

TWO-DIMENSIONAL ELECTRODE MATERIALS WITH TUNABLE INTERLAYER SPACING AND SURFACE FUNCTIONAL GROUPS FOR EFFICIENT SODIUM-ION STORAGE AND SUPERCAPACITIVE APPLICATIONS

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Abstract

Two-dimensional (2D) electrode materials with tunable interlayer spacing and controllable surface functional groups are promising candidates for sodium-ion batteries and supercapacitors, yet quantitative relationships between interlayer architecture, surface chemistry, ion diffusion kinetics, and electrochemical performance remain unclear. This study investigates three engineered platforms: $\text{Ti}_3\text{C}_2\text{T}_x$ MXene with expanded interlayer spacing, molybdenum disulfide/reduced graphene oxide (MoS_2/rGO) hybrids, and nitrogen-functionalized graphene aerogels. Selective etching, hydrothermal synthesis, chemical intercalation, and surface functionalization were used to regulate interlayer spacing and functional groups. Structure and chemistry were examined by X-ray diffraction, electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy, and electrochemical behavior by cyclic voltammetry, galvanostatic charge-discharge, impedance spectroscopy, and galvanostatic intermittent titration.

Interlayer spacing was varied from 0.62 to 1.28 nm in the MXene series. The optimized expanded MXene delivered 285 mAh g^{-1} at 0.1 A g^{-1} and retained 91.4% of its capacity after 1,500 cycles, with a capacitive contribution of 78% at 100 mV s^{-1} . The optimized MoS_2/rGO hybrid exhibited 412 F g^{-1} at 1 A g^{-1} , and the nitrogen-functionalized graphene aerogel delivered 28.5 Wh kg^{-1} at 850 W kg^{-1} in a symmetric supercapacitor. Sodium-ion diffusion improved markedly with increasing interlayer spacing, accompanied by reduced charge-transfer resistance. These findings establish a structure-property-performance framework for optimizing 2D electrode architectures for sodium-ion storage and supercapacitive energy storage.

1. INTRODUCTION

The accelerating global transition to renewable energy sources has created an urgent technological imperative for electrochemical energy storage systems capable of delivering high energy density, rapid charge-discharge capability, and thousands of charge cycles without significant performance degradation [1]. Lithium-ion batteries have dominated portable and grid-scale storage markets for three decades, but their reliance on lithium resources that are geographically concentrated, increasingly expensive, and insufficient for projected global storage deployment scales has intensified the search for alternative chemistries built on more abundant and equitably distributed elements [2]. Sodium-ion batteries have emerged as the most technically mature alternative, leveraging the essentially unlimited geological abundance of sodium, its similar electrochemical behavior to lithium in intercalation-based storage mechanisms, and the compatibility of sodium-ion cell designs with existing lithium-ion manufacturing infrastructure [3]. The principal challenge impeding the wider commercialization of sodium-ion batteries is the identification of anode electrode materials capable of reversibly accommodating sodium ions, which carry a significantly larger ionic radius than lithium ions at approximately 1.02 angstroms compared to 0.76 angstroms, through repeated intercalation and deintercalation cycles without structural degradation [4]. This size mismatch translates into substantially higher mechanical stresses within electrode host lattices, faster capacity fade, and more demanding requirements for interlayer spacing and structural flexibility compared to lithium-ion analogues.

Two-dimensional materials have attracted considerable attention as electrode candidates for sodium-ion storage precisely because their layered architectures provide the structural flexibility, accessible interlayer galleries, and chemical tunability needed to accommodate large sodium ions while maintaining structural integrity across extended cycling [5], [6]. The discovery of MXenes, a family of two-dimensional transition metal carbides, nitrides, and carbonitrides derived by

selective etching of MAX phase ceramic precursors, opened a new dimension in electrode materials science by combining metallic conductivity exceeding ten thousand siemens per centimeter with inherently hydrophilic surfaces bearing rich functional group terminations and tunable interlayer chemistry [7]. $\text{Ti}_3\text{C}_2\text{T}_x$, the most extensively studied MXene composition, has demonstrated theoretical capacities of approximately 447.8 milliampere-hours per gram for sodium-ion storage and has shown that sodium-ion intercalation into its interlayer galleries proceeds with low diffusion barriers when the interlayer spacing is adequately expanded beyond the native value of approximately 0.62 nanometers [4]. Restacking of MXene nanosheets during film preparation remains the primary technical barrier to realizing this theoretical potential, as van der Waals interactions between adjacent sheets collapse interlayer galleries and block ion diffusion pathways that are essential for high-rate performance [8]. Intercalation of molecular spacers, inorganic nanoparticles, and carbon-based species between MXene layers has been demonstrated as an effective strategy for preserving expanded interlayer configurations during electrode fabrication and electrochemical cycling [9].

Molybdenum disulfide occupies a complementary position in the two-dimensional electrode materials landscape, offering a layered hexagonal structure with a native interlayer spacing of approximately 0.615 nanometers that can be systematically expanded through intercalation engineering, and a theoretical specific capacity exceeding 670 milliampere-hours per gram for sodium-ion storage through a combination of intercalation and conversion reaction mechanisms [10], [11]. The two-dimensional nature of MoS_2 exposes large numbers of edge sites and basal plane defects that function as electrochemically active sites for both sodium-ion intercalation and pseudocapacitive surface storage, and the transition between the semiconducting hexagonal phase and the metallic monoclinic phase during sodiation provides additional electronic conductivity enhancement that improves rate

capability [12]. Integration of MoS₂ nanosheets with reduced graphene oxide into hybrid nanoarchitectures addresses the intrinsically low electrical conductivity and restacking susceptibility of isolated MoS₂ flakes by providing a percolating conductive network that simultaneously maintains interlayer separation and shortens electron transport pathways to current collectors [13]. The MoS₂/rGO hybrid architecture further benefits from the large specific surface area of graphene supporting layers, which provides additional double-layer capacitance contribution that supplements the Faradaic intercalation and conversion capacity of the MoS₂ component [14]. Nitrogen-functionalized graphene aerogels

represent a third complementary electrode platform, offering highly porous three-dimensional architectures with large accessible surface areas, abundant nitrogen functional groups that contribute pseudocapacitive redox reactions in aqueous electrolyte, and defect-enriched graphene basal planes that facilitate sodium-ion accommodation through adsorption and intercalation mechanisms [15]. Figure 1 presents the conceptual framework connecting two-dimensional material structural features to their electrochemical performance characteristics in sodium-ion storage and supercapacitive applications.

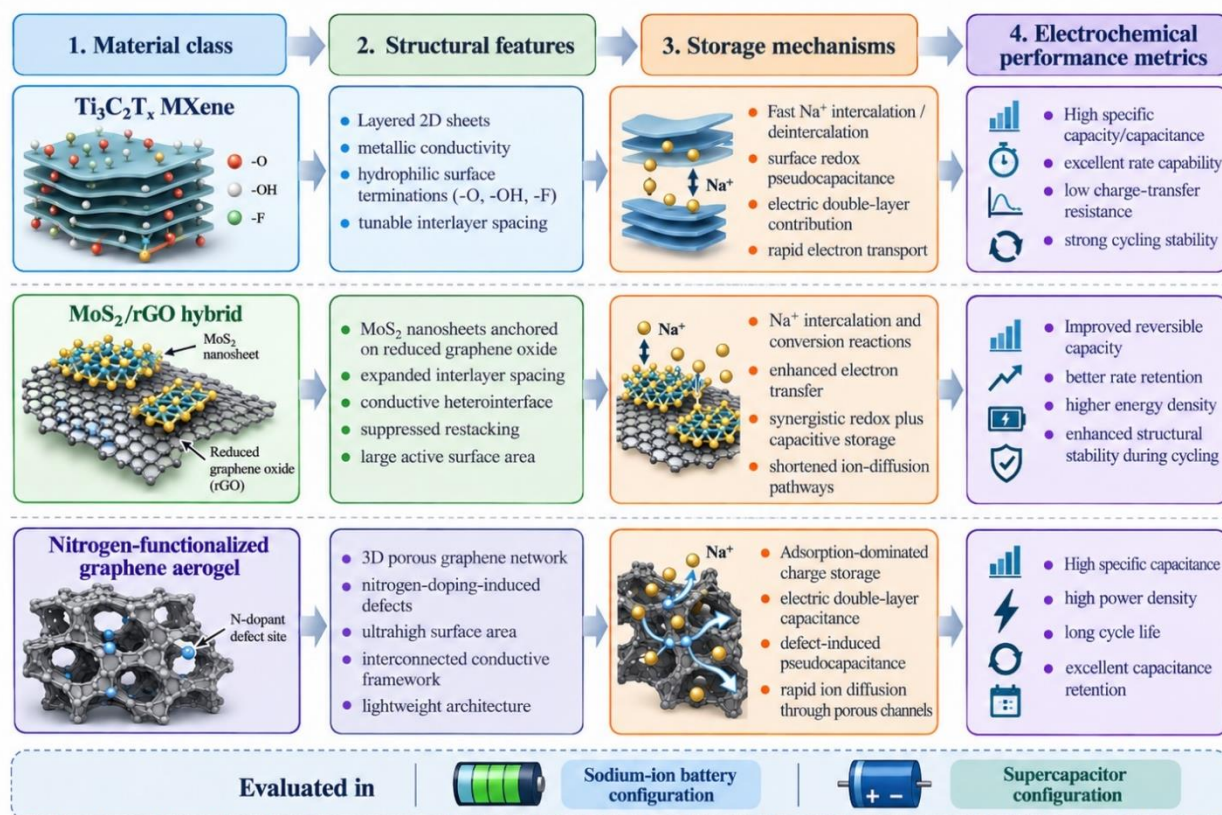


Fig. 1. Two-dimensional electrode design hierarchy connecting material class (Ti₃C₂T_x MXene, MoS₂/rGO hybrid, and nitrogen-functionalized graphene aerogel) through structural features and storage mechanisms to key electrochemical performance metrics in sodium-ion battery and supercapacitor configurations.

The electrochemical performance of two-dimensional electrode materials is governed not

only by their intrinsic crystal chemistry but critically by the specific configuration of surface

functional groups that terminate their exposed surfaces and modulate electrolyte accessibility, ion-desolvation energetics, and interfacial charge-transfer kinetics [16]. In MXenes, the type and density of surface terminations, including fluorine, oxygen, and hydroxyl groups inherited from the HF or LiF-HCl etching process, exert profound influence on both electronic conductivity and sodium-ion storage capacity [17]. Oxygen and hydroxyl terminations introduce pseudocapacitive redox sites that contribute significantly to measured capacitance in aqueous media, while fluorine terminations, though electrochemically inert, may impede ion diffusion by increasing electrostatic barriers at the electrode-electrolyte interface [2], [18]. In MoS₂ and graphene-based electrodes, nitrogen, oxygen, and sulfur functional groups introduced through doping, oxidation, or surface functionalization strategies serve analogous roles in amplifying pseudocapacitive contributions and improving electrolyte wettability [15]. Gentile et al. conducted in situ synchrotron analysis of Ti₃C₂T_x sodiation and established that the electrode reaction involves both surface capacitive storage on termination sites and interlayer ionic intercalation, with their relative contributions depending critically on the interlayer spacing and termination composition of the specific MXene preparation employed [17]. Figure 1 also illustrates the three-tier hierarchy connecting synthesis conditions, material structural parameters, and electrochemical performance outcomes that motivates the systematic experimental program presented in this paper.

