

Article

Binder-Free Two-Dimensional Few-Layer Titanium Carbide MXene Ink for High-Performance Symmetric Supercapacitor Device Applications

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Abstract: A heightened interest in developing MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) for energy storage is evident in binder-free MXene ink being directly applied to current collector Ni-foam. Moreover, 2D titanium carbide MXene, with a few layers of nanostructure, has been prepared for symmetric supercapacitor device applications. As-prepared MXene nanosheets exist in two forms: dried powder and ink, achieved through wet-chemical etching and dimethyl sulfoxide delamination from the MAX (Ti_3AlC_2) phase. This comparative study of electrode devices involves (i) MX-dry powder with binder/additive electrodes and (ii) binder-free MXene inks with directly applied MX-conductive inks. The surface morphological images of pure MX-powder/ink display few layers, and material analysis reveals the good crystalline nature of delaminated MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) inks. The electrochemical symmetric supercapacitor device performances of pure MXene powder and binder-free directly applied/coated MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) ink, in terms of cyclic voltammetry (CV) and impedance spectroscopy (EIS), exhibit galvanostatic charge–discharge (GCD) curves that show high specific capacitance (C_{sp}) at 105.75 F/g at a current density of 1 A/g. A comparison of active material electrodes demonstrated excellent cycle stability. Hence, in this work, we confirmed the superior capacitive behavior of binder-free MXene ink (MX-I) compared to conductive additives with polymeric binders included in MXene electrodes.



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1. Introduction

In recent decades, the pursuit of advanced energy storage solutions has driven noteworthy innovations in the field of supercapacitors, with the aim of enhancing their performance, efficiency, and versatility. Among the myriad materials explored is a new family of 2D materials known as MXene, represented by the formula M_{n+1}X_n . MXene belongs to the MAX phase group, consisting of three-component compounds with layers of transition metal carbides/nitrides (M_{n+1}X_n), where M represents transition metal layers and X denotes carbon/nitrogen [1,2]. The primary MXene, Ti_3C_2 , derived from the selective removal of ‘A’ layers from the MAX phase (Ti_3AlC_2) using wet chemical etching methods, remains widely utilized. Common etchants include acetic solutions, diluted HF [3], LiF/HCl [4], and alkaline solutions, such as NaOH and KOH [5]. Different etching solutions have been achieved through surface functionalization (e.g., with -O, -OH, -F, and -Cl) [6]. MXenes have emerged as a prominent class of two-dimensional materials, drawing attention owing to their unique properties and diverse applications [7,8], particularly in the realm of supercapacitor technology. This remarkable focus on MXenes in the field of supercapacitors is highlighted by their distinctive stacked layered structure and tunable properties [9]. With high electrical conductivity, large surface area, and tailorable surface chemistry, MXenes are promising candidates for energy storage in supercapacitors [10,11]. The transition metal carbide $\text{Ti}_3\text{C}_2\text{T}_x$, a derivative of MXene, has demonstrated both intrinsic electric double-layer capacitance (EDLC) and combined pseudocapacitance mechanisms within

MXene-based electrodes [12]. Ongoing research efforts, as detailed in recent reports, aim to optimize the energy storage performance of two-dimensional layered transition metal carbide materials [13]. The potential of MXenes to advance supercapacitor technology has become evident, offering prospects for high-energy-density and long-lasting energy storage solutions. MXenes, particularly the Ti_3C_2 variant, stand out as strong candidates for electrical energy storage applications [14,15]. This preference stems from their outstanding assets of thermal stability, hydrophilic surface, expansive accessible surface area, significant interlayer spacing, impressive metallic conductivity (approximately 9880 S cm^{-1}), and distinctive optical properties [16,17]. Furthermore, MXenes demonstrate tunable surface states, ensuring adaptability and high mechanical and electrochemical stabilities.

In addition, the discovery of mono-layer graphene nanosheets [18] has been explored in terms of the basics concerning a new variety of 2D family layered materials [19,20] for next-generation energy-effective electrode candidates, such as MXene nanosheets [21]. The incorporation of MXene into supercapacitor electrodes is not only driven by its impressive electrochemical properties but also by the advent of MXene-based inks that facilitate binder-less coating processes. Examples of additive-free graphene 2D material inkjet printing for electronics applications include [22] molybdenum disulfide (MoS_2) [23] and black phosphorous (BP) [24]. Hence, additive and binder-less coatings represent a major advancement in supercapacitor technology, addressing challenges associated with conventional binders, such as reduced electrical conductivity and limited cycling stability [25]. MXene ink, composed of MXene flakes dispersed in a suitable solvent, enables the direct deposition of active materials onto current collectors, eliminating the need for binders. This innovation enhances the overall high-viscosity properties of MXene and the conductivity of the electrode, leading to improved charge-discharge kinetics and increased energy density [26]. Moreover, MXene ink serves as a versatile tool for fabricating symmetric supercapacitor devices. Symmetric configurations involve the use of identical materials as electrodes, presenting an advantageous platform for MXene-based electrodes due to their inherent stability and compatibility [27,28]. The ability of MXene ink to uniformly coat both electrodes can be exploited in the construction of both symmetric and asymmetric flexible and transparent supercapacitors, effectively enhancing both energy and power densities [29]. Furthermore, the Ti sites facilitate reversible redox reactions, contributing to redox capacitance, also known as pseudocapacitance. Additionally, negatively charged MXene nanosheets possess numerous surface terminal groups that enable the creation of a stable and viscous aqueous colloidal solution (ink) without the requirement for surfactants or polymeric binders [30,31]. Therefore, $\text{Ti}_3\text{C}_2\text{T}_x$ ink expanded the layered structure to improve the overall electrochemical performance of symmetric device capacitors. In a comparative analysis, MXene-based binder-less coatings outperformed their traditional binder-containing counterparts, showing superior electrochemical performance in terms of specific capacitance, cycling stability, and rate capability [32]. The binder-less approach not only streamlines the electrode fabrication process but also contributes to the overall sustainability of flexible supercapacitor technology [33–36], and MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) ink has been used as an additive/binder-less coating for batteries and direct coating of electrodes [37–40]. Furthermore, this study explored advancements in energy storage devices, including the integration of Co_3O_4 nanoparticles with carbon composites for enhanced Li-ion storage capabilities, as well as the development of N-doped carbon spheres with MnO_2 composites tailored for high-energy supercapacitor applications [41–43].

