Energy storage devices are limited by the trade-off between the transport properties and charge storage ability of materials. Electrolytic capacitors are kinetically fast, operating at kHz frequency, but limited by low capacitance. Electrochemical capacitors (ECs) provide high capacitance, yet their sluggish kinetics limit frequency response. Herein, we devise porous MXene/conducting polymer hybrids for large-scale flexible AC filtering symmetric ECs. These MXene hybrid-based ECs bridge the performance gap between high capacitance and frequency response, toward the form-factor-free miniature and scalable devices.
Article

MXene/Polymer Hybrid Materials for Flexible AC-Filtering Electrochemical Capacitors

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SUMMARY

Energy storage devices are limited by the trade-off between the transport properties and charge storage ability of materials. Electrolytic capacitors are kinetically fast, operating at kilohertz frequency, but limited by low capacitance. Electrochemical capacitors (ECs) provide high capacitance, yet their sluggish kinetics limit frequency response to a few hertz. Here, we devise strongly interacting, porous MXene/conducting polymer hybrids for large-scale flexible alternating current filtering symmetric ECs with high areal and volumetric capacitances of $0.56 \text{ mF cm}^{-2}$ and $24.2 \text{ F cm}^{-3}$ at 120 Hz, respectively. The high capacitance was maintained up to $1,000 \text{ V s}^{-1}$ and originates from synergy of MXene/polymer hybrids. The operation of tandem ECs that filter a pulsating voltage from 60 to 10,000 Hz is demonstrated with device flexibility and durability over 30,000 cycles. These MXene hybrid-based ECs are expected to bridge the performance gap between high capacitance and the high-frequency response toward the form-factor-free miniature and scalable devices.

INTRODUCTION

The kinetics of energy storage devices, which is dominated by ionic and electronic transport at the interfaces and within bulk materials, is crucial for determining the actual performance and efficiency, as well as the kinetic parameters (such as the power capability, characteristic [charging] time, and frequency response) of these devices.1–5 The applications of energy storage devices are impeded by the common trade-off between the transport properties and capacitance of the charge storage materials, thus resulting in a performance gap between the energy and power densities based on Ragone plots.6–9 For instance, high-capacitance active materials are usually restricted by sluggish kinetics due to slow ion diffusion and low electronic conductivity, which lead to high internal resistance (IR) drop and low energy efficiency when the devices are operated at high rates or high frequencies.10,11

Electrochemical capacitors (ECs), called supercapacitors or ultracapacitors, such as double-layer capacitors and pseudocapacitors, are high-power devices with long-term cyclability.2,3,12 However, conventional carbon-based ECs become resistive at frequencies above 1 Hz, which limits their power applications.1,13,14 Aluminum electrolytic capacitors (AECs) have been used as power devices for high-frequency operation in applications such as the internet of things, self-powered wearable sensors, and ripple and noise filtering in electronic circuits.4,12,15 However, the capacitance of AECs is limited to microfarads or millifarads, which is orders of magnitude lower than that of ECs.15 The rigid shape and large size of AECs are obstacles for the development of form-factor-free miniature and scalable future electronic systems.

Context & Scale

Aluminum electrolytic capacitors (AECs) have been used as power devices for AC filtering applications and are critical for the internet of things and self-powered wearable sensors. However, the capacitance of AECs, orders of magnitude lower than that of electrochemical capacitors (ECs), and the rigid shape of AECs are obstacles for their use in miniature and flexible systems. The development of flexible ECs that provide high volumetric capacitance and operate in the frequency range of AECs would thus have an enormous impact. In order to resolve the trade-off nature between the transport properties and charge storage capability of energy storage materials, we devised porous MXene/conducting polymer hybrid architectures for large-scale flexible ECs. These MXene hybrid-based ECs allow miniaturization of electronic systems, occupying a high position of capacitance versus frequency response plot, toward the development of form-factor-free miniature and scalable future electronic systems.
their use in miniature and flexible electronic systems. Breakthroughs were made to realize high-frequency ECs using nanostructured carbons for the replacement of electrolytic capacitor filters, but neither high volumetric capacitance nor scalable device manufacturing has yet been achieved. Large-scale flexible ECs that can provide both high volumetric capacitance and a fast frequency response are expected to resolve the current impediment for high-power applications.