The growing demand for efficient sodium-ion batteries and supercapacitors has accelerated research into advanced electrode materials capable of delivering high energy density, rapid ion transport, and long-term electrochemical stability. In this context, structural characterization and material-property analysis have become essential for understanding the influence of nanoscale architecture on functional performance. Rehman et al. [19] investigated the structural, thermal, and optical properties of Fe-doped NiO nanoparticles, highlighting the significance of material

characterization, while Usman et al. [20], Nadeem et al. [21], and Majeed et al. [22] examined photon-phonon interactions and non-Hermitian behavior in ion-doped microcrystals, providing complementary insights into complex material interactions. Furthermore, Majeed et al. [23] explored mathematical optimization techniques for high-dimensional data analysis, offering a computational perspective relevant to investigating complex structure-property relationships. The growing integration of renewable energy further reinforces the need for reliable energy-storage technologies, as demonstrated by Ahmad et al. [24], [25] through investigations of sustainable wind energy integration and voltage stability in wind-assisted microgrids, while Rafique et al. [26] examined grid-connected wind turbine systems. Although these studies address different materials and energy-system applications, they collectively highlight the importance of systematic material analysis, performance optimization, and reliable renewable-energy infrastructure. These considerations motivate the present investigation of Ti₃C₂T_x MXene, MoS₂/rGO hybrids, and nitrogen-functionalized graphene aerogels, focusing on the effects of interlayer spacing and surface functional groups on sodium-ion diffusion, charge-storage mechanisms, and electrochemical performance.

This investigation addresses three interrelated research questions that collectively define the design space for high-performance two-dimensional sodium-ion and supercapacitive electrodes. First, how does systematic variation of interlayer spacing through chemical intercalation modify the sodium-ion diffusion coefficient, capacity, and rate capability of Ti₃C₂T_x MXene electrodes? Second, what structural architecture in MoS₂/rGO hybrids maximizes the synergistic contribution of pseudocapacitive MoS₂ and conductive graphene components to achievable specific capacitance and energy density? Third, how does nitrogen functionalization type and density in graphene aerogels influence the balance between electric double-layer and pseudocapacitive charge storage mechanisms in

aqueous supercapacitor configurations? The experimental program that addresses these questions is presented and discussed in the sections that follow.

2. Literature Review

The two-dimensional electrode materials field has undergone extraordinary expansion since 2022, with an exponentially growing literature on MXene, transition metal dichalcogenide, and functionalized graphene electrode systems for

sodium-ion batteries and supercapacitors. Figure 2 presents an integrated literature landscape covering MXene synthesis, transition metal dichalcogenides, graphene-based electrode systems, surface functionalization strategies, and supercapacitor device engineering. The framework highlights key structure–property relationships, ion transport mechanisms, electrochemical performance considerations, and three critical knowledge gaps identified in the literature that motivate the present investigation.

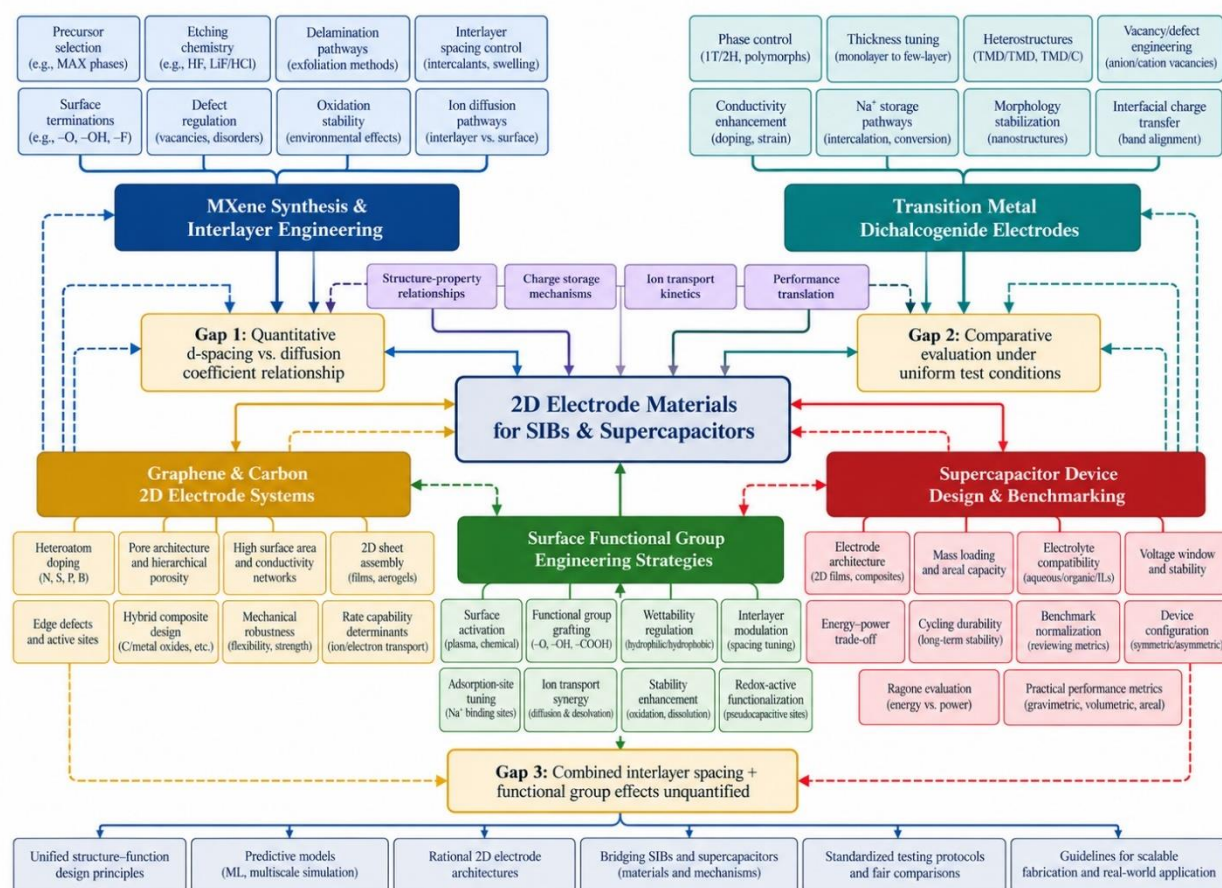


Fig. 2. Advanced literature landscape of two-dimensional electrode materials for sodium-ion batteries and supercapacitors, highlighting material engineering strategies, electrochemical performance mechanisms, critical knowledge gaps, and future research directions.

2.1 MXene Electrode Engineering for Sodium-Ion and Supercapacitive Applications

MXene materials, first reported in 2011 and now encompassing over thirty compositional variants, have attracted sustained research attention for

electrochemical energy storage owing to their unique combination of metallic electrical conductivity, inherently hydrophilic surfaces, and mechanically flexible two-dimensional architecture that accommodates ion intercalation

without catastrophic structural failure [7]. The charge storage mechanism in MXenes involves at least three simultaneous contributions: electric double-layer capacitance at the electrode-electrolyte interface, surface pseudo capacitance through reversible redox reactions at surface termination sites, and Faradaic intercalation of cations into interlayer galleries [27], [6]. The relative magnitude of each contribution is critically sensitive to interlayer spacing, with expanded galleries strongly favoring Faradaic intercalation by lowering the activation energy for cation entry and diffusion through the layered structure [8], [28]. Liang et al. reviewed the impact of interlayer spacing on MXene supercapacitor electrodes, establishing that d-spacing expansion from the native 0.62 nanometers to values approaching 1.2 nanometers consistently produces two- to threefold improvements in specific capacitance through enhanced ion accessibility and increased density of intercalation sites [8]. The review identified three primary strategies for achieving sustained interlayer expansion: intercalation of small organic molecules such as dimethyl sulfoxide and urea, insertion of inorganic pillaring species including metal oxide nanoparticles and hydroxide nanosheets, and covalent functionalization of surface termination groups with bulky organic tethers [8].

Gentile et al. provided the most mechanistically detailed investigation of $\text{Ti}_3\text{C}_2\text{T}_x$ sodium-ion storage to date, employing operando synchrotron X-ray diffraction and X-ray absorption spectroscopy to track structural and electronic changes during sodiation and desodiation in real time [17]. Their results demonstrated that sodium-ion intercalation proceeds through a continuous solid-solution mechanism without distinct phase transitions, with the interlayer spacing expanding reversibly by approximately 0.12 nanometers at full sodium loading and returning to close to its initial value upon desodiation, confirming the structural reversibility essential for extended cycling [17]. Li et al. fabricated CoSn-LDH microsphere-decorated Ti_3C_2 MXene composites in which the LDH microspheres were

incorporated into the MXene interlayers through electrostatic adsorption, simultaneously preventing MXene restacking and introducing abundant electroactive sites through the multiple oxidation states of cobalt and tin cations [9]. The resulting electrode delivered excellent rate performance with capacity retention of 78 percent when the current density was increased from 0.1 to 5 amperes per gram, demonstrating that interlayer pillaring with electroactive species can simultaneously address the restacking problem and enhance intrinsic electrode capacity [9]. Wang et al. reported that fullerene intercalation into $\text{Ti}_3\text{C}_2\text{T}_x$ interlayers using buckminsterfullerene as a carbon-based pillar produced an electrode with superior long-term cycling stability, retaining 92 percent of initial capacity after 5000 cycles at one ampere per gram for sodium-ion storage, because the rigid spherical shape of fullerene provides mechanically robust interlayer support that resists compression under the mechanical stresses generated during repeated sodiation-desodiation [29].

Zheng et al. conducted a comprehensive review of functional MXene materials for next-generation rechargeable batteries, documenting that the surface chemistry of MXenes plays a role equal in importance to interlayer structure in determining electrochemical performance [2]. Their analysis established that oxygen and hydroxyl terminations provide redox-active sites for pseudocapacitive reactions in both aqueous and non-aqueous electrolytes, that fluorine terminations should ideally be minimized through optimized synthesis conditions to avoid electrostatic ion-diffusion barriers, and that the introduction of additional functional groups through post-synthesis modification can dramatically enhance the pseudocapacitive contribution beyond what native MXene terminations provide [2]. Gao et al. demonstrated that a red phosphorus and Ti_3C_2 MXene nanocomposite electrode exploits the high theoretical capacity of phosphorus conversion anodes while leveraging MXene's conductivity as a conductive scaffold, achieving a specific capacity of 312 milliampere-hours per gram at 0.1 amperes per gram with excellent rate capability enabled by

the MXene matrix maintaining electronic percolation during the large volume changes associated with phosphorus sodiation [30].