This paper reports the integration of MXene ink for binder-less coating in supercapacitor electrodes. MXene synthesis from MAX (Ti_3AlC_2) was achieved through selective etching of “Al” phase using diluted HF with HCl mixture of acidic solution. In particular, symmetric device configurations represent a noteworthy step in the development of high-performance energy storage systems. The distinctive electrochemical analysis conducted for $\text{Ti}_3\text{C}_2\text{T}_x$ coupled with the advantages of binder-less coatings make MXene ink-based electrodes frontrunners in the quest for efficient and sustainable symmetric supercapacitor devices. Direct coating ink-based (TiC_2T_x) techniques continue to reveal the full potential

of MXene in energy storage applications for next-generation supercapacitors, driven by the innovative use of MXene ink.

2. Materials and Methods

2.1. Materials Required

Ti₃AlC₂ bulk precursor powders ($\geq 99\%$ purity; particle size 40–60 μm), hydrofluoric acid (HF) solution (48 wt. %), and dimethyl sulfoxide (DMSO) were purchased. Due to the diluted systemic HF toxicity, careful handling with safety data sheets (H330-H314) and exploration of the hazards specific to HF before handling (from Sigma Aldrich, St. Louis, MO, USA) were conducted in a fume hood, and personal protective equipment was used.

2.2. Preparation of MXene

2.2.1. MXene Etching and Delimitations

The MXene (Ti₃C₂T_x) was prepared using a chemical method involving etching and delamination. In a typical procedure, MAX (Ti₃AlC₂) precursor bulk powders were gradually added to a hydrofluoric acid (HF) solution at a concentration of 48%, and the mixture was continuously stirred slowly for 30 h at room temperature. The reaction mixture was transferred to a polypropylene beaker with a Teflon magnetic stirrer in a fume hood. MXene (Ti₃C₂) was prepared via chemical etching. The MAX (Ti₃AlC₂) phase titanium carbide (90% pure Ti₃AlC₂, particle ranges approximately 40 μm) was combined with HF and HCl. In a typical synthesis, 15 mL HF was mixed with 5 mL HCl (6 M) to create an etching solution using proper safety equipment. Additionally, 1 g of MAX (Ti₃AlC₂) was added to the above solution below 20 °C for 24 h. The resulting gel-like liquid suspension was stirred and cleaned. The dark solution of as-prepared Titanium Carbide (Ti₃C₂T_x–T_x) MXene was continuously washed to remove its acidic nature. The MXene solution was cleaned with deionized water (DI) using a centrifuge at 4000 rpm for 20 min, with the anticipation of achieving a pH of approximately 7. The (HF) etched mixture solution was further expanded and delaminated using dimethyl sulfoxide (DMSO) solution, allowing the intercalation of large organic molecules into the as-prepared MXene-MX (Ti₃C₂T_x). Finally, the MXene solution was centrifuged using DI water to remove its active nature and maintain a pH level of approximately 6–7. The as-prepared MXene solution was vacuum-filtered, and the filtered MXene solid was dried at 100 °C for 12 h.

2.2.2. Preparation of MXene Suspension and Ink Formulation

The prepared MXene suspension was subjected to additional sonication to ensure proper dispersion and prevent agglomeration of the MXene flakes. This step is crucial for obtaining a homogeneous ink with well-dispersed MXene nanosheets. The obtained MXene flakes were dispersed in a selected solvent, dimethyl sulfoxide (DMSO), in an MXene-NMP suspension while stirring the mixture continuously. Typically, a mixture of water and an organic solvent, such as 10 mL of DMSO, is used in a controlled environment such as bath sonication for 30 min. The MXene/DMSO solution is then centrifuged to remove the excess DMSO. Finally, 5 mL of the NMP additive was introduced into the MXene suspension of MXene nanosheets dispersed in the solvent to enhance ink stability. The addition of NMP helps to enhance the stability of the ink and improves its wetting properties of MXene to achieve the desired ink with a better gel-like nature. This centrifugation process is continuously repeated approximately 8 to 10 times. Then, the pH level was adjusted to approximately 6.5–7, and MXene was concentrated to achieve the desired ink. The MXene ink formulation enhances the adhesion and stability by mixing to achieve a homogeneous MXene–binder composite ink. The as-prepared MXene ink was stored in a controlled environment to prevent evaporation or degradation. Airtight containers and, if necessary, refrigeration were used to maintain the ink's stability over time, promoting a uniform coating on the substrates.

2.2.3. Material Characterization

The MXene powder and ink materials were comprehensively characterized using various analytical techniques. X-ray diffraction (XRD) analysis was performed using an X'PertPRO PAN-Analytical machine (Philips X'PertPro, Amsterdam, Netherlands) operated at 40 kV and 30 mA, employing Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan rate of $5^\circ/\text{min}$ to investigate the crystallographic structure of the samples. Field-emission scanning electron microscopy (FE-SEM) images were acquired using an FE-SEM S-4800 instrument (FESEM, Hitachi S-4800, Tokyo, Japan), providing detailed insights into the surface morphology and microstructure. Fourier transform infrared (FT-IR) spectroscopy was conducted using a Perkin Elmer instrument (Model no. Spectrum-100, Thermo Scientific, Boston, MA, USA) in the range of $400\text{--}4000 \text{ cm}^{-1}$ to elucidate the functional groups present in the materials. Additionally, high-resolution transmission electron microscopy (FE-TEM) images were obtained using a TECNAI (FEI) TF-20 instrument (FEI Tecnai G2 F20, Eindhoven, The Netherlands) operating at an accelerating voltage of 200 kV to visualize the nanoscale features and structural characteristics. These instrumental analyses collectively provided a comprehensive understanding of the structural, morphological, and chemical properties of the materials. The surface element chemical composition was determined using X-ray photoelectron spectroscopy (XPS) with a Thermo Fisher Scientific-U.K. ESCALAB 250 XPS System with mono-chromatic Al K α radiation ($h\nu = 1486.6 \text{ eV}$) serving as the X-ray energy source, operated at 15 kV and 150 W, with a spot size ranging from 400 to 500 μm .

2.2.4. Electrode Preparation and Coatings

Active materials for dried MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) powder were used for electrode preparation, and an MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) powder composite was formulated by mixing 80% MXene powder, 10% activated carbon (AC), and 10% polyvinylidene fluoride (PVDF) binder. The components were thoroughly mixed to obtain a homogenous composite, ensuring uniform dispersion of the MXene nanosheets and optimal binding with PVDF. Subsequently, the well-mixed composite was coated onto a nickel foam (Ni-foam) substrate to serve as a current collector. The coating process was carefully executed to achieve a consistent and adherent MXene layer on the Ni-foam, promoting efficient charge transfer and enhancing the overall electrode performance. This electrode configuration, with a synergistic combination of MXene, AC, and PVDF, holds promise for advanced energy storage applications, capitalizing on the unique properties of the conductive nature of MXene nanosheets.

