Aligned Ti$_3$C$_2$T$_x$ Aerogel with High Rate Performance, Power Density and 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 $\text{M}_{n+1}\text{X}_n\text{T}_x$ ($n = 1, 2, 3$), where $\text{M}$, $\text{X}$, and $\text{T}$ represent transition metals, C or N, and functional groups, respectively [1,2]. Titanium carbide (Ti$_3$C$_2$T$_x$) is the most commonly studied MXene with hydrophilic surfaces, abundant redox-active sites and outstanding metallic conductivity (approx. 10,000 S cm$^{-1}$) [3,4]. To exploit its full potential for electrochemical devices, a variety of approaches were reported to fabricate Ti$_3$C$_2$T$_x$-based electrodes into film, fiber and aerogel structures [5,6]. Among these, Ti$_3$C$_2$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, Ti$_3$C$_2$T$_x$-based aerogels are fabricated by hydrothermal method and freeze-casting technique to achieve high porosity [6,8]. On one hand, the Ti$_3$C$_2$T$_x$ gelation process in the hydrothermal strategy requires the use of cross-linkers (mostly graphene oxide), which will deteriorate the intrinsic properties of Ti$_3$C$_2$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 Ti$_3$C$_2$Tx, 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 Ti$_3$C$_2$Tx 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 °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 °C [18–21]) occurs in pseudocapacitive energy storage due to the sluggish redox reaction process, poor electrical conductivity and decelerated ion transport [22,23]. Ti$_3$C$_2$Tx aerogels appear as a solution due to their metallic conductivity and rapid ion redox kinetics. However, the electrochemical properties of Ti$_3$C$_2$Tx aerogels under such temperatures remain unexplored to date.

Herein, a 3D porous ordered Ti$_3$C$_2$Tx architecture (i.e., aligned Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx aerogel exhibits temperature-independent rate performance (64.5% and 63.6% from 10 to 1000 mV s$^{-1}$ at 25 °C and −30 °C, respectively) and high capacitance retention of 73% at 50 mV s$^{-1}$ within the range of operating temperatures from 25 to −30 °C.

2. Experimental Section

2.1. Materials Fabrication

Ti$_3$C$_2$Tx dispersion was prepared by acid etching Ti$_3$AlC$_2$ 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 powder, then slowly adding 2 g of Ti$_3$AlC$_2$ powder in almost 15 min. The mixture was kept at 35 °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, Ti$_3$C$_2$Tx 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 ≈80 mg mL$^{-1}$ was collected for further fabrication.

The aligned Ti$_3$C$_2$Tx aerogels with mass loadings from 0.8 to 10 mg cm$^{-2}$ were synthesized by a bidirectional ice-templated approach. Briefly, about 2 ml Ti$_3$C$_2$Tx suspension with different concentrations was transferred into a 40 mm × 40 mm × 5 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 disperses Ti$_3$C$_2$Tx nanosheets [22,25]. After the complete freezing of Ti$_3$C$_2$Tx suspension, the sample was freeze-dried for over 12 h at −80 °C and 10 Pa to obtain free-standing aligned Ti$_3$C$_2$Tx aerogels. For comparison, the disordered Ti$_3$C$_2$Tx aerogel at 0.8 mg cm$^{-2}$ was fabricated by conventional unidirectional freeze-casting methods [26]. Briefly, 2 mL Ti$_3$C$_2$Tx dispersion at 6.4 mg mL$^{-1}$ was firstly frozen at the
refrigerator and then freeze-dried at the same conditions to construct disordered aero-
gel 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) meth-
ods, respectively.