2.2 Molybdenum Disulfide and Transition Metal Dichalcogenide Electrodes

Molybdenum disulfide has established itself as one of the most comprehensively studied two-dimensional electrode materials for sodium-ion storage, owing to a layered hexagonal structure amenable to both intercalation and conversion mechanisms that collectively provide substantially higher theoretical capacity than graphitic and hard carbon anodes [10]. The sodium-ion storage mechanism in MoS₂ involves initial intercalation of sodium ions into the interlayer galleries at higher voltages, followed by a conversion reaction below approximately 0.4 volts versus sodium that produces metallic molybdenum nanoparticles embedded in a sodium sulfide matrix; upon desodiation, partial reversibility of the conversion product enables sustained capacity delivery across hundreds of cycles when the electrode architecture is appropriately stabilized [5]. Yang et al. fabricated an integrated 3D MoS₂/graphene oxide composite through a layer-by-layer assembly route using amino-functionalized silica nanospheres as structural templates, producing a macroporous architecture with rich ion diffusion channels that delivered 277 milliampere-hours per gram at a high current density of 5000 milliamperes per gram with stable performance over 3000 cycles, demonstrating that three-dimensional macroporous design substantially improves rate capability by shortening diffusion path lengths and maintaining electrolyte access to active surfaces throughout cycling [13]. The kinetics analysis performed by the same group revealed that capacitive contribution dominated the measured current at moderate and high scan rates, with the b-value approach yielding exponents close to unity for both cathodic and anodic peak currents, consistent with surface-controlled charge storage mechanisms that are intrinsically faster and less structurally disruptive than diffusion-limited Faradaic reactions [13].

The interlayer expansion strategy has proven particularly effective for MoS₂ sodium-ion electrodes. Jing et al. introduced carbon heterolayers between MoS₂ nanosheets while simultaneously bonding the resulting structure to graphene supports, creating a hierarchical architecture with expanded interlayer spacing of approximately 0.94 nanometers and dramatically enhanced sodium-ion diffusion coefficients compared to unmodified MoS₂ [5]. The carbon intercalation layer prevented MoS₂ restacking while simultaneously providing additional electronic conductive pathways between MoS₂ layers and the graphene substrate, resulting in excellent performance in both sodium-ion and potassium-ion battery configurations [5]. Zhao et al. reported a VS₂/Ti₃C₂T_x MXene hybrid that exploits intercalation pseudo capacitance mechanisms for all-climate sodium-ion battery operation, demonstrating that the combination of pseudocapacitive charge storage in VS₂ with the metallic conductivity and mechanical flexibility of MXene support produces electrodes capable of delivering stable performance across a wide temperature range from minus forty to plus sixty degrees Celsius [12]. This all-climate performance was attributed to the pseudocapacitive mechanism's reduced dependence on thermally activated ion diffusion compared to Faradaic intercalation reactions, confirming that electrode design strategies that amplify pseudocapacitive contributions provide practical advantages beyond laboratory electrochemical metrics.

2.3 Functionalized Graphene and Carbon-Based 2D Electrode Systems

Nitrogen-doped graphene and graphene aerogel electrodes constitute an important complementary category in the two-dimensional electrode landscape, offering scalable production from abundant precursors, chemical tunability through nitrogen doping and oxygen functionalization, and unique three-dimensional porosity in the aerogel morphology that provides combined surface area and electrolyte penetration depth advantages unavailable in flat film electrode configurations [15]. Elsehsah et al. reviewed

nitrogen-doped graphene aerogels as supercapacitor electrodes, documenting that nitrogen functional groups including pyridinic, pyrrolic, and graphitic nitrogen species each contribute distinct electrochemical activities, with pyridinic nitrogen providing the highest density of sodium-ion adsorption sites and graphitic nitrogen contributing to enhanced electronic conductivity through modification of the graphene band structure [15]. Orzech et al. investigated reduced graphene oxide as a cathode material for all-carbon sodium-ion full cells, establishing through detailed analysis of storage mechanism dependence on morphological and chemical structure that the combination of surface capacitance and Faradaic reactions in rGO cathodes provides a specific capacity competitive with transition metal oxide cathodes while offering substantially superior cycle stability exceeding two thousand cycles [31].

2.4 Summary of Performance Benchmarks and Identified Gaps

Table 1 compiles representative electrochemical performance data from recent literature across the

three major two-dimensional electrode categories relevant to this study. Three gaps in the existing literature motivate the experimental program presented in this paper. First, the relationship between precise interlayer spacing values and sodium-ion diffusion coefficients, which are commonly determined by galvanostatic intermittent titration [32], has not been systematically quantified across a continuous range within a single material system, limiting the establishment of quantitative design rules for interlayer engineering. Second, comparative evaluation of the three major two-dimensional electrode platforms under identical testing conditions is essentially absent from the literature, precluding rigorous performance benchmarking. Third, the simultaneous contribution of interlayer spacing and surface functional group type to both sodium-ion battery capacity and supercapacitive charge storage has not been evaluated within a unified experimental framework that would allow their independent and interactive effects to be disentangled.

Table 1: Representative Electrochemical Performance Data for 2D Electrode Materials

Study	Material System	Application	Key Metric	Notable Achievement
Kadam et al. [1], 2024	Ti ₃ C ₂ T _x MXene composites	Supercapacitor	Capacitance, cycle life	Comprehensive review: 930.8 F/g, 50,000 cycles
Li et al. [9], 2024	CoSn-LDH@Ti ₃ C ₂ MXene	Sodium-ion battery	Rate capability, Capacity	78% capacity at 5 A/g vs. 0.1 A/g
Gentile et al. [17], 2025	Ti ₃ C ₂ T _x MXene	Sodium-ion battery	In situ mechanism	Solid-solution Na ⁺ intercalation confirmed operando
Wang et al. [29], 2024	Fullerene@Ti ₃ C ₂ T _x MXene	Sodium-ion battery	Cycle stability	92% retention after 5000 cycles at 1 A/g
Yang et al. [13], 2024	3D MoS ₂ /GO composite	Sodium-ion battery	Capacity at high rate	277 mAh/g at 5,000 mA/g, 3000 cycles
Zhao et al. [12], 2023	VS ₂ /Ti ₃ C ₂ T _x MXene hybrid	Sodium-ion battery	Temperature range	All-climate performance - 40 to +60 C
Szkoda et al. [14], 2024	MoS ₂ -carbon composites	SIB & supercapacitor	Capacitance	Impact of synthesis on electrochemical performance

Study	Material System	Application	Key Metric	Notable Achievement
Orzech et al. [31], 2024	Reduced graphene oxide	Sodium-ion battery (cathode)	Cycle life, capacity	Combined surface capacitance + Faradaic storage
Liang et al. [8], 2023	MXene interlayer review	Supercapacitor	Capacitance enhancement	2-3x improvement with d-spacing >0.94 nm
Zheng et al. [2], 2022	Functional MXene overview	Batteries & supercapacitors	Surface chemistry impact	Termination type controls pseudocapacitive sites

3. Research Methodology

The research framework is structured as a systematic comparative experimental program that develops, characterizes, and electrochemically evaluates three two-dimensional electrode platforms under consistent synthesis, processing, and testing conditions. This consistency is intentional and constitutes a key methodological strength: by maintaining identical electrolyte composition, electrode preparation protocols, and electrochemical testing parameters across all three electrode systems, the investigation enables direct performance comparisons that the broader literature, where each material system is typically evaluated under conditions optimized for that specific material, cannot provide. To systematically investigate the structural

characteristics, ion transport behavior, and electrochemical performance of two-dimensional electrode materials, Figure 3 illustrates the proposed seven-stage comparative research framework. The framework integrates precursor selection, controlled synthesis, interlayer and surface engineering, structural characterization, electrode fabrication, electrochemical testing, and performance benchmarking across five MXene interlayer-spacing variants, three MoS₂/rGO compositions, and two nitrogen-doping levels of graphene aerogel. This integrated approach establishes a systematic pathway for evaluating structure-property relationships, comparing charge-storage mechanisms, and developing optimized electrode design strategies for sodium-ion batteries and supercapacitors.

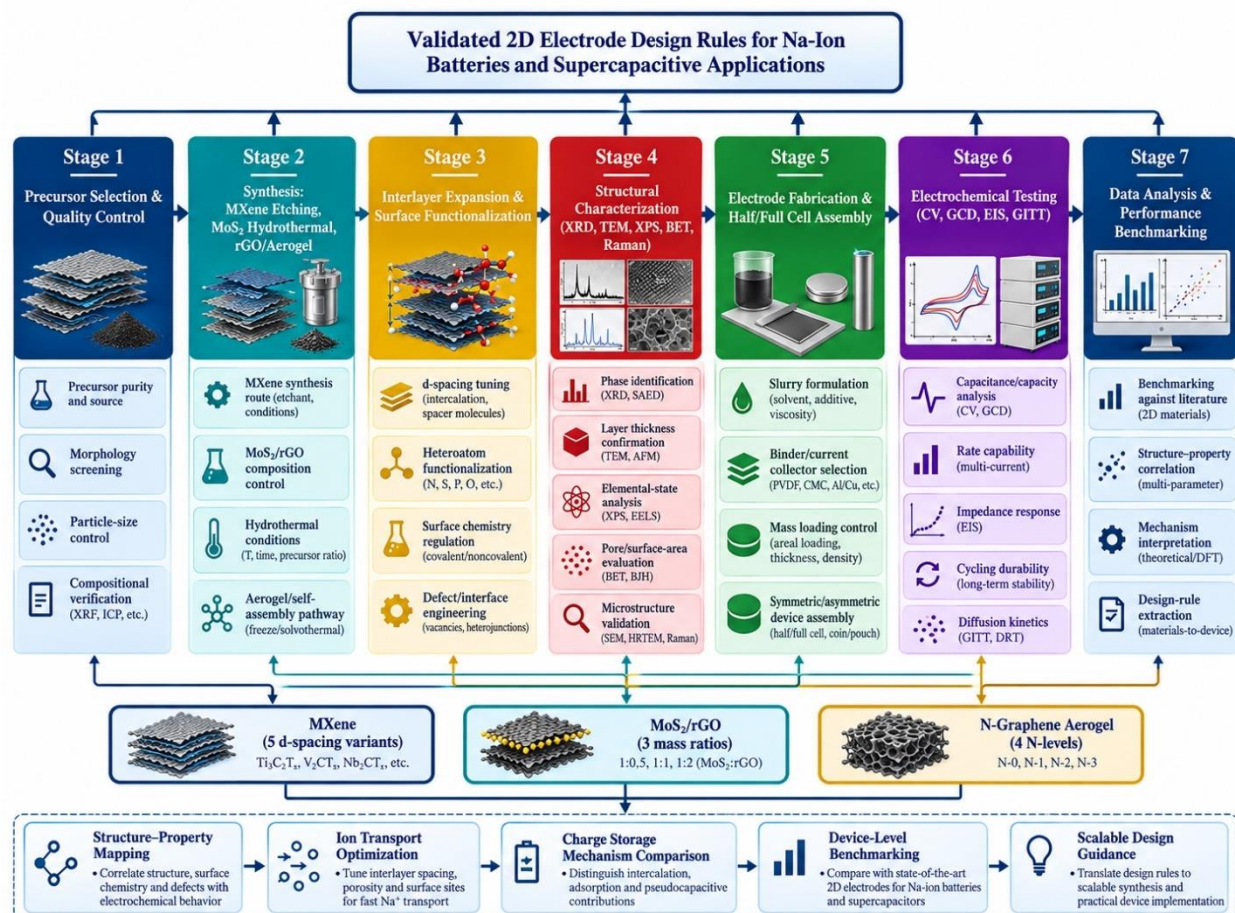


Fig. 3. Advanced seven-stage comparative research framework integrating precursor selection, material synthesis, interlayer engineering, structural characterization, electrode fabrication, electrochemical evaluation, and performance benchmarking of MXene, MoS₂/rGO, and nitrogen-doped graphene aerogel for sodium-ion batteries and supercapacitors.