The as-prepared MXene ink coating technique requires conductive substrate-cleaned Ni-foam. This step ensures optimal film formation during dipping of the brush into the MXene ink and gentle coating of the Ni-foam substrate. An even distribution of MXene ink across the entire surface was ensured. This process was repeated if necessary to achieve the desired thickness. Annealing with coated the Ni-foam was performed overnight at 80°C in an oven to enhance the adhesion and conductivity of the MXene layer. Finally, the coated Ni-foam was uniformly adhered the MXene layer. Finally, the MXene powder forms an electrode prepared with PVDF polymeric binder and is directly coated with MXene ink on a Ni-foam specific active mass of approximately 2–5 mg.

The specific capacitance (Csp) formula for calculating the specific capacitance is given by the electrode (MAX, MXene, MXene-ink) and can be calculated from the galvanostatic charge and discharge via the GCD curves using Equation (1):

$$C_{sp} = (I \times \Delta t) / (m \times \Delta V) \quad \text{F/g} \quad (1)$$

where the applied charge–discharge current is I (mA), Δt is the discharge time (s), ' m ' is the active material mass (mg), and ΔV is the charge–discharge potential window (V). The gravimetric specific capacitance (F/g) of the MXene ink devices was calculated based on the total active mass of both electrodes.

3. Results

3.1. XRD Analysis

The XRD analysis of MAX (Ti_3AlC_2) and its derivative MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) revealed distinct crystalline structures of pure MAX ($\text{Ti}_3\text{AlC}_2\text{T}_x$) and the as-prepared MXene ink. Figure 1 illustrates the MXene preparation process, involving the etching of Al from bulk MAX precursor materials using 48% HF solutions. The XRD pattern of MAX exhibited characteristic diffraction patterns corresponding to the hexagonal crystal lattice of the MAX (Ti_3AlC_2) phase, with high-intensity peaks at $2\theta = 9.47^\circ$, 18.91° , and 38.78° , representing the (002), (004), and (104) planes, respectively. The peak at 38.78° (104) corresponds to the Al peak in the MAX phase XRD results. Furthermore, the MXene powder sample displayed peaks at $2\theta = 8.95^\circ$, 18.91° , 27.60° , 35.95° , 41.43° , and 60.85° , corresponding to the (002), (003), (004), (006), (101), (103), (104), (105), and (110) planes, respectively. Finally, the MXene ink sample exhibited diffraction patterns at $2\theta = 34.08^\circ$, 38.90° , 60.19° , 73.71° , and 75.83° , corresponding to the (002), (101), (105), (110), (118), and (205) planes, respectively [44,45].

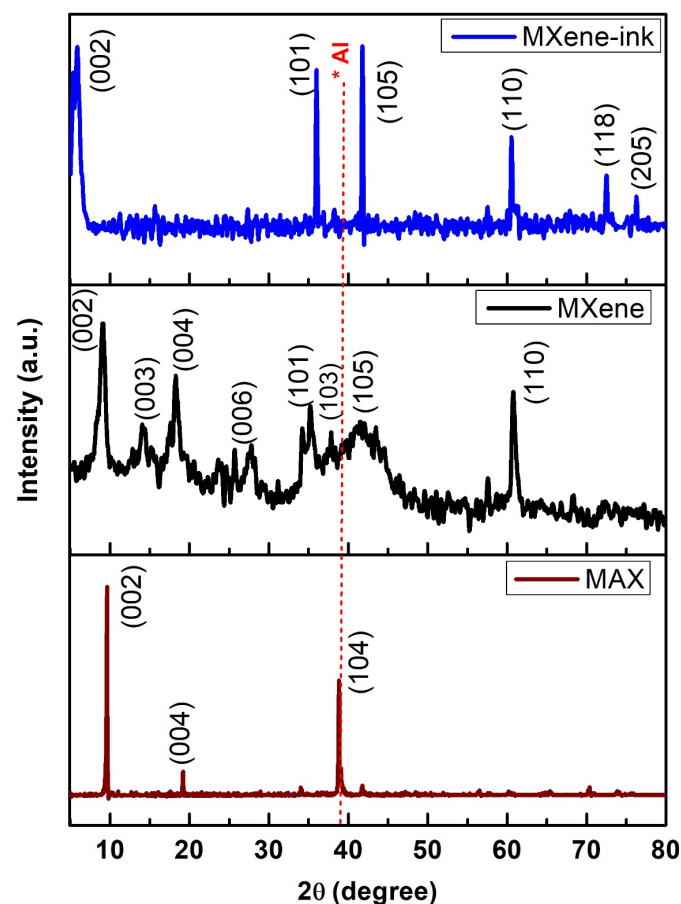


Figure 1. XRD patterns of MAX (Ti_3AlC_2), MXene ($\text{Ti}_3\text{C}_2\text{T}_x$), and MXene ink samples.

Consequently, most of these peaks disappeared from the XRD pattern of MXene, suggesting successful etching with a downward shift in the (002) peak and confirming an increase in the interlayer spacing after Ti_3AlC_2 etching. In the Ti_3AlC_2 XRD pattern, the strong peak corresponding to the (104) plane disappeared in both MXene samples, indicating the successful removal of the Al atomic layer. Simultaneously, $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits a strong diffraction peak after the removal of the Al metal layer. The overall XRD spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes displays a notable shift in peak positions after selective etching to obtain the MXene ink sample, with the peak (002) at $2\theta \sim 6\text{--}7^\circ$ confirming the presence of MXene ($\text{Ti}_3\text{C}_2\text{T}_x$). This shift indicates a structural transformation, with the MXene peaks moving towards lower angles, confirming the successful delamination and formation of $\text{Ti}_3\text{C}_2\text{T}_x$.

The XRD results, consistent with the removal of the aluminum layers, indicate an increased interlayer spacing within the MXene structure. Further analysis allowed the identification of prominent crystallographic planes, such as (002) and (004), which are characteristic of the MXene phase. The observed changes in the XRD pattern confirm the transition from MAX to MXene, signifying the successful synthesis and crystalline transformation of $\text{Ti}_3\text{C}_2\text{T}_x$.

