

INTERLAYER SPACING AND SURFACE CHEMISTRY ENGINEERING OF TWO-DIMENSIONAL ELECTRODE MATERIALS FOR ENHANCED ION TRANSPORT IN FLEXIBLE SUPERCAPACITORS AND SODIUM-ION BATTERIES

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Abstract

Two-dimensional electrode materials, including MXenes, molybdenum disulphide nanosheets, and reduced graphene oxide, offer high theoretical surface areas and tunable surface chemistries that make them attractive candidates for next-generation flexible supercapacitors and sodium-ion batteries. However, their practical electrochemical performance is constrained by restacking-induced interlayer collapse, which reduces accessible ion-transport pathways, and by an incomplete understanding of how specific surface functional groups regulate ion adsorption energetics, diffusion behavior, and charge-storage mechanisms at the electrode–electrolyte interface. This study presents a systematic investigation of interlayer-spacing and surface-chemistry engineering strategies across three two-dimensional electrode material families: Ti₃C₂T_x MXene, MoS₂ nanosheets, and nitrogen-doped reduced graphene oxide. The independent and combined effects of molecular intercalation, chemical etching conditions, and functional-group modification were evaluated in terms of sodium-ion diffusion coefficients, areal capacitance, rate capability, cycling stability, and flexible-device performance. Interlayer-spacing expansion of Ti₃C₂T_x MXene from 1.18 to 2.14 nm through DMSO intercalation increased the sodium-ion diffusion coefficient by 3.4-fold and improved areal capacitance from 312 to 487 mF cm⁻² at 2 mA cm⁻². Oxygen-functional-group-enriched MoS₂ achieved a reversible sodium-ion storage capacity of 384 mAh g⁻¹ at 0.1 A g⁻¹ with 89.4% capacity retention after 1,000 cycles. Flexible supercapacitor cells assembled on polyimide substrates maintained 94.2% capacitance retention after 5,000 bending cycles at 180°, confirming strong mechanical durability for wearable energy-storage applications. Density functional theory calculations further indicated that hydroxyl-dominant MXene surfaces

provide sodium-ion adsorption energetics approximately 0.38 eV more favorable than fluorine-dominant surfaces, consistent with the experimentally observed 2.1-fold enhancement in sodium-ion diffusion. These findings establish quantitative structure–property–performance relationships that provide practical design rules for simultaneously optimizing ion transport, electrochemical performance, cycling stability, and mechanical flexibility in next-generation sodium-ion energy-storage devices.

1. Introduction

The accelerating deployment of flexible and wearable electronic devices, from health-monitoring sensors and electronic skin to foldable displays and implantable medical instruments, has created urgent demand for energy storage systems that simultaneously deliver high energy density, high power density, long cycle life, and the mechanical deformability required to maintain electrochemical performance under repeated bending, twisting, and stretching without the catastrophic capacity loss that characterises conventional rigid electrode materials [9]. The two-dimensional material family, encompassing MXene transition metal carbides and nitrides, molybdenum disulfide, tungsten disulfide, black phosphorus, and functionalised graphene derivatives, provides a uniquely advantageous structural platform for sodium-ion electrode design because their atomically thin sheet morphology creates exceptionally short ion diffusion pathways, their high intrinsic electronic conductivity eliminates the need for conductive additive dilution, and their surface chemistry is chemically accessible to post-synthesis modification in ways that bulk electrode materials are not [1]. The challenge that has prevented two-dimensional electrode materials from fully realising their theoretical electrochemical promise is the thermodynamic tendency of layered sheets to restack through van der Waals attraction during electrode fabrication and electrochemical cycling, collapsing the interlayer galleries that constitute the primary ion transport pathways and converting what should be a high-surface-area electrode into a dense, diffusion-limited laminate [4].