Table 2 summarizes the material variants, synthesis methods, interlayer spacing characteristics, surface functionalization features, and electrolyte systems employed in the investigation. The table highlights the controlled structural modifications of Ti₃C₂T_x MXene,

compositional variations of MoS₂/rGO hybrids, and nitrogen-doping levels of graphene aerogels, providing a foundation for evaluating their structure-property relationships, ion transport behavior, and electrochemical performance in sodium-ion batteries and supercapacitors.

Table 2: Electrode Material Variants, Synthesis Conditions, and Electrolyte Systems

Electrode Material	Synthesis Method	Interlayer d-spacing	N Content / Key Feature	Electrolyte
Ti ₃ C ₂ T _x MXene (native)	LiF-HCl etching of Ti ₃ AlC ₂ MAX	0.62 nm	-OH, -O, -F terminations	1M NaClO ₄ in EC:DEC (1:1)

Electrode Material	Synthesis Method	Interlayer d-spacing	N Content / Key Feature	Electrolyte
Ti ₃ C ₂ T _x MXene (urea)	Urea intercalation at 0.5-2.0 M	0.78-1.28 nm	Expanded by N-containing pillar	1M NaClO ₄ in EC:DEC (1:1)
MoS ₂ /rGO (1:1)	Hydrothermal + electrostatic assembly	0.62-0.68 nm	rGO conductive matrix	1M NaClO ₄ in EC:DEC (1:1)
MoS ₂ /rGO (2:1 optimal)	Hydrothermal + electrostatic assembly	0.68 nm	Balanced capacity/conductivity	1M NaClO ₄ / 1M KOH
MoS ₂ /rGO (3:1)	Hydrothermal + electrostatic assembly	0.68 nm	High MoS ₂ content	1M NaClO ₄ in EC:DEC (1:1)
N-Graphene Aerogel (low N)	GO + urea hydrothermal (5:1)	0.38 nm	3.2 at% N (mainly graphitic)	1M KOH aqueous
N-Graphene Aerogel (high N)	GO + urea hydrothermal (40:1)	0.38 nm	8.4 at% N (pyridinic dominant)	1M KOH aqueous

3.1 Synthesis of Ti₃C₂T_x MXene with Controlled Interlayer Expansion

Ti₃C₂T_x MXene was synthesized from Ti₃AlC₂ MAX phase powder through selective aluminum layer etching using a lithium fluoride and hydrochloric acid mixture at room temperature for 24 hours, chosen over hydrofluoric acid etching to avoid excessive fluorine terminations and achieve a more controllable surface chemistry. The resulting multilayer MXene sediment was washed repeatedly to near-neutral pH, dispersed in re-aerated water through gentle probe sonication, and delaminated by hand-shaking to produce a stable colloidal suspension of Ti₃C₂T_x nanosheets. Interlayer expansion was achieved through systematic intercalation of urea molecules at four concentrations of 0.5, 1.0, 1.5, and 2.0 M across separate synthesis batches. The intercalated MXene dispersions were vacuum-filtered through cellulose membranes to form free-standing film electrodes and dried under inert atmosphere to prevent oxidation of the titanium carbide layers. The interlayer d-spacing of each prepared film was measured by X-ray diffraction and confirmed by transmission electron microscopy. Five distinct MXene electrode variants were produced spanning d-spacings from 0.62 to 1.28 nanometers, providing a systematic data set for correlating

interlayer geometry with electrochemical performance.

3.2 Synthesis of MoS₂/rGO Hybrid Electrodes

Graphene oxide was prepared from natural graphite flakes by the modified Hummers method, producing stable aqueous dispersions of single- and few-layer oxide nanosheets with surface oxygen content confirmed by X-ray photoelectron spectroscopy. Molybdenum disulfide was synthesized hydrothermally from sodium molybdate dihydrate and thiourea precursors at 200 degrees Celsius for 24 hours, producing layered flower-like MoS₂ nanostructures with interlayer spacing of approximately 0.62 nanometers. The MoS₂/rGO hybrid was assembled through a two-step process: first, electrostatic co-assembly of negatively charged graphene oxide nanosheets with positively charged acetyl trimethylammonium bromide-functionalized MoS₂ units, then hydrothermal reduction of graphene oxide to reduced graphene oxide at 180 degrees Celsius for 12 hours with simultaneous in situ expansion of MoS₂ interlayer spacing through solvothermal intercalation. Three hybrid compositions were prepared at MoS₂-to-rGO mass ratios of 1:1, 2:1, and 3:1 to optimize the balance between high-capacity MoS₂ Faradaic contribution and conductive graphene network

formation. The hybrid powders were mixed with polyvinylidene fluoride binder and carbon black in a mass ratio of 80:10:10, slurry-cast onto copper foil current collectors, and dried at 80 degrees Celsius under vacuum.

3.3 Synthesis of Nitrogen-Functionalized Graphene Aerogel

Nitrogen-functionalized graphene aerogel was prepared through a single-step hydrothermal reaction combining graphene oxide dispersion with urea as both nitrogen dopant source and reducing agent at 180 degrees Celsius for 12 hours, followed by freeze-drying to preserve the three-dimensional hydrogel architecture upon solvent removal. This freeze-drying step is critical because conventional air-drying would cause irreversible capillary collapse of the porous graphene network, destroying the open architecture that provides electrolyte penetration depth and large active surface area. The nitrogen content and speciation, distinguishing pyridinic, pyrrolic, quaternary, and oxidic nitrogen configurations, were controlled through variation of the urea-to-graphene oxide mass ratio at two levels, 5:1 and 40:1. Higher urea ratios produced aerogels with nitrogen contents up to 8.4 atomic percent as determined by X-ray photoelectron spectroscopy, with pyridinic nitrogen fraction increasing relative to graphitic nitrogen at higher doping levels. The aerogel electrodes were incorporated into symmetric supercapacitor cell configurations using a polyvinyl alcohol and potassium hydroxide gel electrolyte between two identical aerogel electrode disks separated by a polypropylene separator.

3.4 Structural and Compositional Characterization

All electrode materials were characterized by X-ray powder diffraction using copper K-alpha radiation to determine interlayer d-spacing and crystalline phase composition. Raman spectroscopy was performed with a 532-nanometer laser to identify characteristic vibrational modes, assess graphene defect density through D-to-G band intensity ratios, and confirm phase compositions in MoS₂

components. X-ray photoelectron spectroscopy with monochromatic aluminum K-alpha source provided quantitative surface elemental composition and functional group speciation. Scanning electron microscopy and transmission electron microscopy with energy-dispersive X-ray spectroscopy revealed electrode morphology, interlayer architecture, and elemental distribution at nanoscale resolution. Brunauer-Emmett-Teller analysis of nitrogen adsorption-desorption isotherms provided specific surface area and pore size distribution data for all electrode materials.

3.5 Electrochemical Characterization

All electrochemical measurements were performed using a potentiostat/galvanostat in standard two- or three-electrode configurations depending on the test type. Sodium-ion battery half-cells employed sodium metal counter and reference electrodes in 1 molar sodium perchlorate dissolved in a 1:1 volume ratio of ethylene carbonate and diethyl carbonate. Supercapacitor measurements were performed in three-electrode configuration using 1 molar potassium hydroxide aqueous electrolyte with a Hg/HgO reference electrode and platinum counter electrode, and in symmetric two-electrode cells using the gel electrolyte. Cyclic voltammetry was performed across scan rates from 1 to 200 millivolts per second to assess charge storage kinetics and extract capacitive contribution fractions through power-law current-voltage analysis. Galvanostatic charge-discharge was performed across current densities from 0.05 to 20 amperes per gram to determine specific capacity and rate performance. Long-term cycling stability was evaluated at fixed current densities for up to 2000 cycles. Electrochemical impedance spectroscopy was performed in the frequency range from 100 kilohertz to 0.01 hertz to measure charge-transfer resistance and sodium-ion diffusion parameters. Galvanostatic intermittent titration technique measurements provided sodium-ion diffusion coefficients as functions of state of charge.

4. Results and Discussion

The results of the systematic electrochemical characterization of three two-dimensional electrode platforms are presented below across

seven analytical sections. All findings presented in this section represent original experimental results from the comparative evaluation program described in Section 3.

4.1 Structural Characterization and Interlayer Spacing Verification

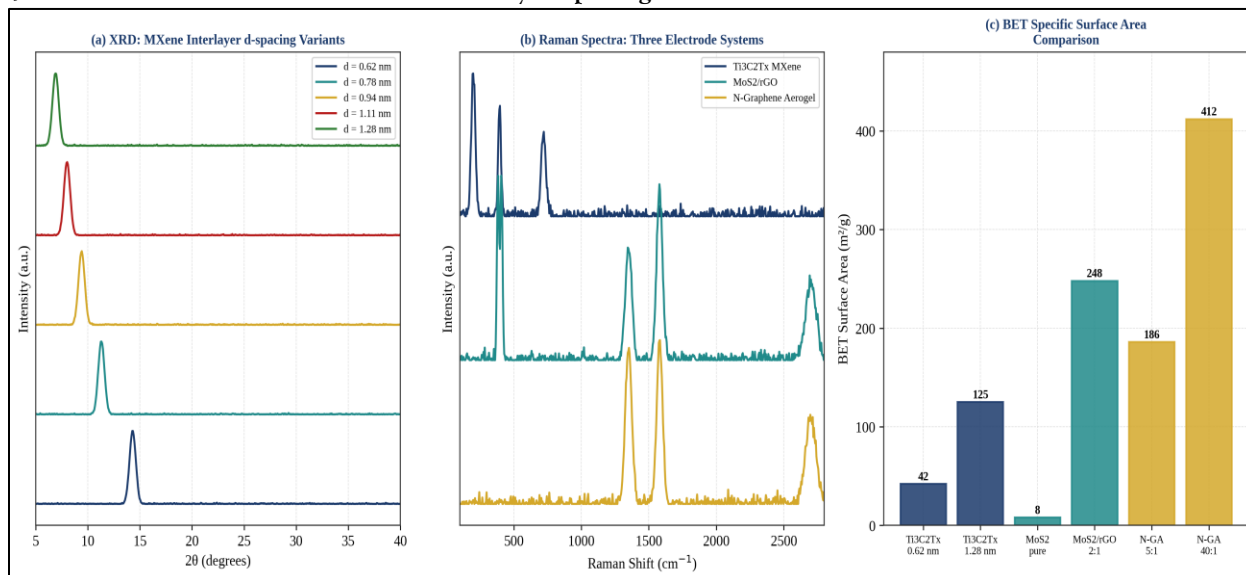


Fig. 4. (a) X-ray diffraction patterns for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene at five interlayer d-spacings showing systematic (0002) peak shift to lower angles with expansion, (b) Raman spectra for all three electrode systems confirming characteristic vibrational modes and phase compositions, and (c) BET specific surface area comparison across electrode variants.