3.2. FT-IR Functional Group Analysis

FTIR spectroscopy was used to characterize the surface functional groups of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets, as illustrated in Figure 2. The FT-IR transmittance (T %) peaks of the characteristic MAX, MXene, and MXene-ink materials were observed at 1102 cm^{-1} , 1405 cm^{-1} , 1628 cm^{-1} , 2355 cm^{-1} , 2920 cm^{-1} , and 3428 cm^{-1} , corresponding to the C-O bond, carbonate (CO_3^{2-}) species bond, C-OH stretch, CO_2 , C-H bonds, and -OH stretching, respectively [46]. These peaks are attributed to the stretching vibration of the strongly hydrogen-bonded -H group and bending vibration of the C-OH bond, associated with absorbed water molecules. In addition, the MXene-ink FT-IR data revealed a strong peak at 1405 cm^{-1} , assigned to the carbonate (CO_3^{2-}) species antisymmetric stretching modes. The surface functionalization of $\text{Ti}_3\text{C}_2\text{T}_x$ resulted in high transmittance peaks at 2920 cm^{-1} and 3428 cm^{-1} , corresponding to the symmetric and asymmetric stretching vibrations of C-H and -OH bonds, respectively. Furthermore, the main IR transmittance characteristic peaks at 620 cm^{-1} and 626 cm^{-1} can be attributed to the deformation vibration of the Ti-O-Ti linkage with Ti-O and Ti-C bonds [47], respectively. Additionally, the appearance of peaks at 1405 cm^{-1} was assigned to the stretching vibration of the O-H bond. From the FT-IR results, more functional groups conformed after etching MXene and MXene-ink compared to the MAX phase.

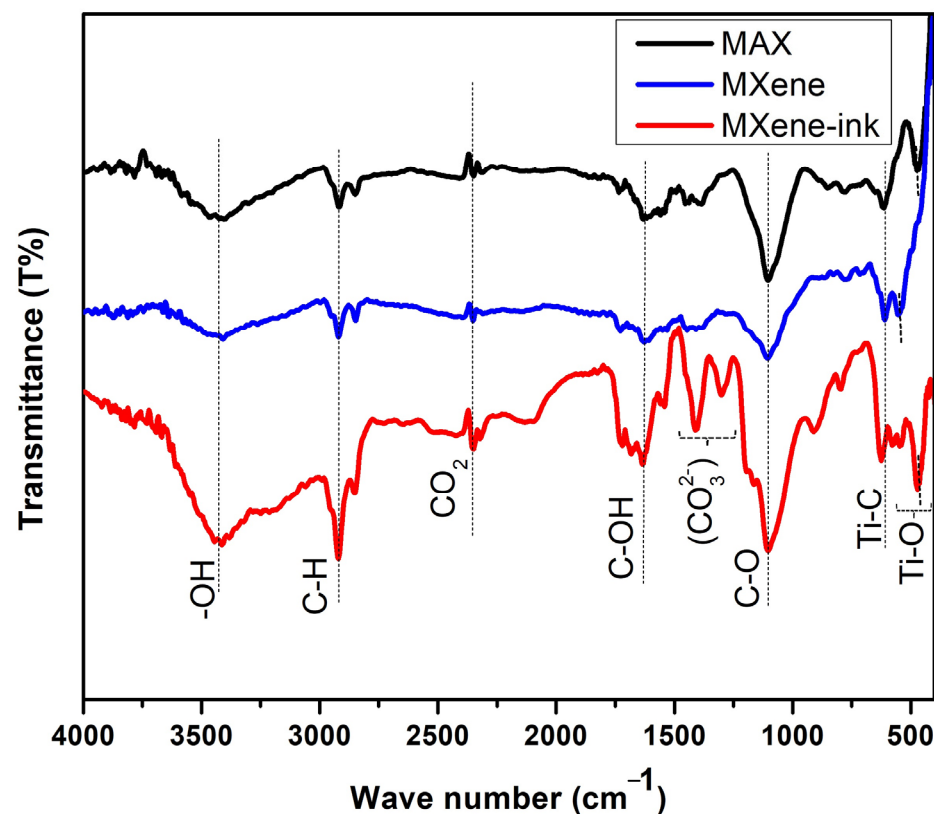


Figure 2. FT-IR spectrum of the pristine MAX (Ti_3AlC_2) after etching/delaminated MXene nanosheet and MXene ink.

3.3. FE-SEM Analysis

The FE-SEM results revealed distinctive features in the microstructures of the MAX (TiAlC_2) bulk material and MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) derivatives, indicating a transformation from the precursor to MXene nanosheets. Figure 3a,b shows a layered structure in the MAX bulk, with a pronounced lamellar arrangement, which is consistent with the inherent stacked bulk structure of the MAX phase. Conversely, Figure 3c,d shows the MXene powder, whose FE-SEM images exhibited a more exfoliated morphology with discernible stacked few-layer nanosheets, indicating successful delamination during the etching process. Furthermore, when transitioning to the MXene ink (Figure 3e,f), the surface micrographs demonstrated enhanced dispersion and uniform few-layer delamination of the MXene nanosheets, highlighting the effectiveness of the ink formulation in promoting a well-coated and interconnected structure. This comparative FE-SEM analysis not only elucidates the morphological evolution from the MAX precursor to MXene but also underscores the favorable characteristics of the MXene ink in achieving a desirable surface architecture for potential applications in energy storage devices and beyond. The electrode surface morphology of the MXene ink after cycling is shown in Figure S1.