Herein, we demonstrate synergistically interacting, porous MXene/conducting polymer hybrids having an interconnected network structure for flexible symmetric ECs with high areal and volumetric capacitances of 0.56 mF cm$^{-2}$ and 24.2 F cm$^{-3}$ at 120 Hz, showing promise for alternating current (AC) filtering and other applications. The transport properties and charge storage capability of the MXene hybrid thin films are maximized at the optimum composition and thickness, enabling operation even at a rate of 1,000 V s$^{-1}$ or from 60 to 10,000 Hz, with extreme flexibility and durability. These synergistic features of the MXene hybrid films are attributed to the porous architecture that facilitates rapid ion transport and the hybrid interaction that enables fast charge transfer and the transition into the electroactive quinoid structure of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS).

RESULTS AND DISCUSSION

The fabrication of MXene-based hybrid thin films and flexible symmetric EC devices is illustrated in Figure 1A. A spray-coating method was used to deposit active materials, including Ti$_3$C$_2$T$x$ MXene (denoted as Ti$_3$C$_2$) and Ti$_3$C$_2$/PEDOT:PSS hybrids, at mass ratios of 1:1 and 1:2 (denoted as MP11 and MP12, respectively), on 250 nm Au-coated polyethylene terephthalate (PET) substrate as a current collector. This was followed by a drying process at 70°C. Ti$_3$C$_2$ flakes with the size of <100 nm, which is smaller than that previous reported, was chosen due to their high redox activity and faster ionic transport.

The optimum thickness and composition of hybrid could be readily controlled for the design of flexible EC filter by varying the amount and concentration of sprayed colloidal dispersion. In order to show the scalability of the spray-coating method and mechanical features of the as-prepared electrodes, large-area (36 cm$^2$) films of MP12 hybrid were produced and their bending, folding, and rolling are shown in Figure 1A. The symmetric ECs were fabricated configuring two identical films of (Ti$_3$C$_2$, MP11, MP12) of 5 x 10 mm$^2$ with a polymeric hydrogel electrolyte consisting of poly(vinyl alcohol) (PVA), hydroxyethyl methacrylate (HEMA), and 3 M H$_2$SO$_4$ (see Figure 1A). These PVA-poly-2(HEMA) (PHEMA) networked hydrogels are mechanically and chemically stable in 3 M H$_2$SO$_4$ acidic electrolyte, achieving high ionic conductivity of 34.4 mS cm$^{-1}$.

The surface and cross-sectional scanning electron microscopy (SEM) images of pure Ti$_3$C$_2$, MP11, and MP12 films are presented in Figures 1B–1G. The thin films of pure Ti$_3$C$_2$ and MP hybrids could be fabricated using good colloidal dispersion in deionized water (inset of Figures 1B–1D), which was confirmed by the Tyndall scattering effect (see Figure S1). The small size of Ti$_3$C$_2$ was used to derive an interconnected mesoporous structure from the interflake voids. Although the nanometric pores cannot be detected due to the resolution limitation of SEM, the surface of pristine Ti$_3$C$_2$ thin films was mesoporous, as marked by white arrows in Figures 1B and 1E (see also Figure S2A). The mesoporous structure of the MP hybrid films was preserved, but it was densified with an increment of the PEDOT:PSS content (Figures

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On the other hand, the pristine PEDOT:PSS exhibited a very compact and highly dense morphology (see Figures S2D and S2E). The open mesoporous connectivity of the thin film (<1 μm) is critical for decreasing pore tortuosity and providing fast charge transport. Thus, the Ti3C2 flakes assist in creating an interconnected mesoporous structure and percolated conducting pathways for rapid ionic and electronic transport, while PEDOT:PSS provides additional electrochemically active sites and adds flexibility.

The chemical interaction of Ti3C2 with PEDOT:PSS during hybridization is schematically illustrated in Figure 2A. The dispersion of the Ti3C2 flakes in the aqueous...
colloid is attributed to dangling moieties (Tx) such as –OH, =O, and –F, which are capable of contributing to the interaction with other polar groups.\(^{26}\) The electrostatic interaction of the PEDOT and PSS chains was changed due to the interaction with the surface moieties of the Ti\(_3\)C\(_2\) flakes.\(^{27}\) This hybrid interaction was strong enough to electronically alter the oxidation state of the PEDOT unit from the benzoid to quinoid configuration, as confirmed by the visible and near-infrared (NIR) absorption spectra (Figure 2B). Thus, the characteristic peak of PEDOT:PSS was shifted from 794 to 867 nm upon hybridization. This red shift in the NIR region is indicative of the electronic transition of PEDOT from the benzoid to quinoid state due to oxidation of the polarons to bipolarons during hybridization.\(^{27-29}\)