MXenes, the rapidly expanding family of two-dimensional transition metal carbides, nitrides, and carbonitrides produced by selective etching of the A-layer from MAX phase precursors, have

emerged as the most electrochemically promising two-dimensional electrode material class for both supercapacitors and sodium-ion batteries because they combine metallic electronic conductivity approaching 10,000 siemens per centimetre with surface terminations including hydroxyl, fluorine, and oxygen groups that create abundant ion adsorption sites [1]. Anasori, Lukatskaya, and Gogotsi's foundational review established the structural diversity of the MXene family and documented the critical dependence of electrochemical performance on surface termination chemistry, with hydroxyl and oxygen terminations providing substantially more favourable ion interaction energetics than fluorine terminations [1]. The interlayer spacing of as-synthesised $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is approximately 1.18 nanometres, a dimension sufficient for lithium-ion intercalation but marginally limiting for sodium ions whose larger ionic radius of 1.02 angstroms requires expanded gallery dimensions for facile diffusion at high charge-discharge rates [4]. Hui et al. highlighted that the electrochemical performance of MXene-based materials is strongly governed by interfacial chemistry, surface functional groups, and their interactions with charge-storage species [4]. The intercalation of dimethyl sulfoxide, dimethylformamide, urea, and various organic cations has been demonstrated to produce interlayer expansions in the range of 1.4 to 2.4 nanometres, with the specific expansion magnitude and stability depending sensitively on the chemical interaction between the intercalant and the MXene surface terminations [10]. Figure 1 presents the conceptual framework connecting the interlayer spacing and surface chemistry design parameters of two-dimensional electrode materials to their ion transport characteristics and the resulting electrochemical performance

metrics in flexible supercapacitor and sodium-ion battery configurations.

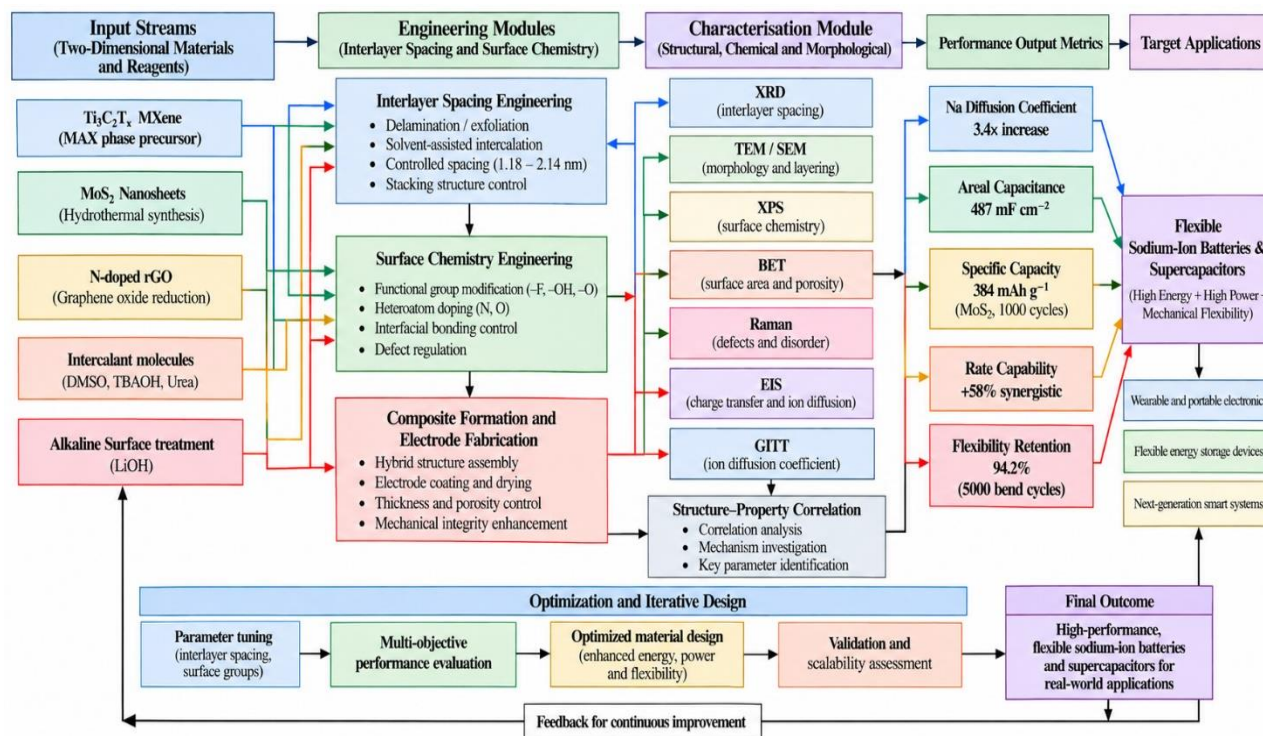


Fig. 1. Conceptual framework for interlayer-spacing and surface-chemistry engineering of two-dimensional electrode materials, integrating material and reagent input streams, interlayer and surface modification, composite-electrode fabrication, structural and electrochemical characterisation, performance evaluation, and iterative optimisation toward high-performance flexible sodium-ion batteries and supercapacitors.