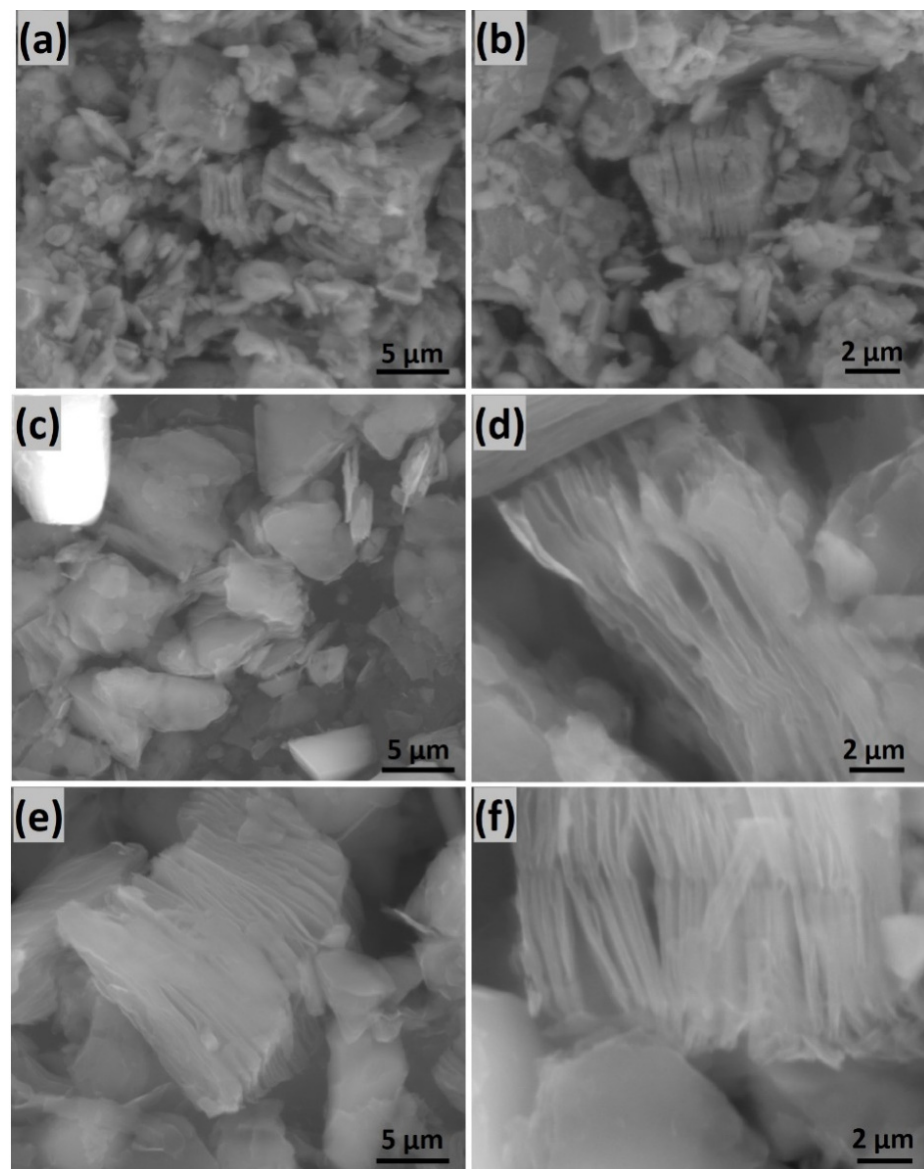


Figure 3. (a,d) FE-SEM surface morphological images of (a,b) MAX phase, (b–d) MXene, and (e,f) MXene-ink.

3.4. FE-TEM Analysis

The FE-TEM results revealed crucial insights into both the structural characteristics of the MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) powder and the surface morphology of the MXene ink composed of few-layer nanosheets (Figure 4a–d). For the MXene powder, the FE-TEM images exhibited distinct layers with well-defined edges, indicative of the typical accordion-like structure inherent to MXene nanosheets, as shown in Figure 4a,b. The powder exhibited a stacked arrangement, confirming successful delamination from the MAX phase precursor. In contrast, Figure 4c,d displays the FE-TEM analysis of the MXene ink surface, exhibiting a unique morphology characterized by the dispersion of few-layer nanosheets. The nanosheets demonstrated a more disordered and interconnected arrangement on the ink surface, highlighting the influence of the ink formulation on the few-layer MXene surface morphology. This comparative discussion underscores the impact of the ink preparation method on the spatial organization of the MXene nanosheets, suggesting that the ink formulation introduces a degree of interconnectivity and disorder compared to the more stacked and layered structures observed in the MXene powder.

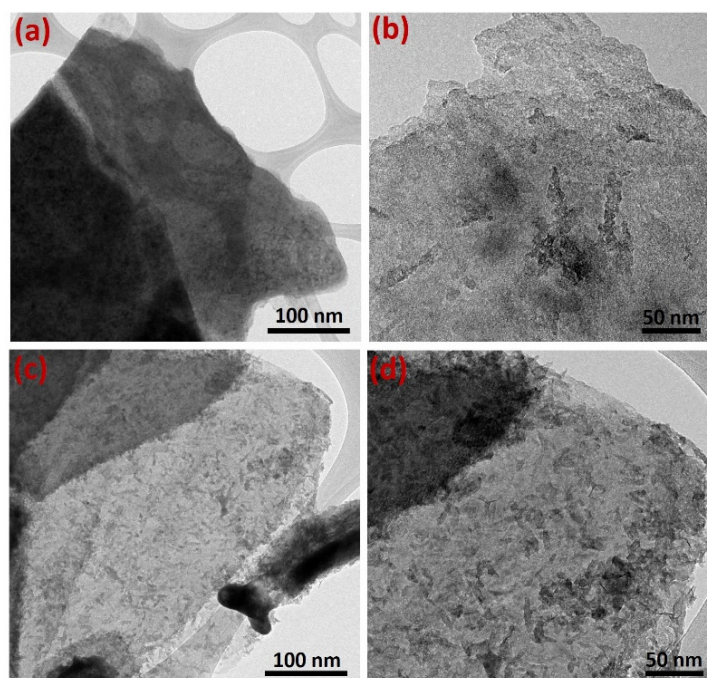


Figure 4. FE-TEM surface morphology image of (a,b) $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and (c,d) MXene ink.

Figure 5a shows HR-TEM surface morphology images with a higher magnification fringe pattern. Through this, researchers can gain insights into the morphology, orientation, and quality of the material under investigation. This transformative process converts the Fourier transform of the original image back to its spatial domain, enabling direct visualization of the spatial arrangement of atoms within the MXene TiC layers' fringe pattern. In Figure 5b, the resulting fringe pattern grayscale image with a threshold in the FFT reveals a d-spacing of 0.23 nm, indicative of lattice interfaces without surface structural defects. However, variations in the d-spacing values of fringes may provide insights into the grain size distribution [48]. Furthermore, discontinuities observed in the fringe patterns could signify interfaces within the material (enlarged original IFFT fringe pattern images provided in Figure S2).