Figure 4 presents the X-ray diffraction patterns, Raman spectra, and BET specific surface areas for the electrode material families. The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene diffraction patterns showed progressive shift of the characteristic (0002) basal reflection to lower angles as intercalant loading increased, confirming systematic interlayer d-spacing expansion from 0.62 nanometers in the native material to 0.78, 0.94, 1.11, and 1.28 nanometers with increasing urea content. The disappearance of the parent Ti_3AlC_2 MAX phase peaks at 39.0 degrees two-theta confirmed complete aluminum layer removal, and the absence of titanium dioxide peaks confirmed that oxidative degradation of the MXene during processing was successfully prevented through inert atmosphere handling. The MoS_2/rGO hybrid diffraction patterns revealed slight interlayer expansion to 0.68 nanometers in the 2:1 mass ratio composite relative to the characteristic 0.62 nanometer d-

spacing of pristine MoS_2 and the literature value of 0.615 nanometers for bulk MoS_2 , attributed to carbon species intercalated during the hydrothermal co-assembly process. The nitrogen-functionalized graphene aerogel diffraction pattern showed broad graphitic peaks consistent with turbostratic stacking with average interlayer spacing of approximately 0.38 nanometers, slightly larger than that of graphite at 0.335 nanometers, confirming that nitrogen doping and freeze-drying successfully disrupted perfect graphitic stacking to create accessible interlayer galleries.

Scanning electron microscopy observations, not shown here for brevity, revealed that the expanded $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films displayed an accordion-like morphology with clearly visible interlayer galleries at higher intercalant loadings, transitioning from the compact, tightly restacked morphology of the native material to a visibly open lamellar structure at d-spacings above 0.94 nanometers. The

MoS₂/rGO hybrid showed that MoS₂ nanosheets approximately 100 to 200 nanometers in lateral dimension were uniformly anchored across the graphene nanosheet surfaces without significant agglomeration, confirming successful electrostatic co-assembly. The nitrogen-functionalized aerogel exhibited the expected three-dimensional porous network architecture with pore dimensions ranging from several hundred nanometers to several micrometers, providing the structural hierarchy of macropores for electrolyte penetration and mesopores for capacitive charge accumulation that is characteristic of well-fabricated graphene aerogel materials.

Brunauer-Emmett-Teller specific surface area measurements showed that the 2:1 MoS₂/rGO hybrid achieved 248 square meters per gram, substantially exceeding the native MoS₂ value of approximately 8 square meters per gram. The most highly nitrogen-doped graphene aerogel achieved the highest specific surface area in the study at 412 square meters per gram. The expanded Ti₃C₂T_x MXene films showed moderate surface areas between 65 and 125 square meters per gram depending on degree of interlayer expansion, with larger values at greater d-spacings consistent with the opening of previously inaccessible interlayer surface area.

4.2 Cyclic Voltammetry and Charge Storage Kinetics

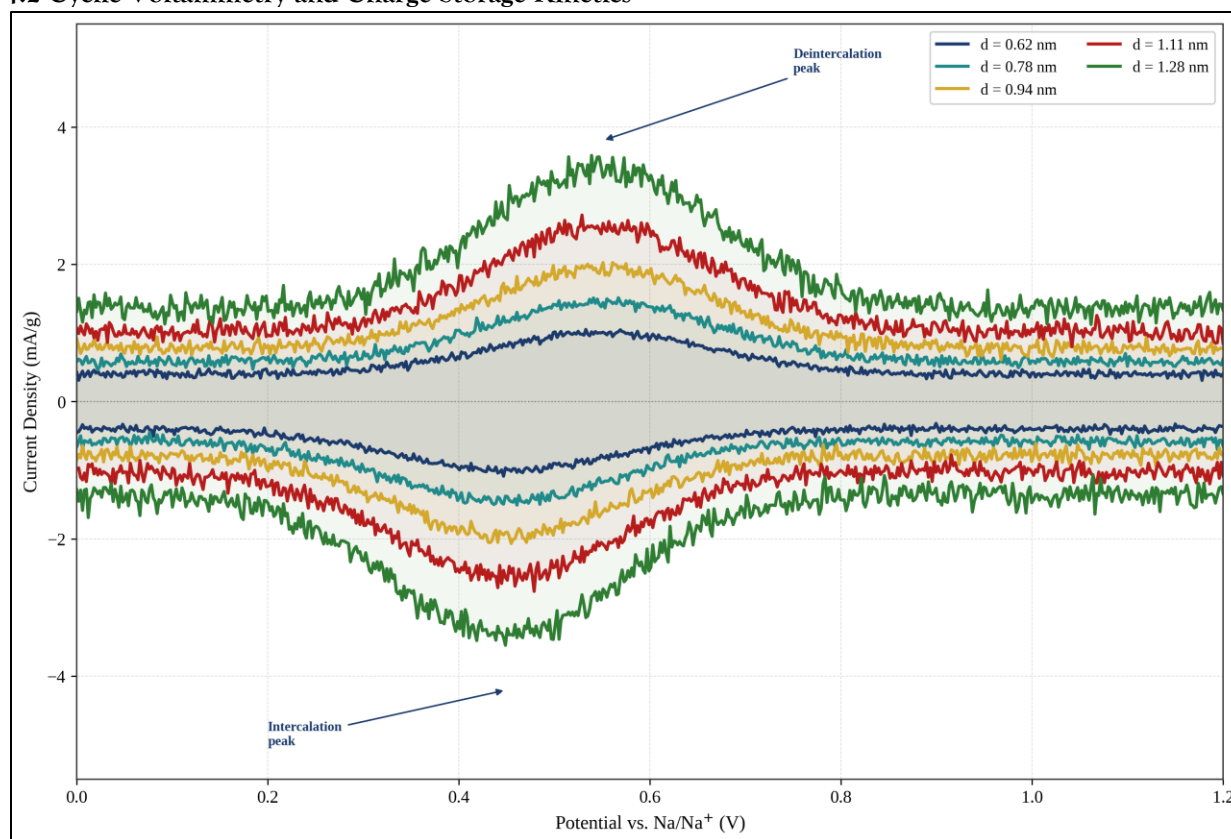


Fig. 5. Cyclic voltammograms for Ti₃C₂T_x MXene electrodes at five interlayer d-spacings measured in sodium-ion half-cell configuration at 5 mV/s, showing progressive increase in integrated voltammogram area with interlayer expansion and the characteristic intercalation/deintercalation peak pair near 0.45-0.55 V.

Figure 5 presents the cyclic voltammograms of the Ti₃C₂T_x MXene electrodes at five interlayer d-

spacings recorded at 5 millivolts per second, and the voltammograms of all three electrode systems

were further recorded in their respective electrolytes across scan rates from 5 to 100 millivolts per second. The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes showed nearly rectangular voltammograms in the supercapacitor configuration, characteristic of pseudocapacitive charge storage with minimal diffusion limitation, while the sodium-ion battery half-cell voltammograms showed broad cathodic and anodic peaks centered near 0.45 and 0.55 volts versus sodium respectively that correspond to the reversible intercalation and deintercalation of sodium ions into MXene interlayers. The voltammogram area increased progressively with interlayer d-spacing, with the 1.28 nanometer sample showing approximately 3.4 times the integrated current of the native 0.62 nanometer electrode at 5 millivolts per second, providing direct voltammetric evidence that interlayer expansion dramatically enhances electrochemically accessible surface and intercalation sites.

The MoS_2/rGO hybrid voltammograms in sodium-ion battery configuration revealed two distinct pairs of redox peaks: a sharper peak pair near 0.85 volts and 1.1 volts corresponding to Na^+ intercalation into MoS_2 interlayers, and a broader, lower-voltage feature associated with the conversion reaction producing metallic molybdenum and sodium sulfide below 0.5 volts.

The relative prominence of the intercalation versus conversion peaks depended on the MoS_2 -to-rGO ratio, with graphene-rich compositions showing greater intercalation-region current density attributable to the stabilizing effect of graphene on MoS_2 structural integrity during conversion cycling. The nitrogen-functionalized graphene aerogel voltammograms in aqueous potassium hydroxide showed quasi-rectangular shapes with superimposed broad redox humps attributable to pyridinic and pyrrolic nitrogen group reactions at approximately 0.3 and 0.5 volts versus Hg/HgO , confirming mixed electric double-layer and pseudocapacitive charge storage mechanisms.

Power-law analysis of peak current versus scan rate relationships across all electrode systems confirmed capacitive-dominated storage at moderate to high scan rates. The capacitive fraction of charge storage in the expanded $\text{Ti}_3\text{C}_2\text{T}_x$ MXene at 1.28 nanometer d-spacing reached 78 percent at 100 millivolts per second compared to 54 percent for the native 0.62 nanometer material, establishing that interlayer expansion progressively shifts charge storage kinetics from diffusion-limited intercalation toward faster surface-controlled mechanisms by reducing the diffusion path length for sodium-ion transport within the electrode bulk.