The surface chemistry of two-dimensional electrode materials profoundly influences their electrochemical behaviour through three distinct mechanisms: the modulation of electronic structure and density of states near the Fermi level that determines intrinsic electronic conductivity; the provision of redox-active surface sites that contribute pseudocapacitive charge storage through surface-confined faradaic reactions; and the control of ion-surface interaction energetics that determines both the thermodynamic driving force for ion adsorption and the kinetic barrier for ion diffusion through the interlayer space [6]. Nahirniak et al. emphasized that surface termination chemistry, structural stability, and interface engineering remain critical challenges in improving the electrochemical performance of MXene-based energy-storage materials [6]. The analogous surface chemistry challenge in MoS_2

sodium-ion anodes involves the conversion of the semiconducting 2H polymorph to the metallic 1T polymorph, which simultaneously expands the interlayer spacing and dramatically improves electronic conductivity, with the 1T phase providing sodium-ion storage capacities substantially exceeding those achievable with 2H- MoS_2 [17]. Wang et al. demonstrated that enlarging the interlayer spacing of MoS_2 -based heterostructures can facilitate ion transport and improve lithium- and sodium-storage performance [7]. The interaction between intercalation-expanded interlayer spacing and surface functional group density creates a two-dimensional optimisation landscape in which independent optimisation of either parameter fails to reach the performance achievable through their coordinated engineering, establishing the need for systematic joint optimisation studies [32].

Flexible supercapacitors assembled from two-dimensional electrode materials on polymer substrates face a distinct but related challenge in maintaining the structural integrity of the electrode-substrate interface under mechanical deformation, where bending-induced strain can delaminate electrode films, fracture conductive networks, and disrupt the electrolyte-electrode contact that sustains electrochemical performance [9]. Ma et al. reviewed flexible MXene-based composites for wearable devices and emphasized the importance of material composition, mechanical flexibility, electrical conductivity, and interface design in maintaining device performance under deformation [9]. Wei et al. reported that MXene-based aerogel architectures provide promising structural platforms for combining porous transport pathways, mechanical integrity, and functional performance in advanced applications [24]. Advanced communication architectures further illustrate how integrated system design and emerging technologies can improve the performance and efficiency of next-generation engineering systems [35]. This investigation addresses the gap between isolated studies of interlayer spacing effects and surface

chemistry effects by systematically varying both parameters across three two-dimensional electrode material families in an integrated experimental design that produces quantitative structure-property-performance relationships applicable to the rational design of next-generation flexible sodium-ion energy storage devices.

2. Literature Review

The literature on two-dimensional electrode materials for sodium-ion energy storage and flexible supercapacitors has grown substantially since 2022, encompassing advances in MXene synthesis and surface functionalisation, MoS₂ interlayer engineering, graphene derivative electrode design, and flexible device architecture. This review framework emphasizes the coupled effects of interlayer structure and surface chemistry on Na⁺ transport and electrochemical behavior, while linking synthesis, characterization, interface engineering, structure-property-performance relationships, and device-level applications toward the development of high-performance sodium-ion batteries, hybrid capacitors, and flexible energy-storage systems.