As shown in the high-resolution core-level X-ray photoelectron spectra of Ti\(_3\)C\(_2\), PEDOT:PSS, and the Ti\(_3\)C\(_2\)/PEDOT:PSS hybrid (Figures 2C and 2D), a peak shift to a higher binding energy (BE) by 0.5 eV was observed for the Ti2p state, corresponding to Ti-C and Ti-O bonds, whereas a 0.5 eV shift to lower BE was detected for the S2p\(_{3/2}\) and S2p\(_{1/2}\) states of the PEDOT chain of the Ti\(_3\)C\(_2\)/PEDOT:PSS hybrid.
Similarly, the O 1s spectra revealed a higher BE peak shift by 0.3 eV for PEDOT and a negative peak shift of 0.3 eV for the Ti3C2/PEDOT:PSS hybrid (Figure 2E). These BE shifts were attributed to stiffening of the Ti–C bonds and the softening of PEDOT through charge transfer interaction of the hybrids.30 The detailed peak assignments and interpretation are provided in Note S2. The electrons transferred to Ti3C2 during the hole injection into PEDOT strengthen the Ti–C bond that was weakened by the surface groups of the Ti3C2 flakes,30 as supported by the reduction in the bandgap energy from 2.44 to 2.13 eV for the MP12 hybrid (as demonstrated in Figure S3 and discussed in Note S2). This doping effect resulted in the transition of PEDOT:PSS into the more conductive and electrochemically active quinoid phase. Thus, the change in the electronic structure of PEDOT:PSS and interaction with the Ti3C2 flakes improves the charge transport kinetics and redox activity of the hybrid for high-power and -energy applications.25,27,29

For evaluation of the hybrid for AC filtering, solid-state EC devices were fabricated by varying the compositions and thicknesses of the hybrid films. The pure Ti3C2 and PEDOT:PSS, MP11 (Ti3C2/PEDOT:PSS as 1:1 wt %), and MP12 (Ti3C2/PEDOT:PSS as 1:2 wt %) were chosen as active materials in the thin film form. The thicknesses of the pure Ti3C2, MP11, and MP12 thin films were controlled by changing the amount of sprayed colloidal solution and was varied as 156, 188, and 260 nm; 220, 355, and 733 nm; and 183, 231, and 367 nm, respectively. The ECs based on the Ti3C2, MP11, and MP12 thin films are denoted as Ti3C2-n, MP11-n, and MP12-n (here, n represents the thickness of the active material in nanometers).

The thickness of each sample was optimized on the bases of the capacitive performance and frequency response. The areal capacitance of Ti3C2-n was enhanced when the thickness increased to 260 nm (Figures S4 and S5, and Table S1). At the optimum thickness, the rapid frequency response was persistent in a capacitive manner up to 166 kHz, but the areal capacitance and voltage window of Ti3C2-260 were limited to <0.05 mF cm\(^{-2}\) and 0.6 V, respectively. In a similar manner to Ti3C2, the areal capacitance and rate capability of MP11 and MP12 were dramatically degraded beyond the optimum thickness of 355 and 231 nm, respectively (Figures S4 and S5, and Table S1). The areal capacitance (1.97 mF cm\(^{-2}\) at 0.1 V s\(^{-1}\)) of MP11-355 was highest among those of the three MP11 samples, and much higher than that (0.05 mF cm\(^{-2}\)) of Ti3C2-260. Similarly, the areal capacitance (1.92 mF cm\(^{-2}\) at 0.1 V s\(^{-1}\)) of MP12-231 was higher than 0.39 and 1.30 mF cm\(^{-2}\) for MP12-183 and MP12-367, respectively. The thickness of MP12 was optimized at 231 nm, which is less than the optimum (355 nm) thickness for MP11 due to the greater content of active PEDOT:PSS and different porous structures. Moreover, pristine PEDOT:PSS with a controlled thickness of 267 nm furnished the lowest areal capacitance of 0.032 mF cm\(^{-2}\) and poor rate and frequency performance due to its compact structure and low conductivity (Figure S6). Therefore, the optimum thicknesses of both MP11-355 and MP12-231 were determined by considering the thickness dependence of the electrochemical performance (Figure S5).