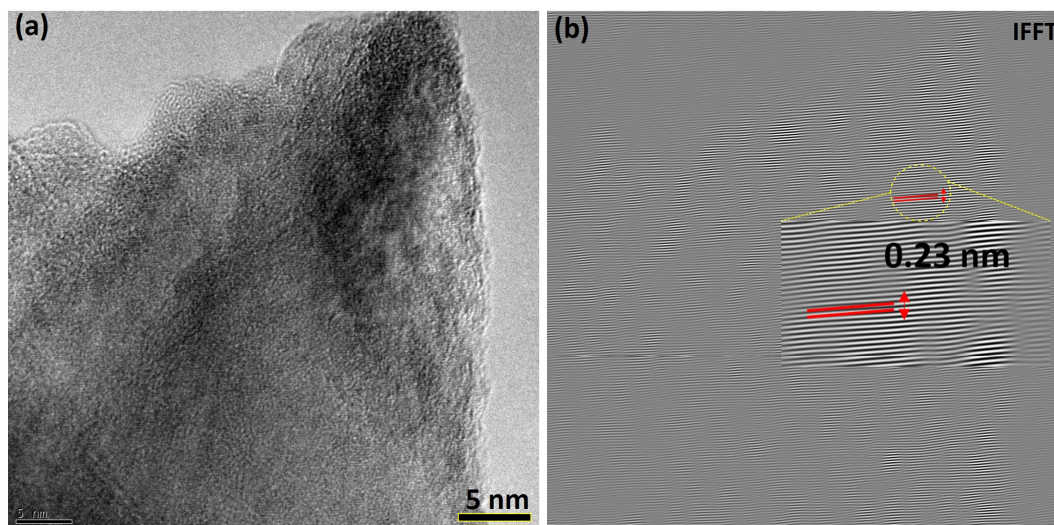


Figure 5. (a) Fringe pattern observed in the HR-TEM surface image, (b) After applying the inverse fast Fourier transform (IFFT), revealing intricate details of the specimen's nanostructure.

3.5. Electrochemical Symmetric Device Performance

The utilization of MXene ink in a two-electrode device configuration for symmetric supercapacitors is a promising approach in the field of energy storage systems. MXenes used in ($\text{Ti}_3\text{C}_2\text{T}_x$ // $\text{Ti}_3\text{C}_2\text{T}_x$) were demonstrated using three different sets of materials: (i) before-etching (MAX phase) Ti_3AlC_2 , (ii) MXene after etching ($\text{Ti}_3\text{C}_2\text{T}_x$), and (iii) delaminated MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) ink. Cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) curves were obtained for the symmetric system over a wide potential range of 0–1.4 V, as shown in Figure 5. Figure 5a,b shows the symmetrical MXene-ink direct coating binder-less device for the electrochemical performance of such a configuration using cyclic voltammetry (CV) at scan rates ranging from 10 to 110 mV/s, electrochemical impedance spectroscopy (EIS), and the analysis of charge–discharge curves with a particular focus on specific capacitance. Figure 5a shows the CV obtained at various scan rates, providing valuable insights into the electrochemical behavior of the MXene ink-based symmetric supercapacitor. The observed rectangular shape of the CV curves suggests the ideal capacitive behavior of the device. As the scan rate increases, the deviation from a perfect rectangular shape becomes more apparent, indicating the presence of some pseudocapacitive contributions. This behavior is often attributed to faradaic reactions occurring at the surface of the MXene electrodes. The electrochemical analysis of the bare Ni-foam substrate is shown in Figure S4.

The electrochemical impedance spectroscopy (EIS) measurements offer a deeper understanding of the charge transfer and ion diffusion processes within the symmetric supercapacitor. The Nyquist plots reveal semicircles at higher frequencies, indicating the presence of charge transfer resistance. The Nyquist plot semicircles represent the charge transfer resistance values of $9.7\ \Omega$ to the smaller semicircle region corresponding to the better electrochemical performance of the electrode–electrolyte interface. The Warburg impedance at lower frequencies signifies ion diffusion within the electrode material. The EIS results confirm the capacitive nature of the MXene ink-based symmetric supercapacitor. Z-fit analysis results for MXene-ink symmetric device for the inset fitted Randle's circuit values are in the Supporting Information (SI) File (Table S1).

The galvanostatic charge–discharge curves (Figure 6c) obtained at different current densities provide critical information about the energy storage capacity of the device. The symmetric behavior of the curves indicates balanced charge storage in both electrodes, which is a characteristic feature of well-designed symmetric supercapacitors. The specific capacitance, calculated from the charge–discharge curves, reflects the ability of the device to store charge per unit mass. The MXene ink-based symmetric supercapacitor demonstrated

commendable specific capacitance values, highlighting its potential for high-performance energy storage applications. The specific capacitance of the MXene ink was investigated across a range of current densities (1–5 A/g) to assess its performance in different charge–discharge curves. The obtained results shed light on the electrochemical behavior of the material and its suitability for various energy storage applications. The observed current density-dependent behavior of the specific capacitance is critical for understanding the practical applicability of MXene ink in various energy storage systems. The MXene ink exhibited remarkable specific capacitance values at lower current densities. The charge–discharge profiles in Figure 6c show that as current density increased to 1, 2, 3, 4, and 5 A/g, a gradual decrease in specific capacitance of 105.75 F/g, 78.42 F/g, 53.10 F/g, 34.85 F/g, 19.43 F/g was calculated from Equation (1). Figure S6 shows that various specific capacitance (C_{sp}) values correspond with the current densities (A/g) of the MXene-ink symmetry device. This reduction can be attributed to the good diffusion of ions within the MXene ink structure at higher charge–discharge rates. The analysis of the charge–discharge curves shows good electrochemical stabilities for delivering and storing electrical energy efficiently. MXenes, a family of 2D transition metal carbides interconnected layer by layer with high electrochemical ionic storage have gained attention owing to their excellent electrical conductivity, large surface area, and remarkable electrochemical properties that increase specific capacitance. Additionally, the results and discussion of the MAX (Ti_3AlC_2) symmetric device’s electrochemical performance are presented in Figure S5.