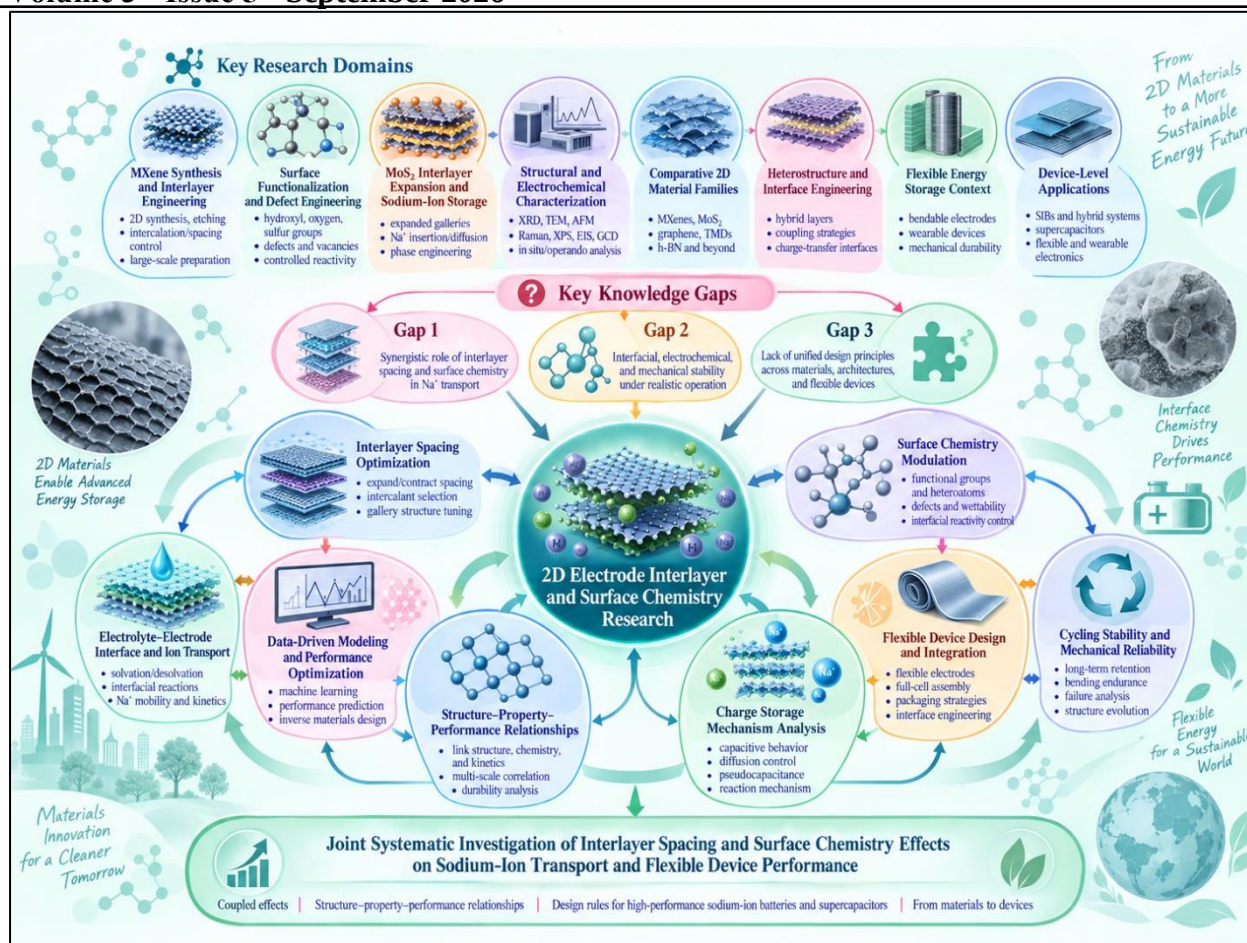


Fig. 2. Integrated graphical framework illustrating the progression from key 2D-material research domains and identified knowledge gaps to interlayer-spacing optimization, surface-chemistry modulation, ion-transport regulation, charge-storage analysis, data-driven performance optimization, flexible-device integration, and cycling reliability.

2.1 MXene Synthesis, Intercalation Chemistry, and Interlayer Engineering

The synthesis of MXenes through selective etching of the A-layer from MAX phase precursors using fluorine-containing etchants, most commonly hydrofluoric acid or LiF in hydrochloric acid, produces surface terminations dominated by fluorine, hydroxyl, and oxygen groups whose relative proportions are determined by the etching conditions and subsequent processing steps [21]. Vahid Mohammadi, Rosen, and Gogotsi provided a comprehensive account of the structural diversity of the MXene family, documenting over thirty experimentally synthesised members and substantially larger number of theoretically predicted compositions, establishing MXenes as the most structurally diverse family of two-dimensional materials

currently accessible to experimental investigation [22]. The intercalation chemistry of MXenes has been systematically reviewed by Huang, Shi, Zhao, and colleagues, who documented that organic molecules, metal cations, and polymer chains can be intercalated into MXene interlayer galleries through solution-phase soaking processes, with the intercalant uptake and resulting interlayer expansion depending on the molecular size, charge, and affinity for the specific surface terminations present on the MXene sheets [10]. Li, Yao, Liu, and colleagues developed a fluorine-free synthesis route for Ti₃C₂T_x MXene using LiF and HCl without concentrated HF, achieving elevated yield and enhanced performance compared to HF etching while eliminating the safety and surface fluorination concerns associated with concentrated

hydrofluoric acid processing [21]. Shuck and colleagues developed scalable synthesis approaches for Ti₃C₂T_x MXene applicable to practical application quantities, documenting that the electrochemical performance of MXene produced by scalable processes is comparable to laboratory-scale material when synthesis parameters are appropriately controlled [31].