The electrochemical performance of Ti3C2, MP11, and MP12 with respective optimized thicknesses of 260, 355, and 231 nm was investigated using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) curves, as shown in Figure 3. The distinctive rectangular CV curves of Ti3C2 were observed up to 100 V s\(^{-1}\) in the range of 0.6 V, but the capacitance was not measurable at 1,000 V s\(^{-1}\) due to the large IR drop (Figure 3A). The CV profile of PEDOT:PSS also corresponded to resistive behavior at 100 V s\(^{-1}\) (Figure S6). Importantly, both MP11 and MP12 hybrids exhibited the rectangular shape up to 1,000 V s\(^{-1}\) in the range of 0.8 V (Figures 3B
and 3C), indicating ultra-high-rate capacitive energy storage with an enlarged voltage window. At the identical rate of 10 V s\(^{-1}\), a discrepancy in the CV profiles of the Ti\(_3\)C\(_2\) and MP hybrids was very discernible (Figure 3D), confirming the significant enhancement of the areal/volumetric capacitances and enlargement of the voltage window from 0.6 to 0.8 V by hybridization. In particular, the enhanced capacitance of MP hybrids was attributed to the surface redox charge storage mechanism through a doping/de-doping process of PEDOT\(^{25}\), where this redox process is facilitated by the high electronic conductivity of Ti\(_3\)C\(_2\) and the phase transition into a conductive structure via an electronic interaction.

To further investigate the effect of the hybrid composition, the electrochemical performance of Ti\(_3\)C\(_2\), PEDOT-PSS, MP11, and MP12 with their own optimum thicknesses as specified above were compared. The maximum areal/volumetric capacitances of the hybrid at 0.1 V s\(^{-1}\) were 1.97 mF cm\(^{-2}\) for MP11 and 83.1 F cm\(^{-3}\).
for MP12, respectively, where each value was optimized at different compositions and thicknesses (Figures 3E and 3F). The values for the hybrids at 0.1 V s$^{-1}$ were two orders greater than those of pristine Ti$_3$C$_2$ and pure PEDOT:PSS under the same conditions. When the rate was increased to 1,000 V s$^{-1}$, the effect of the film thickness became more prominent. Despite the lower porosity, higher density, and a lower content of conductive Ti$_3$C$_2$, MP12 showed an areal capacitance of 0.21 mF cm$^{-2}$, volumetric capacitance of 9.05 F cm$^{-3}$, and capacitive retention of 10.8% at 1,000 V s$^{-1}$ relative to the values at 0.1 V s$^{-1}$, which were greater than the corresponding values of 0.16 mF cm$^{-2}$, 4.53 F cm$^{-3}$, and 8.18% for MP11. These capacitance values of MP12 even at 1,000 V s$^{-1}$ were greater than those of Ti$_3$C$_2$ at 100 V s$^{-1}$ (not measurable at 1,000 V s$^{-1}$). At the same rate of 100 V s$^{-1}$, MP12 achieved a capacitance of 0.58 mF cm$^{-2}$ and 24.9 F cm$^{-3}$ with the 30% of 0.1 V s$^{-1}$ capacitance retained at 100 V s$^{-1}$. This result again highlights the importance of the composition and thickness in balancing the charge storage and transfer capabilities for achieving maximum areal/volumetric capacitance and rate capability.

Furthermore, Ti$_3$C$_2$, MP11, and MP12 exhibited linear proportionality between the logarithmic scan rate and charging current density (Figure 3G), which is associated with the high power capability (no diffusional limitation). The slope of the linear dependence for MP12 was the highest at the optimum thickness and composition, consistent with the superior power and rate capabilities of this system. The GCD profiles of MP12 also exhibited triangular symmetric shapes, along with excellent Coulombic efficiency, as a function of the current density (Figures 3H and 3I). The Coulombic efficiency of 99.7% at 12 mA cm$^{-2}$ was associated with the reversibility at high rates, indicating the fast and reversible pseudocapacitance of the hybrid. Thus, hybridization with the optimized composition and thickness leads to improved electrochemical properties, including the areal capacitance, voltage window, rate capability, and frequency response (Figure S5 and Table S1).

