mV s^{-1} ; GCD profiles (b) from 1 to 20 mA cm^{-2} and (c) from 40 to 200 mA cm^{-2} ; (d) Cycling stability and coulombic efficiency with (e) typical GCD profiles at 100 mA cm^{-2} ; (f) Ragone plot.

3.4. Sub-Zero-Temperature Stability

Generally, compared to the enhanced capacitive performance exhibited at elevated temperatures (e.g., from 25 to 60 °C), large capacitance decay at sub-zero temperatures is a major challenge [22,49]. To demonstrate the excellent sub-zero-temperature stability in ordered architectures, electrochemical measurements of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at 0.8 mg cm^{-2} are conducted in two-electrode configurations with a potential window of 0.7 V (Figure S8) and operating temperatures ranging from 25 to -30 °C. 3 M H_2SO_4 aqueous solution is still applied as an electrolyte owing to its ultrahigh ionic conductivity over the common organic electrolytes, which can remain unfrozen even at -30 °C [17].

When the temperature drops from 25 to -30 °C at 10 mV s^{-1} (Figure 5a), redox/intercalation peaks of CV shapes weaken due to the dominance of the double-layer component in energy storage at sub-zero temperatures [23]. At the scan rate up to 1000 mV s^{-1} , aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel displays almost identical rectangular-like curves (Figure 5b), revealing the temperature-insensitive capacitive behavior. The shapes of CV curves remain almost unchanged and only a small decrease of the integral area is detected at room temperature (Figure S9a), suggesting the fast electrolyte ions transport and diffusion in the unique architecture. When the temperature decreases to -30 °C, the CV curves maintained similar shapes without any obvious distortion at the same scan rate ranges (Figure S9b), a clear indication of the remarkable sub-zero-temperature tolerance.

Figure 5. Low-temperature stability of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel electrode in a two-electrode configuration. CV curves at (a) 10 and (b) 1000 mV s^{-1} at different temperatures; (c) Specific capacitance versus scan rate from 25 to -30 °C; (d) Comparison of specific capacitance near room temperature (in the range of 20 and 30 °C) and capacitance retention with previously reported supercapacitors.

Figure 5c provides the specific capacitance derived from CV results at different operating temperatures. Specifically, the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel exhibits the specific capacitance of 154 F g^{-1} at 10 mV s^{-1} and high-rate capability of 63.6% from 10 to 1000 mV s^{-1} at -30 °C. Meanwhile, an almost identical capacitance retention of 64.5% is obtained at 25 °C, demonstrating a temperature-independent rate performance. Furthermore, the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel possesses a capacitance of 214 F g^{-1} at 50 mV s^{-1} under room temperature as well as temperature-relevant retentions of 83% and 73% for 25 to 0 °C and 25 to -30 °C, respectively. Such capacitance and retention are substantially higher than those of previously reported electric double-layer capacitors and pseudocapacitors with similar temperature ranges in Figure 5d [19,20,23,50].

In addition, Figure S10a displays GCD profiles of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at different temperatures tested at 10 A g^{-1} . Slight charge/discharge time decreases are observed and capacitance retentions of 75–77% at -30°C are obtained from 1 to 100 A g^{-1} (Figure S10b), in great accordance with CV results. Such outstanding low-temperature performance demonstrates the potential of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel electrodes to deliver stable and reliable operation under harsh sub-zero-temperature conditions.

To further understand the temperature-relevant capacitive behavior, the Arrhenius-type equation is assumed to investigate the process kinetics [51]:

$$\ln C = \ln C_0 - Q/RT \quad (7)$$

where C is specific capacitance, Q denotes activation energy, T refers to absolute temperature, C_0 and R are the preexponential parameter and universal gas constant, respectively. The calculated activation energy from CV results is in the range of $3.42\text{--}3.52 \text{ kJ mol}^{-1}$ (Figure 6a), lower than that of MnO_2 (32.8 kJ mol^{-1}) [52] and comparable to that of graphene ($3.01\text{--}7.87 \text{ kJ mol}^{-1}$) [53]. Such low activation energy validates the temperature-insensitive charge storage processes in the ordered architecture.