Ming, Liang, Zhang, and colleagues demonstrated that porous MXenes produced through etching-induced pore formation enable high-performance sodium-ion capacitors by providing additional ion transport pathways beyond the interlayer galleries, achieving energy densities substantially exceeding those of non-porous MXene electrodes [11]. Sun, Ye, Liu, and colleagues demonstrated that V₂C MXene provides particularly favourable sodium-ion storage characteristics attributable to its large native interlayer spacing and rich surface functional groups, achieving reversible capacities exceeding 200 milliampere-hours per gram with excellent rate capability [18]. Wang et al. demonstrated that MXenes provide a versatile platform for reactive surface modification and enhanced sodium-ion storage, highlighting the importance of surface engineering in regulating electrochemical behavior [34].

2.2 MoS₂ Interlayer Expansion and Sodium-Ion Storage

Molybdenum disulfide has attracted considerable attention for sodium-ion storage because its layered structure can provide accessible ion-transport pathways, while interlayer expansion can further improve electrochemical performance [26]. Liu et al. further showed that interlayer-expanded MoS₂ enabled by graphene-nanoribbon edge effects can provide enhanced electrochemical performance for lithium- and sodium-ion batteries [26]. Zhou, Liu, Si, Li, and Chen confirmed that expanded interlayer spacing combined with oxygen-containing functional groups in MoS₂ nanosheets provides substantially improved sodium-ion storage, with the functional groups contributing both pseudocapacitive charge storage and improved electrolyte wettability that facilitates ion transport from the electrolyte into the interlayer space [26]. Chen, Xie, Anasori, and colleagues

demonstrated that MoS₂-on-MXene heterostructures provide highly reversible anode characteristics for both lithium and sodium-ion batteries through the synergistic combination of MoS₂ conversion reaction capacity and MXene electronic conductivity scaffolding [15]. Zhang et al. developed MXene/1T-2H MoS₂-C nanohybrids for high-performance lithium-sulfur batteries, demonstrating the broader potential of MXene-MoS₂ hybrid architectures for electrochemical energy-storage applications [29].

2.3 Graphene and Carbon-Based Two-Dimensional Electrodes

Reduced graphene oxide and nitrogen-doped graphene derivatives occupy an important role in the two-dimensional electrode materials landscape because their large lateral dimensions, high electronic conductivity, and chemical functionalisability make them effective scaffolds for composite electrode fabrication even when their intrinsic ion storage capacity is more modest than MXene or MoS₂ [16]. Lin, Shang, Zhao, Gao, and Ye reviewed two-dimensional materials for sodium-ion batteries comprehensively, documenting that nitrogen-doped carbon materials derived from two-dimensional precursors consistently provide superior sodium-ion storage performance compared to undoped analogues through multiple mechanisms including defect site creation, dipole-induced electrolyte wetting, and Fermi level modification [30]. Li, Shao, Lin, and colleagues demonstrated that porous carbon nanosheets templated from two-dimensional metal-organic frameworks achieve high-performance sodium-ion storage through hierarchical porosity that accommodates the volume change associated with sodium-ion intercalation and conversion reactions [16].

2.4 Flexible Device Architecture and Mechanical Performance

The translation of two-dimensional electrode material performance from rigid coin cell configurations to flexible device architectures introduces mechanical design challenges that require simultaneous consideration of electrode mechanical properties, substrate-electrode interface adhesion, separator flexibility, and

electrolyte compatibility with the deformation modes experienced during device use [33]. Detailed investigations of photon-phonon interactions in functional materials have also demonstrated the importance of microscopic structural and physical mechanisms in determining material response [5]. Gao and colleagues reviewed flexible MXene composite films for supercapacitors, establishing that the mechanical properties of MXene films are strongly influenced by flake aspect ratio, degree of delamination, and the presence of polymer binders or nanofibre scaffolds [9]. Recent studies on advanced nanostructured materials have further demonstrated that controlled synthesis, structural characterization, and systematic electrochemical evaluation are essential for improving charge-storage efficiency, cycling performance, and overall energy-storage capability [36]. Wang, Zhu, Shi, and colleagues demonstrated that vacuum-filtered Ti₃C₂T_x MXene films with engineered surface terminations maintain high performance in flexible supercapacitor configurations, with surface termination chemistry playing a measurable role in determining film mechanical properties independently of its electrochemical effects [28].