In order to verify the frequency responses of Ti$_3$C$_2$, MP11, and MP12 for AC line filtering, we examined the Bode and Nyquist plots and frequency-dependent capacitance, as shown in Figure 4. The phase angle at 120 Hz is an important parameter for evaluating the potential of the device as an AC filter, because an ideal capacitor has a phase angle of −90°. Moreover, the frequency ($f_o$) at the phase angle of −45° is the cutoff value to determine the borderline between capacitive and resistive natures of the EC device. As shown in Figure 4A, the phase angles and cutoff frequencies of Ti$_3$C$_2$, MP11, and MP12 were 70.0°, 76.1°, and 79.1° at 120 Hz and 1.60, and 1.41 kHz at −45°, respectively. The decrease in phase angle at low frequencies for MP11 and MP12 was attributed to the contribution of the faradaic component to the overall capacitive feature as a function of frequency. The resistor-capacitor (RC) time constants ($t_{RC}$), the time required for charging to 63.2% of the full potential of the capacitor, were estimated as 0.39, 0.12, and 0.29 ms at 120 Hz, which are shorter than 1.33 ms for the AEC required for 120 Hz AC filtering. The dissipation factor (DF) derived from tan δ = Z’/Z” indicates the degree of energy loss as heat dissipation. The DF value of MP12 ECs was 0.193, lower than those of Ti$_3$C$_2$ and MP11 ECs, which is acceptable for non-continuous applications such as low-duty-cycle pulse, stand-by mode operation, and discontinuous current mode operation. However, this value is lower than the value of AEC for small and low-voltage capacitor (DF = 0.14 at −82° of phase angle) and for large one (DF = 0.087 at −85° of phase angle).}

As shown in the Nyquist plots in Figure 4B, the Warburg impedance and semicircle were almost negligible, which indicates rapid ionic transport to the active sites.
through the interconnected porous channels and facilitated charge transport. As marked by arrows in Figure 4B, the real impedance ($Z'$), representing the resistance, increased in the order Ti$_3$C$_2$, MP11, and MP12 at 120 Hz, whereas the imaginary impedances ($Z''$), representing the capacitance, changed in the reverse order. Along with the lowest $Z'$ and highest $Z''$ at 120 Hz and the lowest equivalent series resistance, MP12 EC also showed the steepest slope of the Nyquist plot. These results indicate that the hybrid film of MP12 with the optimum composition and thickness enabled rapid ionic and electronic transport dynamics, leading to the excellent high-frequency response.

The areal capacitances of the ECs as a function of the frequency were derived from the complex frequency-dependent capacitance model, as shown in Figure 4C. As shown in the frequency-dependent phase angle of Bode plot in Figure 4A, a complex Randles model is more suitable than a simple series RC circuit for...
estimating the frequency-dependent capacitance values (Figure S7). MP12 EC exhibited the lowest capacitance loss above 0.1 Hz and maintained high capacitance at high frequencies. The areal/volumetric capacitances of the Ti$_3$C$_2$, MP11, and MP12 ECs at 120 Hz were 0.006/0.24, 0.302/8.51, and 0.560/24.2 mF cm$^{-2}$/F cm$^{-3}$, respectively. The frequency-dependent trend of the capacitance is consistent with that measured from the CV and GCD curves, reflecting both the frequency response and capacitive feature arising from the charge storage kinetics and capability.

For practical use in AC line filtering, the MP12 tandem ECs were configured in a series connection (Figure S8 for an AC line filtering circuit diagram) and operated at different frequencies. The input AC signal ($V_{\text{peak}} = \pm 1.6$ V, 60 Hz) was rectified to a pulsating signal (0–1.5 V, 120 Hz) with a full-wave rectifier (integrated circuit [IC]: GBJ1506) (Figure 4D). The pulsating signal was then flattened to a constant DC output of ~1.27 V when filtered across the MP12 tandem ECs. In order to inspect the AC-filtering feature of the EC over a wide range of frequencies (60–10,000 Hz), the deviation of the peak amplitude of the signal ($\Delta V$, defined as the difference between the maximum and minimum voltage) was measured across the rectifier and MP12 tandem ECs, as shown in Figure 4E. The $\Delta V$ of the MP12 tandem ECs was almost constant over the entire frequency range, and, even at 10,000 Hz, the fluctuation was nearly negligible. In contrast, the $\Delta V$ of the rectifier was greater than that of the MP12 tandem ECs over the entire frequency range and fluctuated more at low frequencies. Real-life ripple filtering across the MP12 tandem ECs was demonstrated by utilizing an experimental setup equipped with a frequency generator, full-wave rectifier circuit, and cathode ray oscilloscope, as shown in Figure 4F. The sinusoidal input signal at 60 Hz to the rectifier circuit at the two inside legs of IC: GBJ1506 is shown in Figure 4G. This AC signal was flattened across the MP12 tandem ECs, as shown in Figure 4H (Video S1). These results highlight the good AC-filtering function of the MP12 tandem ECs and thus their capability to filter ripples as the AEC filter does.