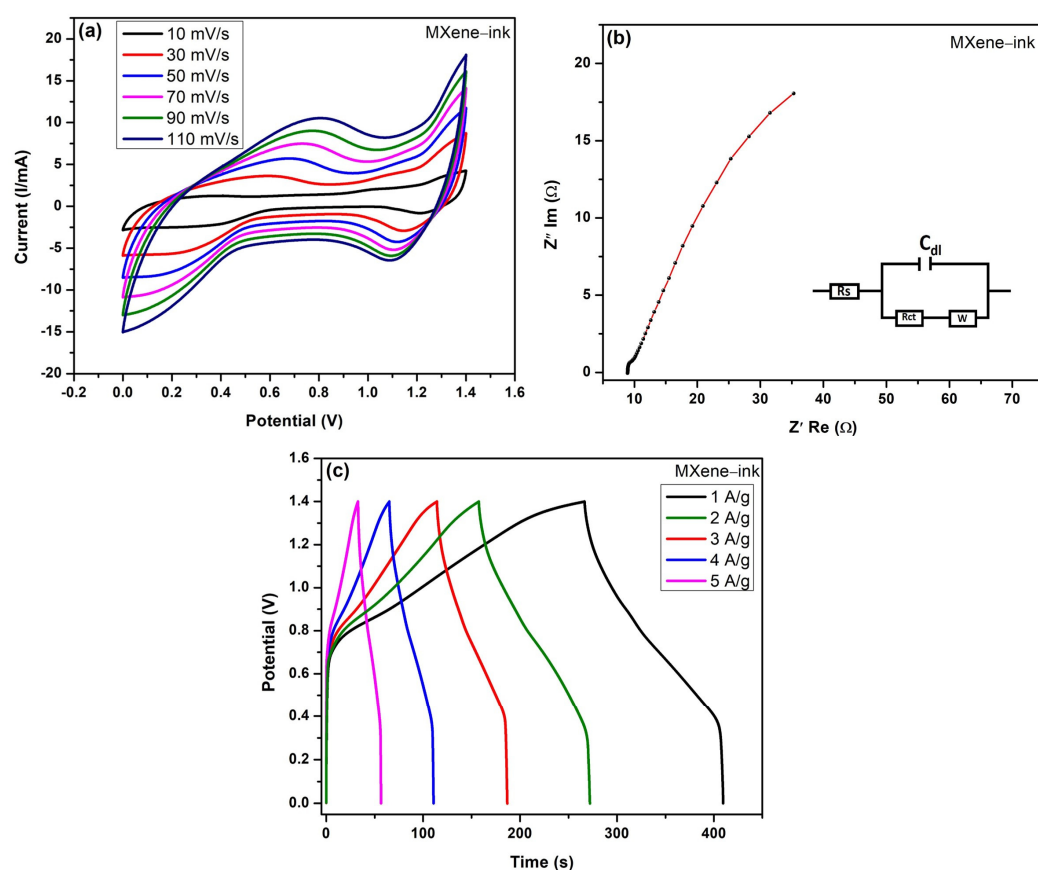


Figure 6. (a) CV, (b) EIS, and (c) GCD curves for the performance of the MXene ink symmetric device at 0–1.4 V, and electrochemical impedance Nyquist plot with Randles circuit (inset).

In a comparative analysis of delaminated MXene powder samples with conductive polymeric binder-based symmetric supercapacitor configurations, the incorporation of a polyvinylidene fluoride (PVDF) binder resulted in a notable enhancement in performance compared with its binder-less counterpart. The combined analysis of the CV, EIS, and GCD demonstrated the promising electrochemical performance of the MXene powder symmetric

supercapacitor. As shown in Figure 7a, CV measurements were performed at various scan rates (10–110 mV/s) to investigate the electrochemical behavior of the MXene-based symmetric supercapacitor. The results revealed that the shape of the CV curves provide insights into the capacitive behavior and potential window within which the supercapacitor operates (0–1.4 V).

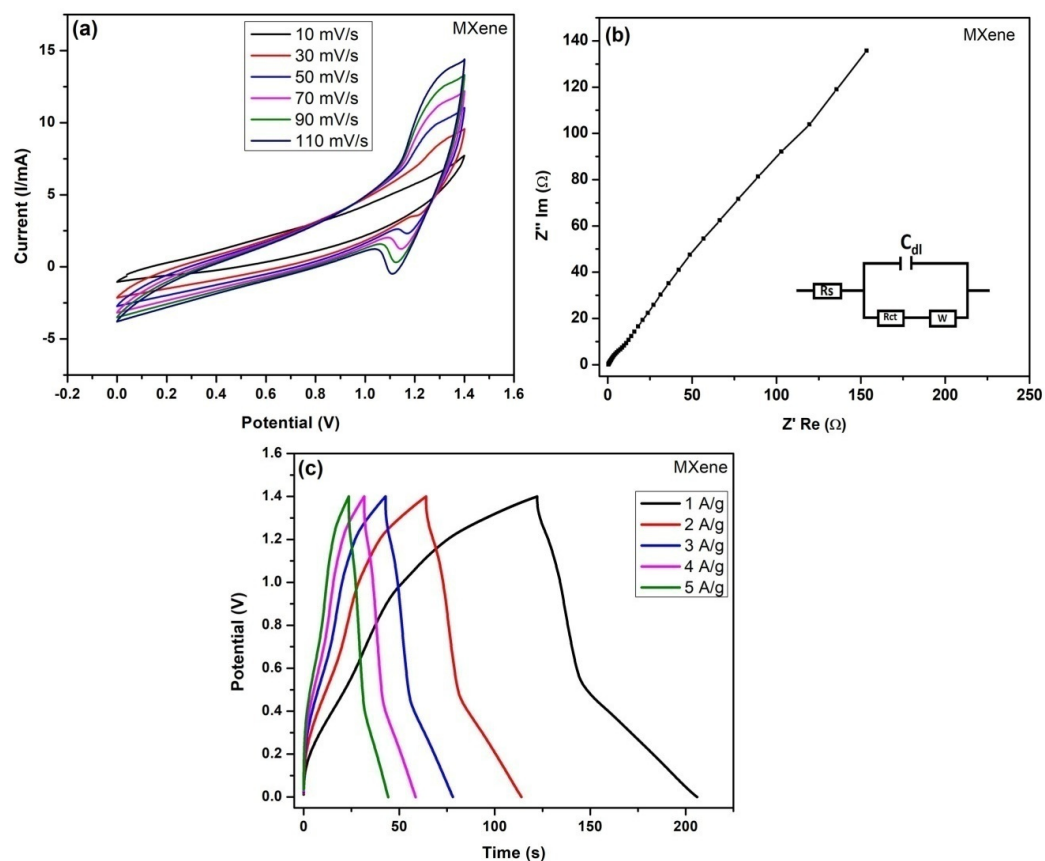


Figure 7. (a) CV, (b) EIS, and (c) GCD curves for the performance of the MXene ink symmetric device at 0–1.4V, and electrochemical impedance Nyquist plot with Randles circuit (inset).