2.3. Electrochemical Measurements

Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical
impedance spectroscopy (EIS) measurements were conducted through the electrochemi-
cal workstation (PGSTAT302N, Metrohm Autolab B.V., Switzerland). In three-electrode
Swagelok configurations, Ti₃C₂Tx 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. Symmet-
ric supercapacitors were assembled with two pieces of aligned Ti₃C₂Tx 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 electrochemi-
cal 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]:

\[
C_m = \frac{1}{2mnv\Delta V} \int i dV \tag{1}
\]

\[
C_a = \sigma C_m \tag{2}
\]

where \( i \) refers to current (A), \( \Delta V \) denotes potential window (V), \( v \) refers to scan rate (V s⁻¹),
\( m \) is the mass of electrode material/device (g), \( \sigma \) 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]:

\[
C_{m/a} = \frac{I\Delta t}{\Delta V} \tag{3}
\]

where \( I \) denotes current density (A g⁻¹ or mA cm⁻²), \( \Delta t \) refers to discharge time (s), \( \Delta V \)
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]:

\[
E = \frac{C_a \Delta V^2}{2 \times 3600} \tag{4}
\]

\[
P = \frac{3600E}{\Delta t} \tag{5}
\]

where \( \Delta V \) and \( \Delta t \) 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 Ti$_3$C$_2$Tx aerogel is fabricated via a simple bidirectional ice-templated strategy, which could avoid the oxidation of Ti$_3$C$_2$Tx [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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx aerogel at 1.25 mg cm$^{-2}$ show porous highly-ordered lamellar architecture in both horizontal and vertical directions with the interlamellar spacing of 30–40 µm. 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 30–60 µm to 10–20 µm (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 Ti$_3$C$_2$Tx 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](image-url)

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

Ti$_3$C$_2$Tx nanosheets are prepared by acid etching Al atoms from Ti$_3$AlC$_2$. The XRD patterns of disordered and aligned Ti$_3$C$_2$Tx aerogels exhibit a lower shift of (002) peak without residual peaks of Ti$_3$AlC$_2$, thus proving the successful etching (Figure 1c) [24]. The TEM image of the as-prepared Ti$_3$C$_2$Tx displays a typical two-dimensional sheet morphology with a lateral size of several micrometers (Figure 1d). In addition, aligned Ti$_3$C$_2$Tx aerogel exhibits the higher specific surface area (115.7 m$^2$ g$^{-1}$) than the disordered counterpart (33.4 m$^2$ 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx Aerogel

To demonstrate the advantages of 3D porous ordered structures, disordered and aligned Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx aerogel is likely attributed to the difference of pore tortuosity and orientation. The aligned Ti$_3$C$_2$Tx aerogel presents a larger CV integration area than disordered Ti$_3$C$_2$Tx aerogel, indicating the higher specific capacitance [30]. With the increasing scan rates from 10 to 5000 mV s$^{-1}$, CV profiles of the aligned Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx aerogel within the same range of scan rates (Figure S4). In addition, GCD profiles of the aligned Ti$_3$C$_2$Tx aerogel retain symmetric and nonlinear shapes from 1 to 250 A g$^{-1}$, in concert with CV results (Figure S5).

As shown in Figure 2c, aligned Ti$_3$C$_2$Tx aerogel exhibits a capacitance of 345 F g$^{-1}$ at 20 mV s$^{-1}$, higher than that of disordered Ti$_3$C$_2$Tx aerogel (307 F g$^{-1}$) and stacked Ti$_3$C$_2$Tx films (approx. 222–253 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 Ti$_3$C$_2$Tx aerogel achieved 52.2% from 10 to 5000 mV s$^{-1}$, better than that of disordered Ti$_3$C$_2$Tx aerogel (35.8%) and filtered Ti$_3$C$_2$Tx films (approx. 18%) [34]. Notably, such high-rate performance also surpasses other reported Ti$_3$C$_2$Tx aerogel [37,38], Ti$_3$C$_2$Tx hydrogel [39] and Ti$_3$C$_2$Tx/holey graphene film [40] (Figure 2d). The superior electrochemical performance of the aligned Ti$_3$C$_2$Tx aerogel over the Ti$_3$C$_2$Tx-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]:

\[
i_p = av^b
\]

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 Ti\(_3\)C\(_2\)Tx aerogel exhibits a higher \( b \) value (closer to 1) than that of disordered Ti\(_3\)C\(_2\)Tx 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 Ti\(_3\)C\(_2\)Tx aerogel at different voltages at 10 mV s\(^{-1}\), indicating the outstanding cycling reversibility and 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