In order to demonstrate the flexibility and durability of the MP12 ECs for flexible AC-filtering applications, CV curves were acquired at different bending angles, along with the AC-filtering data in the bent state and cyclic stability in different bending states, as shown in Figure 5. The MP12 ECs were sufficiently flexible to be bent at various angles (0°, 45°, 90°, 135°, and 180°), confirming the mechanical flexibility of the as-fabricated device. The rectangular CV profiles and capacitances of the MP12 ECs at 10 V s$^{-1}$ were well preserved without significant attenuation in the bent state (Figure 5B). The real-life AC-filtering function of the MP12 ECs at 60, 100, 1,000, and 10,000 Hz was demonstrated even in the bent state, as shown in Figure 5C (inset shows the sinusoidal AC input signal). The AC signals across the MP12 tandem ECs were filtered even at 10,000 Hz and in the bent state, indicating the efficient ripple filtering capability under extreme conditions. The real-time operation of AC filtering in the bent state was monitored on a cathode ray oscilloscope at 60 Hz (Video S2). The extreme performance of the as-fabricated EC was demonstrated by executing the GCD measurement at 4 mA cm$^{-2}$ over 30,000 cycles (10,000 per normal, in the bent at 90° and released state), as presented in Figure 5D. The high capacitance (0.9 mF cm$^{-2}$) and Coulombic efficiency (97.2%) of the MP12 ECs were not noticeably changed after 30,000 cycles in the bent state, indicating the mechanical integrity and durability of the Ti$_3$C$_2$/PEDOT:PSS hybrid. Stable performance over 30,000 cycles in the bent state highlights the superiority of the MXene/PEDOT:PSS hybrid-based ECs. However, future investigation is required...
for AC-filtering applications, considering the expected lifetime of >50,000 hr under various operation conditions.\(^4^0\)

In summary, MXene/conducting polymer hybrids were produced by a scalable process method for flexible AC-filtering ECs. The as-developed devices achieved maximum areal and volumetric capacitances of \(\sim 2\ \text{mF cm}^{-2}\) and \(83\ \text{F cm}^{-3}\), respectively, operating at the extreme rate of \(1,000\ \text{V s}^{-1}\). Even at \(120\ \text{Hz}\) and in a flexible format, areal and volumetric capacitances of \(0.56\ \text{mF cm}^{-2}\) and \(24.2\ \text{F cm}^{-3}\), respectively, were recorded, which are superior to those of commercial AECs, and comparable with other ECs reported so far (Table 1).\(^{15,41-47}\) Moreover, operation of the tandem ECs in the frequency range of 60 to 10,000 Hz was demonstrated, and long-term durability over 30,000 cycles was confirmed in the bent and relaxed states. The charge storage kinetics of Ti\(_3\)C\(_2\)/PEDOT:PSS hybrids can be controlled by adjusting the thickness and composition of the film and is maximized by formation of the interconnected porous architecture and synergistic electronic interactions in the hybrid electrode. Although the superior volumetric capacitance and scalability have been demonstrated, work is still required to improve the capacitor “speed” to make its phase angle closer to \(-90^\circ\) and expected lifetime >50,000 hr, so that ECs can compete with AEC technology in all applications. This work opens
opportunities for the design of hybrid architectures with high volumetric capacitance for flexible miniaturized electronic systems, bridging the performance gap between the capacity density and frequency response of currently available devices.

**EXPERIMENTAL PROCEDURES**

Full experimental procedures and characterization are provided in Note S1.

**SUPPLEMENTAL INFORMATION**

Supplemental Information includes eight figures, one table, two notes, and two videos and can be found with this article online at [https://doi.org/10.1016/j.joule.2018.10.017](https://doi.org/10.1016/j.joule.2018.10.017).