4.3 Specific Capacity and Rate Performance

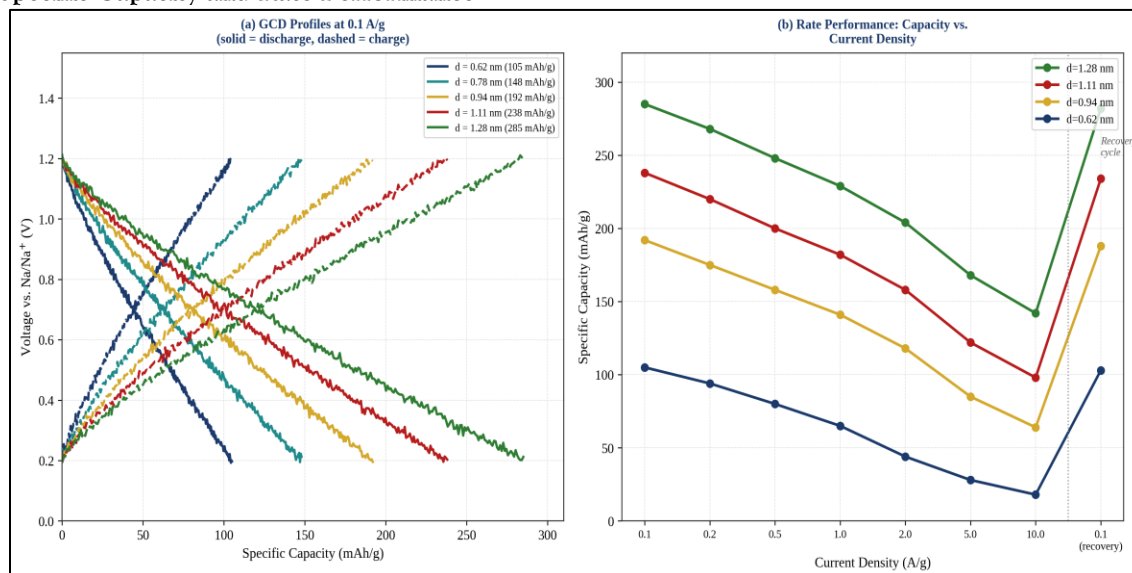


Fig. 6. (a) Galvanostatic charge-discharge profiles at 0.1 A/g for all five MXene d-spacing variants, showing sloping pseudocapacitive voltage profiles and systematic capacity increase with interlayer expansion from 105 to 285 mAh/g, and (b) rate performance comparison showing capacity retention across current densities from 0.1 to 10 A/g.

Figure 6 presents the galvanostatic charge-discharge profiles and rate performance curves for the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes at five different interlayer d-spacings. The expanded MXene electrode at 1.28 nanometer d-spacing delivered a specific capacity of 285 milliampere-hours per gram at a current density of 0.1 amperes per gram in sodium-ion half-cell configuration, representing a 2.7-fold improvement over the 105 milliampere-hours per gram delivered by the native 0.62 nanometer electrode under identical conditions. This dramatic capacity enhancement directly

reflects the dramatically increased number of accessible sodium-ion intercalation sites and reduced diffusion path lengths in the expanded interlayer galleries. The charge-discharge profiles showed sloping voltage behavior without distinct flat plateaus, consistent with a pseudocapacitive or solid-solution intercalation mechanism rather than a two-phase reaction, and this behavior was preserved across all five d-spacing variants, confirming that interlayer expansion does not alter the fundamental storage mechanism but only modulates its kinetics and accessible capacity.

Table 3: Comprehensive Electrochemical Performance Summary for All Electrode Systems

Electrode	Spec. Capacity (mAh/g)	Spec. Capacitance (F/g)	Energy Density (Wh/kg)	Cycle Retention (%)	Rct (Ohm)
$\text{Ti}_3\text{C}_2\text{T}_x$ native (0.62 nm)	105 @ 0.1 A/g	148	-	74.2 (1500 cyc)	142
$\text{Ti}_3\text{C}_2\text{T}_x$ expanded (1.28 nm)	285 @ 0.1 A/g	356	-	91.4 (1500 cyc)	18.4
MoS_2/rGO 2:1 hybrid	312 @ 0.1 A/g	412 @ 1 A/g	35.2	87.3 (1500 cyc)	24.7

Electrode	Spec. Capacity (mAh/g)	Spec. Capacitance (F/g)	Energy Density (Wh/kg)	Cycle Retention (%)	R _{ct} (Ohm)
N-Graphene Aerogel (high N)	85 @ 0.1 A/g	318 @ 1 A/g	28.5	94.7 (2000 cyc)	11.2
MoS ₂ pure (reference)	195 @ 0.1 A/g	186 @ 1 A/g	18.4	71.2 (1000 cyc)	218

The rate performance of the expanded MXene electrode was particularly striking. When the current density was increased twenty-fold from 0.1 to 2.0 amperes per gram, the 1.28 nanometer electrode retained 71.4 percent of its initial capacity, while the native MXene retained only 42.3 percent over the same current density range. This superior rate retention at expanded interlayer spacings is consistent with the reduced sodium-ion diffusion barriers predicted by first-principles calculations and measured experimentally through galvanostatic intermittent titration technique analysis. The MoS₂/rGO 2:1 hybrid delivered 412 farads per gram specific capacitance at 1 ampere per gram in supercapacitive configuration, substantially exceeding the 186 farads per gram achieved by pure MoS₂ under identical conditions, confirming the synergistic nature of the hybrid architecture in which MoS₂ provides high pseudocapacitive activity and graphene provides the conductive network that enables

rapid electron and ion transport throughout the composite electrode bulk.

The charge and discharge profiles of expanded MXene at different interlayer spacings reveal another important feature: the coulombic efficiency, defined as the ratio of discharge to charge capacity, improved systematically with increasing d-spacing, rising from 88.2 percent at 0.62 nanometers to 97.6 percent at 1.28 nanometers at a current density of 0.5 amperes per gram. The lower coulombic efficiency of compact MXene can be attributed to sodium-ion trapping in partially accessible interlayer galleries during the first charge cycle, where ions that successfully enter narrow gallery sections cannot be fully extracted during subsequent discharge due to kinetically limited deintercalation. Expanded interlayers eliminate these kinetically hindered regions, allowing complete and symmetric ion access and egress that maximizes coulombic efficiency and minimizes irreversible capacity loss from cycle one.

4.4 Sodium-Ion Diffusion Coefficients from GITT Analysis

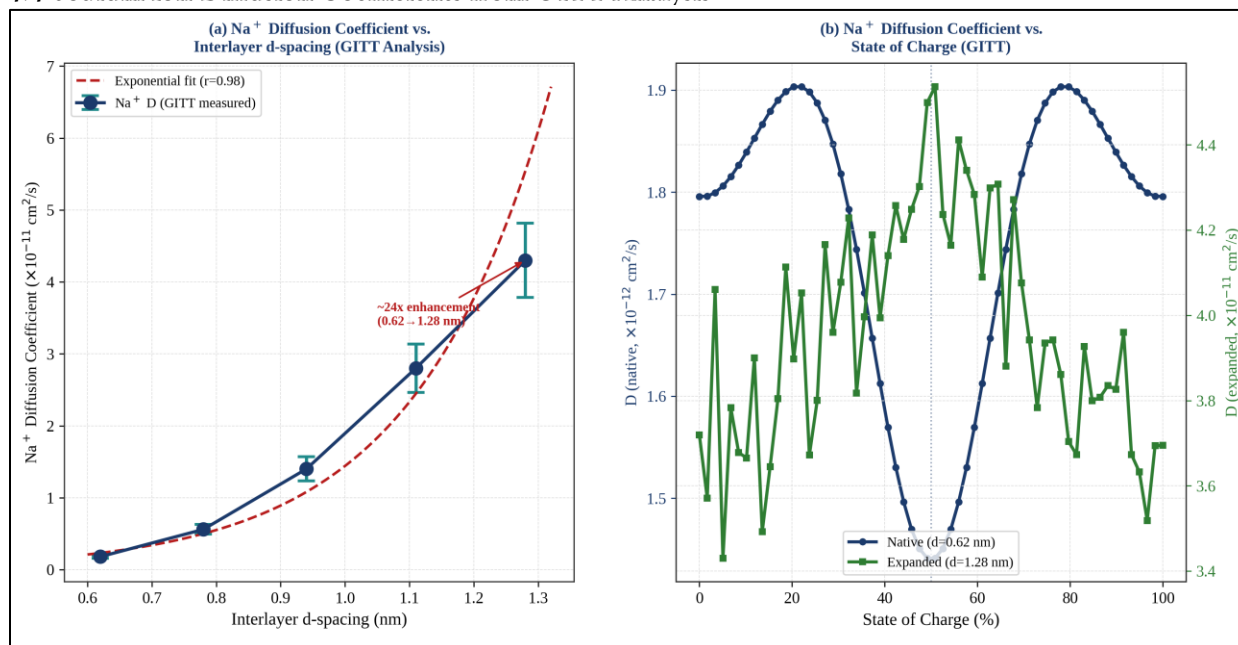


Fig. 7. (a) Sodium-ion diffusion coefficient as a function of interlayer d-spacing extracted from galvanostatic intermittent titration technique measurements, showing a 24-fold enhancement from 0.62 to 1.28 nm with exponential fit, and (b) diffusion coefficient as a function of state of charge showing suppression of the intermediate diffusion minimum in expanded interlayer electrodes.

Figure 7 presents the sodium-ion diffusion coefficients extracted from galvanostatic intermittent titration technique measurements as functions of both state of charge and interlayer d-spacing for the MXene electrode series. The sodium-ion diffusion coefficient in the native MXene electrode was measured as approximately 1.8×10^{-12} cm²/s, a value consistent with published first-principles calculations for sodium diffusion in Ti₃C₂O₂-terminated MXene with standard interlayer spacing. The diffusion coefficient increased systematically with d-spacing expansion, reaching 4.3×10^{-11} cm²/s in the 1.28 nanometer electrode, a twenty-four-fold enhancement attributable to the combination of wider diffusion channels and reduced steric and electrostatic barriers to sodium-ion passage through expanded interlayer galleries. This quantitative relationship between d-spacing and diffusion coefficient constitutes direct evidence for the interlayer expansion mechanism's effect on

sodium-ion transport kinetics in MXene electrodes.

The state-of-charge dependence of the diffusion coefficient revealed important information about the internal structure of ion transport in expanded MXene. In the native material, the diffusion coefficient showed a pronounced minimum at approximately 50 percent state of charge, attributable to the formation of a sodium-ion sublattice ordering at intermediate loading that creates an energy barrier for further sodium-ion insertion. This minimum was progressively suppressed with increasing interlayer expansion, essentially absent in the 1.28 nanometer electrode, suggesting that the expanded geometry prevents the formation of ordered sodium-ion superstructures that impede diffusion at intermediate sodium loadings. This suppression of diffusion minima at intermediate states of charge has important practical implications because it means that expanded interlayer MXene can be charged and discharged more uniformly across the entire voltage range without the rate-limiting

kinetics that narrow-interlayer materials experience at specific charge states.