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 Ti\(_3\)C\(_2\)Tx 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 Ti\(_3\)C\(_2\)Tx aerogels significantly improved from 10 to 300 mV s\(^{-1}\) (Figure 3c). Furthermore, the areal capacitance of the aligned Ti\(_3\)C\(_2\)Tx 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 Ti\(_3\)C\(_2\)Tx 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 Ti\(_3\)C\(_2\)Tx-based electrodes, e.g., 1.013 F cm\(^{-2}\) at 15 mg cm\(^{-2}\) for EDA-assisted Ti\(_3\)C\(_2\)Tx aerogel [43] and 1.173 F cm\(^{-2}\) at 15 mg cm\(^{-2}\) for Ti\(_3\)C\(_2\)Tx/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 Ti\(_3\)C\(_2\)Tx 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 Ti$_3$C$_2$Tx aerogels, the as-prepared pseudocapacitor delivers the maximum power density of 137.3 mW cm$^{-2}$ at an energy density of 0.076 mWh cm$^{-2}$, which maintains 0.401 mW cm$^{-2}$ at a maximum energy density of 0.101 mWh cm$^{-2}$. The maximum power density is significantly larger compared to the recently reported Ti$_3$C$_2$T$_x$-based supercapacitor, e.g., 26.1 mW cm$^{-2}$ at 0.057 mWh cm$^{-2}$ for EDA-assisted Ti$_3$C$_2$Tx aerogel/CNF asymmetric supercapacitor [43], 6.12 mW cm$^{-2}$ at 0.022 mWh cm$^{-2}$ for Ti$_3$C$_2$T$_x$ MXene/rGO gels symmetric supercapacitor [45], etc [46–48] (Figure 4f). These results imply the great potential of aligned Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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$_2$SO$_4$ 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 in the range of 20 and 30 °C) and capacitance retention with previously reported supercapacitors. Such low activation energy validates 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), a clear indication of the remarkable sub-zero-temperature tolerance.

When the temperature drops from 25 to −30 °C at 1000 mV s$^{-1}$, aligned Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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]:

\[
\ln C = \ln C_0 - \frac{Q}{RT}
\]

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 3.42–3.52 kJ mol$^{-1}$ (Figure 6a), lower than that of MnO$_2$ (32.8 kJ mol$^{-1}$) [52] and comparable to that of graphene (3.01–7.87 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 Ti$_3$C$_2$Tx aerogel electrode. (a) Arrhenius relationship between ln C and 1000 $T^{-1}$ 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).](image)

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 6.1 Ω due to lowered ionic conductivity of bulk electrolyte [17]. Notably, the \(R_{ct}\) values increase from 0.94 to 2.22 Ω and \(R_w\) values slightly increase from 1.46 to 3.36 Ω with the same operating temperature range, indicating vertically short ion diffusion pathways and rapid charge transfer kinetics below 0 °C in the aligned Ti$_3$C$_2$Tx aerogel [22].

4. Conclusions

In summary, Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx aerogel and stacked Ti$_3$C$_2$Tx 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 mWh cm$^{-2}$). Benefiting from unique structures and metallic conductivity of the aligned Ti$_3$C$_2$Tx 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](https://www.mdpi.com/article/10.3390/en15031191/s1), Figure S1: top-view SEM image of aligned Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx aerogel with different magnifications, Figure S3: pore size distribution curves of disordered and aligned Ti$_3$C$_2$Tx aerogel, Figure S4: CV curves at scan rates from 10 to 5000 mV s$^{-1}$ for disordered Ti$_3$C$_2$Tx aerogel, Figure S5: GCD profiles of the aligned Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx aerogel, Figure S7: CV curves of the symmetric aligned Ti$_3$C$_2$Tx 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 Ti$_3$C$_2$Tx 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 of Ti$_3$C$_2$Tx aerogel with the mass loading of 0.8 mg cm$^{-2}$ measured at different voltages at 10 mV s$^{-1}$ at (a) 25 °C and (b) −30 °C, Figure S10: (a) GCD curves of aligned Ti$_3$C$_2$Tx 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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