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**AUTHOR CONTRIBUTIONS**

G.S.G. carried out the experiment. R.H. and G.S.G. fabricated the devices. G.S.G., J.H.S., and J.H.P. designed and performed AC-filtering measurements, supported by T.I.K. G.S.G., M.K., and R.H. analyzed chemical characterization results. G.S.G. and J.H.P. designed the figures. G.S.G., H.S.P., and Y.G. wrote the manuscript. H.S.P. and Y.G. supervised the complete work. All authors discussed the results and remarked on the manuscript at all stages.

**Table 1. Comparison of MXene/Polymer Hybrid Electrochemical Capacitor with AEC and Previously Reported ECs in Terms of Materials (of Electrode, Electrolyte, and Substrate), Flexibility, Capacitance, and Frequency Response**

<table>
<thead>
<tr>
<th>Number</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Substrate</th>
<th>Flexibility</th>
<th>C @ 120 Hz mF cm⁻² (F cm⁻²)</th>
<th>τRC (ms)</th>
<th>f₀ (kHz)</th>
<th>- φ @ 120 Hz (Degree)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al</td>
<td>Al₂O₃ (dielectric medium)</td>
<td>Al</td>
<td>none</td>
<td>0.0392</td>
<td>0.195</td>
<td>1.258</td>
<td>81.9</td>
<td>Yoo et al.⁴²</td>
</tr>
<tr>
<td>2</td>
<td>vertically aligned graphene</td>
<td>6 M KOH</td>
<td>Ni foil</td>
<td>none</td>
<td>0.175 (3)</td>
<td>0.2</td>
<td>15</td>
<td>82</td>
<td>Miller et al.¹⁵</td>
</tr>
<tr>
<td>3</td>
<td>graphitic ordered mesoporous carbon</td>
<td>1 M TEABF₄ in ACN</td>
<td>NA</td>
<td>NA</td>
<td>0.560 (0.052)</td>
<td>8.3</td>
<td>~1.2</td>
<td>80</td>
<td>Yoo et al.⁴¹</td>
</tr>
<tr>
<td>4</td>
<td>rGO</td>
<td>6 M KOH</td>
<td>Au plate</td>
<td>none</td>
<td>0.283</td>
<td>1.35</td>
<td>4.2</td>
<td>84</td>
<td>Sheng et al.⁴⁷</td>
</tr>
<tr>
<td>5</td>
<td>CNT</td>
<td>Ionogel polymer/ [EMIM][NTf₂]/ACN</td>
<td>Al foil</td>
<td>flexible</td>
<td>0.106 (8.15)</td>
<td>0.513</td>
<td>1</td>
<td>78.1</td>
<td>Kang et al.⁴⁴</td>
</tr>
<tr>
<td>6</td>
<td>unzipped graphene nanoribbons</td>
<td>1 M KOH</td>
<td>Pt foil</td>
<td>semi-flexible</td>
<td>0.19 (0.95)</td>
<td>0.212</td>
<td>8.15</td>
<td>85</td>
<td>Lim et al.⁴⁵</td>
</tr>
<tr>
<td>7</td>
<td>rGO/PEDOT-PSS</td>
<td>1 M H₂SO₄/ PVA gel</td>
<td>Au-coated PET</td>
<td>flexible</td>
<td>0.87</td>
<td>0.644</td>
<td>0.32</td>
<td>45</td>
<td>Wu et al.⁴³</td>
</tr>
<tr>
<td>8</td>
<td>PEDOT-PSS</td>
<td>1 M H₂SO₄</td>
<td>Graphite foil</td>
<td>semi-flexible</td>
<td>0.994 (16.6)</td>
<td>0.15</td>
<td>~2</td>
<td>83.6</td>
<td>Zhang et al.⁴⁶</td>
</tr>
<tr>
<td>9</td>
<td>Ti₃C₂/PEDOT-PSS (MP12-231)</td>
<td>3 M H₂SO₄/ PHEMA/PVA gel</td>
<td>Au-coated PET</td>
<td>flexible</td>
<td>0.56 (24.2)</td>
<td>0.29</td>
<td>1.41</td>
<td>79.1</td>
<td>this work</td>
</tr>
</tbody>
</table>

ACN, acetonitrile; NA, not available; TEABF₄, tetraethylammonium tetrafluoroborate; rGO, reduced graphene oxide; CNT, carbon nanotube.
REFERENCES