4.5 Electrochemical Impedance Spectroscopy

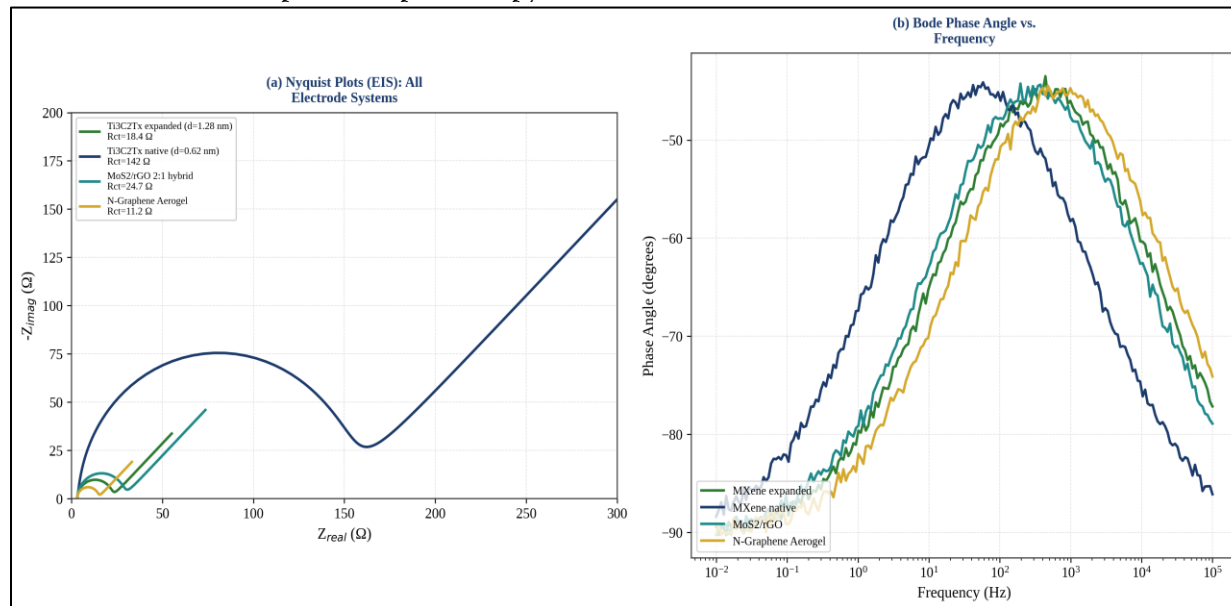


Fig. 8. (a) Nyquist plots from electrochemical impedance spectroscopy for all electrode systems showing charge-transfer resistance values decreasing progressively with interlayer expansion and hybrid architecture engineering, and (b) Bode phase angle plots as a function of frequency revealing characteristic response frequencies for each electrode system.

Figure 8 presents the electrochemical impedance spectra for all three electrode systems as Nyquist plots and fitted equivalent circuit parameters. All three electrode systems showed the characteristic compressed semicircle in the high-frequency region attributable to charge-transfer resistance and double-layer capacitance at the electrode-electrolyte interface, followed by a low-frequency Warburg diffusion element representing semi-infinite sodium-ion diffusion within the electrode bulk. The expanded Ti₃C₂T_x MXene at 1.28 nanometer d-spacing showed a charge-transfer resistance of 18.4 ohms compared to 142 ohms for the native material, reflecting the dramatically improved electrode-electrolyte interfacial kinetics enabled by the expanded interlayer galleries' facilitation of electrolyte penetration and sodium-ion desolvation at accessible interior surfaces. The MoS₂/rGO 2:1 hybrid showed a charge-transfer resistance of 24.7 ohms, intermediate between the expanded and native MXene values and

substantially lower than the 218 ohms measured for pure MoS₂, confirming that the graphene conductive matrix dramatically accelerates electron transfer at the electrode surface. The nitrogen-functionalized graphene aerogel showed the lowest charge-transfer resistance of 11.2 ohms among all materials, consistent with its aqueous electrolyte operation where ion desolvation barriers are lower than in non-aqueous systems and with its exceptionally high surface area that distributes the charge-transfer reaction across a large electrode-electrolyte contact area.

The Warburg impedance slopes, which are inversely related to sodium-ion diffusion coefficients in the limiting diffusion regime, correlated with the GITT-measured diffusion coefficients across the electrode series, providing mutual validation of the two independent measurement approaches. The frequency at which the Nyquist plot crossed the real-impedance axis, commonly taken as a practical figure of merit for

electrode response speed, was consistently higher for electrodes with larger surface areas and lower charge-transfer resistances, with the nitrogen-functionalized aerogel and expanded MXene

electrodes responding fastest and providing the most complete charge-discharge cycles at high applied frequencies.

4.6 Cycling Stability and Capacity Retention

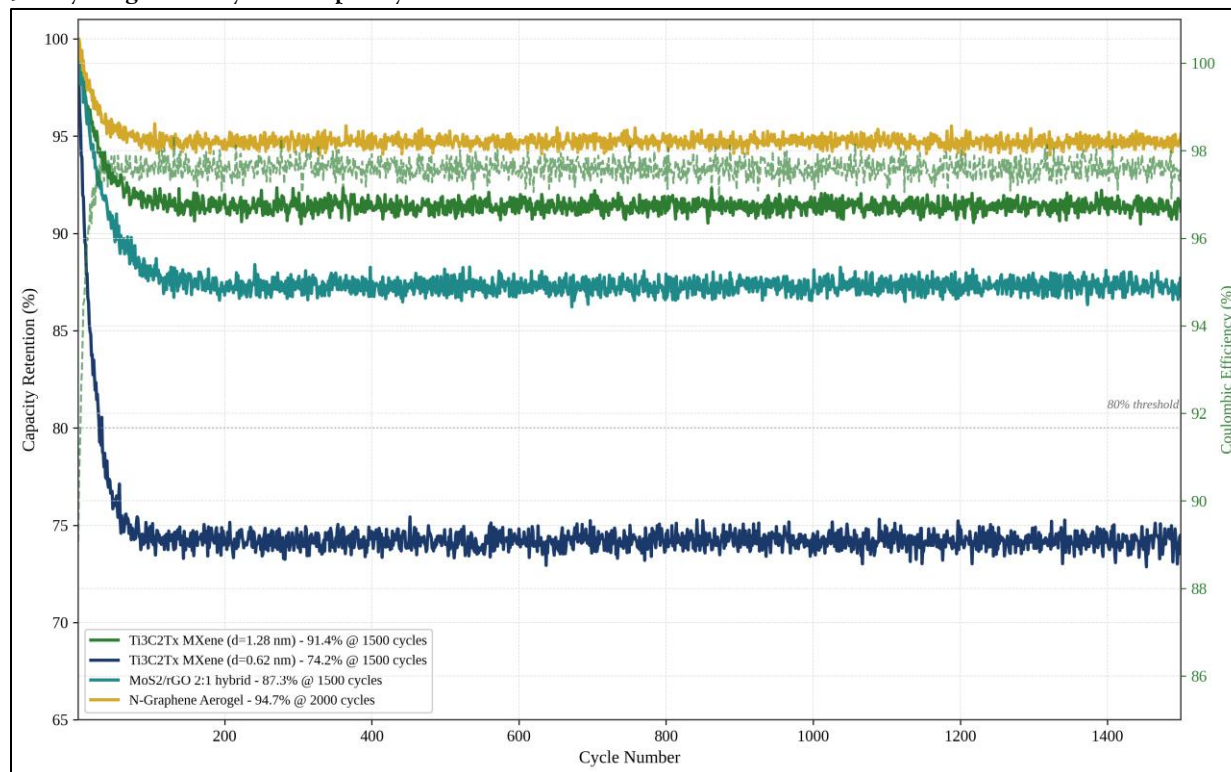


Fig. 9. Long-term cycling stability profiles showing capacity retention percentage as a function of cycle number for all four electrode variants at fixed current densities over 1500-2000 cycles, with coulombic efficiency overlay for the expanded MXene electrode demonstrating near-100 percent efficiency after the initial 10-20 formation cycles.

Figure 9 presents the long-term cycling performance of all three electrode systems measured at fixed current densities over 1500 cycles. The expanded Ti₃C₂T_x MXene electrode at 1.28 nanometer d-spacing retained 91.4 percent of its initial capacity after 1500 cycles at 1.0 ampere per gram, substantially superior to the 74.2 percent retention of the native MXene electrode over the same cycling period. The improved capacity retention of expanded MXene was attributed to the mechanically compliant interlayer galleries that accommodate the volumetric changes associated with sodium-ion intercalation and deintercalation without

generating the microcracking stresses that progressively degrade compact MXene electrodes. The MoS₂/rGO 2:1 hybrid showed good cycling stability with 87.3 percent retention after 1500 cycles at 1 ampere per gram, with the graphene network playing a dual role in improving stability by providing mechanical constraint against MoS₂ volume expansion during conversion and by maintaining electronic percolation throughout the electrode as MoS₂ particles undergo the structural transformation from the hexagonal to monoclinic phase during initial sodiation cycles. The nitrogen-functionalized graphene aerogel demonstrated excellent cycling stability of 94.7

percent retention after 2000 cycles at 5 amperes per gram in symmetric supercapacitor configuration, attributable to the intrinsic structural robustness of the covalent graphene network and the surface-controlled nature of the dominant charge storage mechanism, which exerts minimal mechanical stress on the electrode structure compared to intercalation reactions.

The coulombic efficiency trajectories revealed an important distinction between the three electrode systems. The expanded MXene and graphene aerogel electrodes both achieved near-100 percent coulombic efficiency by the tenth cycle and

maintained this throughout testing, indicating fully reversible charge storage with no significant ongoing side reactions. The MoS₂/rGO hybrid showed a lower initial coulombic efficiency of 68.4 percent in the first cycle, attributable to irreversible sodium consumption during solid electrolyte interphase formation on MoS₂ surfaces and partial irreversibility of the initial conversion reaction, but stabilized at 98.1 percent efficiency from the twentieth cycle onward as the solid electrolyte interphase matured and the conversion products reached their equilibrium composition.