EIS was employed to study the MXene symmetric supercapacitor's impedance characteristics. The Nyquist plots obtained from EIS analysis allowed the determination of the equivalent circuit parameters, providing information about the charge transfer resistance, electrolyte resistance, and double-layer capacitance. The low charge transfer resistance indicated that the EIS Nyquist plot data with charge transfer resistance showed values of 10.7Ω R_{ct} ; hence, compared to MXene ink, it shows a higher R_{ct} value. The supporting information (Table S2) shows the Z-fit analysis with Randles' circuit value results for the MXene device. GCD measurements were performed to assess the specific capacitance of the charge–discharge curves, where current densities of 1, 2, 3, 4, 5 A/g correspond to specific capacitance values of 63.92 F/g, 38.73 F/g, 27.44 F/g, 20.60 F/g, 15.44 F/g, respectively. Figure S6 shows specific capacitance (C_{sp}) versus current densities (A/g) of the MXene device. The MXene/PVDF symmetric device showed lower energy storage performance compared to MXene. The addition of PVDF binder counterparts contributes to less electrode integrity, but the MXene ink enhanced adhesion between MXene nanosheets, thereby facilitating a more robust and stable charge storage environment. This result is reflected in the superior specific capacitance values and enhanced cyclic stability, thus emphasizing the positive impact of binder utilization. The PVDF binder's role in mitigating electrode material detachment and promoting better structural integrity enhances the overall efficiency of the symmetric device, positioning the MXene-PVDF composite as a promising configuration for high-performance supercapacitor applications. These findings underscore

the importance of binder selection in electrode fabrication and highlight the positive impact of PVDF on the electrochemical performance of MXene-based symmetric supercapacitors. Finally, Table S3 compares MXene with a metallic nanocomposite supercapacitor with different electrodes.

Overall, the results of cyclic voltammetry, electrochemical impedance spectroscopy, and charge–discharge curve analysis collectively suggest that the MXene ink is a promising material for the construction of efficient and high-performance symmetric supercapacitors. MXene powders have emerged as promising materials for high-performance symmetric supercapacitor devices. Figure 8 demonstrates exceptional capabilities over 10,000 cycles, showing a capacitance retention (CR%) of 97.72% and coulombic efficiency (CE%) of 98.7%. In addition, the comparative MXene symmetric device exhibited cycling stability, with a capacitance retention (CR%) of 92.22%. This enhanced cycle stability, reflecting the superior number of charge–discharge cycles in binder-less MXene-ink symmetric devices, can be attributed to the direct conduction between the MXene layers and conductive substrate (Ni-foam). This direct conduction facilitates a strong interface, ensuring robust adhesion and stability during cycling. Compared to conventional binder-based electrodes, the absence of binders eliminates the potential interfacial resistance and improves the electron/ion transport pathways. Consequently, the MXene layers maintained their structural integrity layer by layer, leading to an enhanced cycling stability and superior capacitance retention performance in comparative cycling tests. This direct contact between the MXene layers and conductive substrate not only ensures improved electrical conductivity but also promotes mechanical integrity, making binder-less MXene-ink symmetric devices an attractive choice for high-performance energy storage applications.

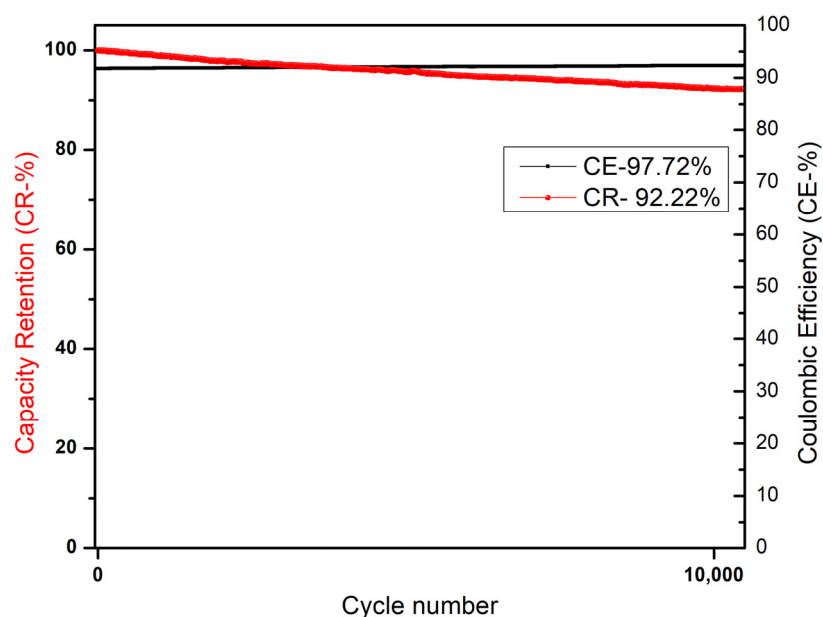


Figure 8. Comparative analysis of MXene and MXene ink symmetric device cycle number versus capacitance retention (CR%) and coulombic efficiency (CE%) performance.

4. Conclusions

We successfully prepared an MXene delaminated powder with a polymeric binder and few-layer MXene sheets to form an ink-based MXene symmetric supercapacitor device. Structural confirmation through XRD and FETEM analyses validated the successful synthesis and structural integrity of the MXene ink and MXene powder. XRD provided detailed crystallographic information, revealing the phase purity and crystalline structure of the material. The FE-TEM images offer insights into the morphology and dispersion of the MXene nanosheets. The integration of the MXene ink and MXene powder into a symmetric supercapacitor, supported by electrochemical analyses, underscores their potential for use

in high-performance energy storage devices. These findings highlight the versatility and potential of MXene-based materials for advanced energy storage technologies. In conclusion, the investigation of the electrochemical behavior of MXene ink revealed a specific capacitance (C_{sp}) of 105.75 F/g at a current density of 1 A/g. Additionally, the electrode cycling stability over 10,000 cycles demonstrated a capacitance retention of 97.72%. These trends highlight the potential of the material for applications with varying direct coatings of binder-less electrodes, paving the way for future practical energy storage applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst14030261/s1>, Figure S1: Surface morphology images of MXene-ink for after 10,000 cycling FE-SEM images; Figure S2: Inverse Fast Fourier Transform (IFFT) fringe images of magnified view (original source from MXene-ink HR-TEM images); Figure S3: (a) XPS survey of MXene-ink sample, de-convoluted XPS spectra of (b) Ti2p, (c) C1s, and (d) O1s; Figure S4: (a) CV of the bare Ni foam (current collector substrate) and (b) comparative bare Ni-foam with the as-prepared MXene-ink electrodes at a fixed scan rate of 100 mV/s in 3 M KOH aqueous electrolyte; Figure S5: (a) CV curves with various scan rate for the MAX (Ti_3AlC_2) symmetric device with different scan rate. (b) EIS Nyquist plot with Randel circuit (inset) and (c) charge-discharge curves current densities in symmetric device; Figure S6: Relationship between specific capacitance (C_{sp}) versus current densities (A/g) for all electrode; Table S1: Z-fit analysis results for MXene-ink symmetric device: relative parameters relative error with stop fit at 1×10^{-3} , and Weight: $|Z|^2$; Table S2: Z-fit analysis for MXene symmetric device; Table S3: Comparison of MXene with metallic nanocomposite supercapacitor different electrode [25,33,49–57].

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