Figure 6. Temperature-insensitive electrochemical mechanism of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel electrode. (a) Arrhenius relationship between $\ln C$ and $1000/T$ at different scan rates; (b) Nyquist plots with the inset of enlarged mid-high-frequency regions at different temperatures; (c) Fitted values of resistive elements in the equivalent circuit (inset).

To further understand the charge transfer and ion diffusion processes at sub-zero temperatures, EIS measurements are performed and the corresponding Nyquist plots are provided in Figure 6b. All Nyquist plots display almost identical shapes with nearly vertical lines in low-frequency range and depressed semicircles in high-frequency region. Equivalent circuits with well-fitted values and lines for Nyquist plots are presented in Figure 6c and Figure S11, respectively. When temperatures decrease from 25°C to -30°C , the R_s values increase from 4.2 to 6.1Ω due to lowered ionic conductivity of bulk electrolyte [17]. Notably, the R_{ct} values increase from 0.94 to 2.22Ω and R_w values slightly increase from 1.46 to 3.36Ω with the same operating temperature range, indicating vertically short ion diffusion pathways and rapid charge transfer kinetics below 0°C in the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel [22].

4. Conclusions

In summary, $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels are promising candidates for high-performance energy storage devices (e.g., supercapacitors) and the persistent problem of the commonly appearing disordered tortuous porous structure of $\text{Ti}_3\text{C}_2\text{T}_x$ aerogels is resolved by a simple bidirectional ice-templated approach. The new fabrication approach based on customized temperature gradients has been developed to fabricate the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel with ordered and aligned porous structures. The porous aerogel exhibits a specific capacitance of 345 F g^{-1} at 20 mV s^{-1} and a high-rate performance of 52.2% from 10 to 5000 mV s^{-1} . The excellent capacitance and rate performance over disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel and stacked $\text{Ti}_3\text{C}_2\text{T}_x$ films are attributed to the sufficient ion-accessible redox sites, short ion diffusion pathways and unobstructed ion transport. Such architecture can be scaled to 10 mg cm^{-2}

without apparent capacitance decay even at 100 mV s^{-1} and deliver a maximum power density of 137.3 mW cm^{-2} (at $0.076 \text{ mWh cm}^{-2}$). Benefiting from unique structures and metallic conductivity of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel, temperature-independent rate capability and high temperature-relevant capacitance retention (73% at 50 mV s^{-1}) are obtained with operating temperatures ranging from 25 to -30°C . Considering the diversity of MXenes and related materials, this work opens new opportunities to fabricate 3D porous ordered MXene aerogels for high-rate energy storage devices (supercapacitors, lithium-ion batteries, lithium-sulfur batteries, etc) in sub-zero-temperature environments.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/en15031191/s1>, Figure S1: top-view SEM image of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel with mass loadings of (a) 0.8, (b) 1.25, (c) 2.5, (d) 5, (e) 7.5, and (f) 10 mg cm^{-2} , Figure S2: top-view SEM image of disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel with different magnifications, Figure S3: pore size distribution curves of disordered and aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel, Figure S4: CV curves at scan rates from 10 to 5000 mV s^{-1} for disordered $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel, Figure S5: GCD profiles of the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at (a) low current densities from 1 to 20 A g^{-1} and (b) high current densities from 50 to 250 A g^{-1} , Figure S6: fitted values of the resistive elements in the equivalent circuit (inset) for the Nyquist spectra of disordered and aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel, Figure S7: CV curves of the symmetric aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel pseudocapacitor with the mass loading of 10 mg cm^{-2} measured at different voltages at 10 mV s^{-1} , Figure S8: CV curves of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel with the mass loading of 0.8 mg cm^{-2} measured at different voltages at 10 mV s^{-1} in a two-electrode configuration, Figure S9: CV profiles from 10 to 1000 mV s^{-1} at (a) 25°C and (b) -30°C , Figure S10: (a) GCD curves of aligned $\text{Ti}_3\text{C}_2\text{T}_x$ aerogel at different temperatures with a current density of 10 A g^{-1} and (b) capacitance retention with operating temperatures from 25 to -30°C at different current densities, Figure S11: nyquist plots at different temperatures (scatter represents raw data, and line represents fitting data).

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