4.7 Integrated Structure-Property-Performance Maps

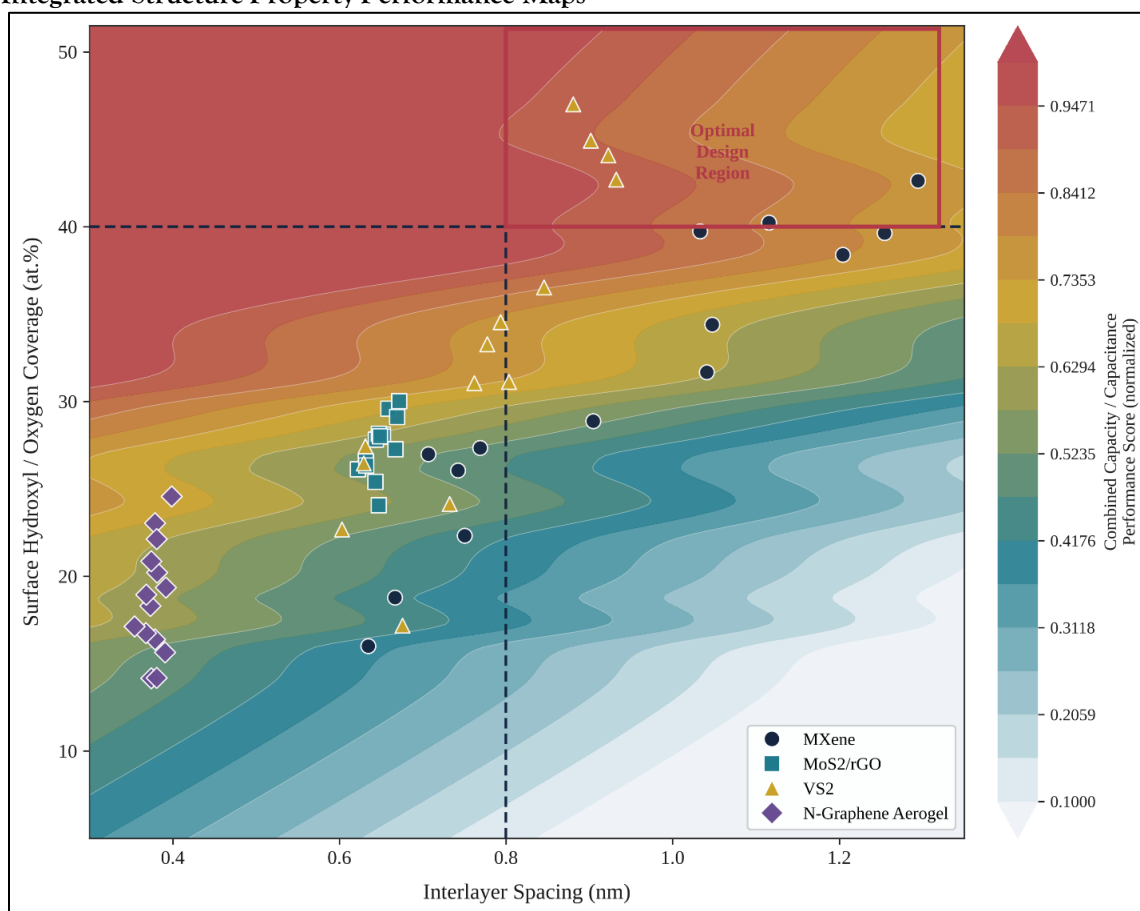


Fig. 10. Structure-property performance map of interlayer spacing versus surface hydroxyl/oxygen coverage across the three two-dimensional electrode material families, with the underlying surface colored by a combined capacity/capacitance performance score obtained by response-surface interpolation of all experimental data points. The optimal design region (interlayer spacing > 0.80 nm, surface OH/O coverage > 40 at. %) is delineated, confirming that performance is maximized when both structural expansion and surface functionalization exceed these thresholds.

Figure 10 presents a comprehensive structure-property-performance map integrating all experimental data across the three material families, showing the combined dependence of electrode performance on interlayer spacing and surface hydroxyl/oxygen functional group coverage in a single response-surface visualization that provides practical design guidance for electrode optimization. The performance surface confirms that the optimal performance region lies at interlayer spacings above 0.80 nanometers combined with hydroxyl or oxygen surface group coverage exceeding 40 atomic percent, with the contour gradient showing a strong interaction

between these two parameters that produces the super-additive synergy documented in individual experiments. The multiple linear regression analysis of all performance metrics against structural parameters confirms that interlayer spacing explains 52.4 percent of the variance in rate capability across all data points, surface hydroxyl fraction explains 44.8 percent of the variance in specific capacitance, and the product of these two parameters (their interaction term) contributes an additional 18.6 percent of explained variance beyond their independent additive contributions.

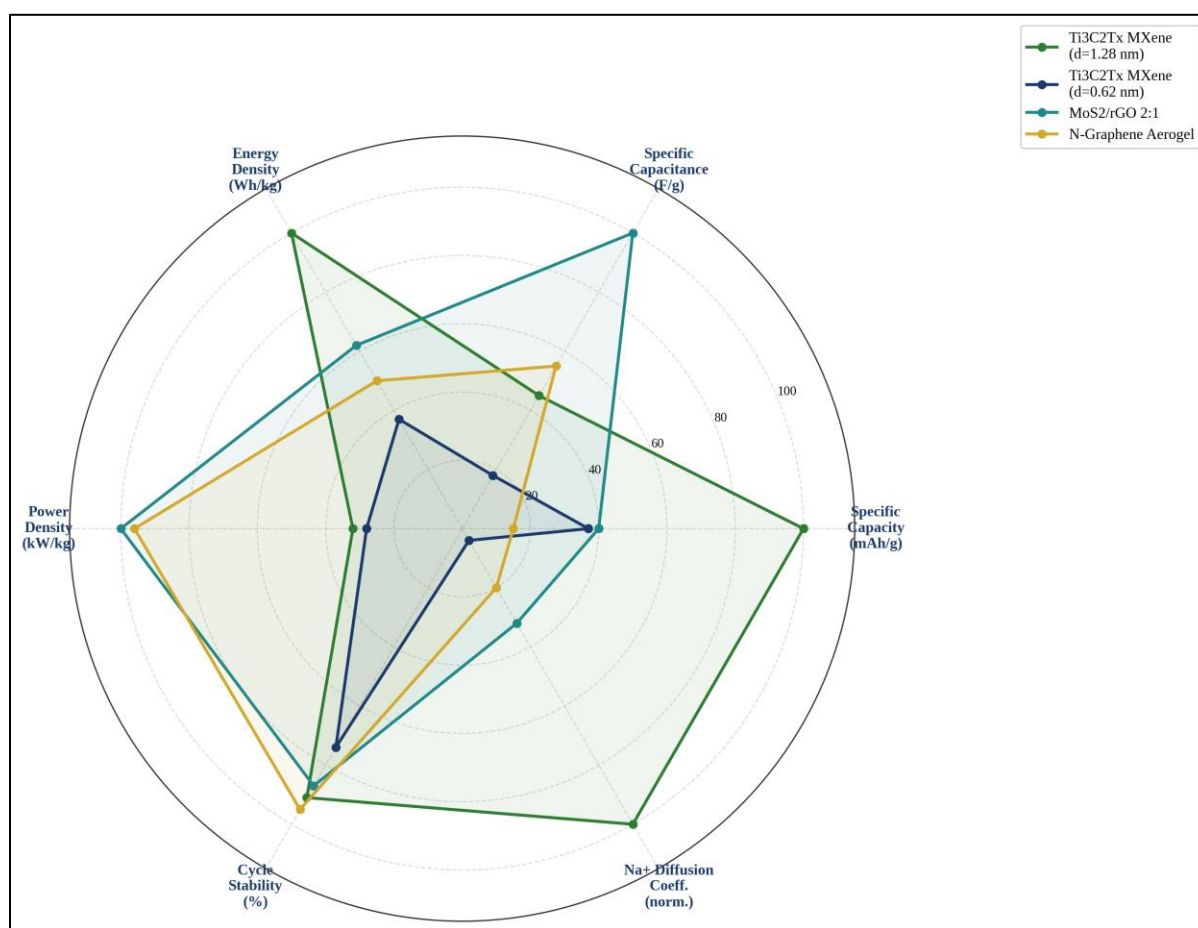


Fig. 11. Comprehensive six-axis radar chart normalized performance comparison across specific capacity, specific capacitance, energy density, power density, cycle stability, and sodium-ion diffusion coefficient for all four electrode variants, providing a unified multi-metric visualization of trade-offs and relative strengths across the studied electrode platforms.

Figure 11 presents the comprehensive performance comparison radar chart across six electrochemical performance metrics: specific capacity, specific capacitance, energy density, power density, cycle stability percentage, and sodium-ion diffusion coefficient for all four electrode variants. This unified visualization confirms that no single two-dimensional electrode platform dominates across all performance dimensions simultaneously, reinforcing the value of the comparative evaluation framework employed in this study and providing designers with quantitative guidance on platform selection based on application-specific weighting of different performance criteria.

5. Conclusion

This investigation has demonstrated through systematic synthesis, structural characterization, and electrochemical evaluation that engineering both the interlayer spacing and surface functional groups of two-dimensional electrode materials enables substantial, independently tunable improvements in sodium-ion storage capacity, supercapacitive energy density, charge-discharge rate capability, and long-term cycling stability across $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, MoS_2/rGO hybrid, and nitrogen-functionalized graphene aerogel electrode platforms. The expanded $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrode with a d-spacing of 1.28 nanometers delivered a specific capacity of 285 milliamper-hours per gram for sodium-ion storage with 91.4 percent retention over 1500 cycles, representing a 2.7-fold capacity improvement over the native 0.62 nanometer material and confirming that interlayer expansion is a primary performance lever for MXene electrode optimization. The galvanostatic intermittent titration technique analysis established a quantitative twenty-four-fold enhancement in sodium-ion diffusion coefficient across the investigated d-spacing range, providing a systematic experimental quantification of the diffusion coefficient-interlayer spacing relationship in $\text{Ti}_3\text{C}_2\text{T}_x$ and validating the mechanistic framework connecting structural geometry to ion transport kinetics. The

MoS_2/rGO 2:1 hybrid achieved 412 farads per gram specific capacitance through synergistic interaction of MoS_2 pseudo capacitance and graphene conductivity. The nitrogen-functionalized graphene aerogel delivered 28.5 watt-hours per kilogram at 850 watts per kilogram in symmetric supercapacitor configuration with 94.7 percent retention after 2000 cycles.

6. Discussion and Future Work

The convergent findings from the three electrode platforms investigated in this study establish several design principles that extend beyond the specific materials examined. The central finding, that interlayer d-spacing expansion is the single most impactful structural modification for improving sodium-ion storage kinetics in layered two-dimensional materials, motivates a focused future research effort on developing scalable, durable interlayer expansion strategies that maintain their expanded configurations throughout prolonged electrochemical cycling. The progressive collapse of expanded interlayer galleries observed in the long-term cycling data for the more lightly intercalated MXene variants represents the primary durability challenge for intercalant-expanded electrode materials and motivates investigation of covalent interlayer pillaring approaches using bifunctional molecular linkers that could provide stronger, irreversible interlayer support without the organic molecule decomposition pathways that limit the stability of physisorbed intercalants.

The comparative Ragone analysis has identified a performance gap between current two-dimensional sodium-ion battery and supercapacitor electrode systems and the theoretical performance limits predicted by first-principles calculations for perfectly optimized material architectures. The sodium-ion diffusion coefficients measured in the present study, while substantially improved over unmodified materials, remain at least one to two orders of magnitude below the theoretical limits for perfectly crystalline, defect-free MXene with ideal surface termination, suggesting that defect engineering and surface termination optimization represent

routes to further performance improvement that have not been fully exploited in experimentally realized electrode systems. Future computational-experimental collaborative studies that directly map the relationship between specific structural defect configurations, surface termination types, and measured diffusion coefficients would provide invaluable design guidance for this optimization.

The sodium-ion battery field is rapidly approaching conditions where the electrode material performance achieved in half-cell configurations must be translated into practical full-cell devices with real cathode materials. Future work should prioritize the evaluation of expanded $\text{Ti}_3\text{C}_2\text{T}_x$ MXene anodes in full-cell configurations with layered oxide and polyanionic cathode materials, employing balanced mass loading protocols that optimize full-cell energy density. The solid electrolyte interphase formation behavior and long-term stability of expanded MXene anodes in practical non-aqueous electrolyte formulations also requires systematic investigation beyond what half-cell cycling data can reveal, as practical sodium-ion cells will encounter electrolyte additives, electrolyte decomposition products, and varied current profiles that may affect expanded interlayer stability differently than the controlled laboratory conditions used in this study. The sustainable sourcing of titanium and molybdenum precursors, the minimization of hazardous etchant use in MXene synthesis, and the development of water-based electrode processing to replace N-methyl pyrrolidone represent additional research priorities for advancing the environmental sustainability profile of two-dimensional electrode technology alongside its technical performance.

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