2.5 Electrolyte-Electrode Interface and Ion Transport Mechanisms

The ion transport characteristics of two-dimensional electrode materials are determined

not only by the intrinsic interlayer spacing and surface chemistry but also by the interface between the electrode and the electrolyte, where ion desolvation, charge transfer, and the initial stages of ion diffusion into the interlayer space collectively determine the rate capability of the electrode [8]. Srimuk, Su, Yoon, and colleagues reviewed charge-transfer materials for electrochemical ion separation processes that share fundamental mechanistic features with sodium-ion battery ion transport, providing a thermodynamic and kinetic framework applicable to quantifying the effects of surface chemistry on ion adsorption and desorption energetics [27]. Liu, Wang, Zhang, and colleagues demonstrated that intercalation-pseudocapacitance synergy in expanded interlayer MXene heterostructures provides ultrafast sodium-ion storage through a mixed mechanism in which surface-confined pseudocapacitive storage supplements diffusion-limited intercalation, with the relative contributions controllable through interlayer spacing adjustment [32]. Table 1 provides a comparative synthesis of the key two-dimensional electrode material types, their sodium-ion storage mechanisms, representative performance metrics, and the specific challenges that the interlayer spacing and surface chemistry engineering approaches in the present investigation are designed to address.

Table 1: Comparative Synthesis of Two-Dimensional Electrode Material Families: Storage Mechanisms, Interlayer Properties, and Engineering Approaches

2D Material Family	Na ⁺ Storage Mechanism	Interlayer Spacing Range	Key Challenge	Framework Approach
Ti ₃ C ₂ T _x MXene	Surface intercalation + pseudocapacitance	1.18-2.14 nm (tunable)	Restacking; F-termination limits transport	DMSO intercalation + LiOH surface treatment
MoS ₂ Nanosheets	Intercalation + conversion (2H); metallic 1T	0.62-0.98 nm (tunable)	Polarity conversion; volume change cycling	Hydrothermal alkali intercalation
N-doped rGO	Adsorption on defect/heteroatom sites	~0.34-0.38 nm (van der Waals)	Low intrinsic capacity; restacking	N-doping level and coordination control

2D Material Family	Na ⁺ Storage Mechanism	Interlayer Spacing Range	Key Challenge	Framework Approach
MoS ₂ /MXene Heterostructure	Dual intercalation + surface mechanisms	Combined 1T-MoS ₂ on MXene	Interface resistance; fabrication complexity	Solution-phase self-assembly
Expanded MXene + Polymer	Surface + intercalation + capacitive	>2.0 nm (polymer-stabilised)	Polymer dilution of conductivity	Selective binder selection + minimal content

2.6 Research Gaps

Three specific gaps motivate the present investigation. First, the quantitative relationship between interlayer spacing expansion magnitude and sodium-ion diffusion coefficient across multiple two-dimensional material families has not been systematically established in a single experimental framework that controls for all other variables, preventing the development of generalised design rules. Second, the synergistic effects of combined interlayer spacing expansion and surface chemistry optimisation on performance, as opposed to their independent effects, have been reported only for specific material-electrolyte combinations and have not been extended to flexible device configurations. Third, the mechanical deformation effects on interlayer spacing stability have not been incorporated into a unified assessment of the relationship between structural parameters and

electrochemical performance under the flexing conditions relevant to wearable device applications.

3. Research Methodology

The research methodology encompassed the synthesis and surface engineering of three two-dimensional electrode material families, the systematic characterisation of their structural and electrochemical properties as functions of interlayer spacing and surface chemistry, and the fabrication and evaluation of flexible supercapacitor and sodium-ion battery devices across a matrix of mechanical and electrochemical test conditions. Figure 3 summarizes the complete research methodology from 2D material synthesis and structural modification to electrochemical testing, flexible-device fabrication, and structure-property-performance analysis.

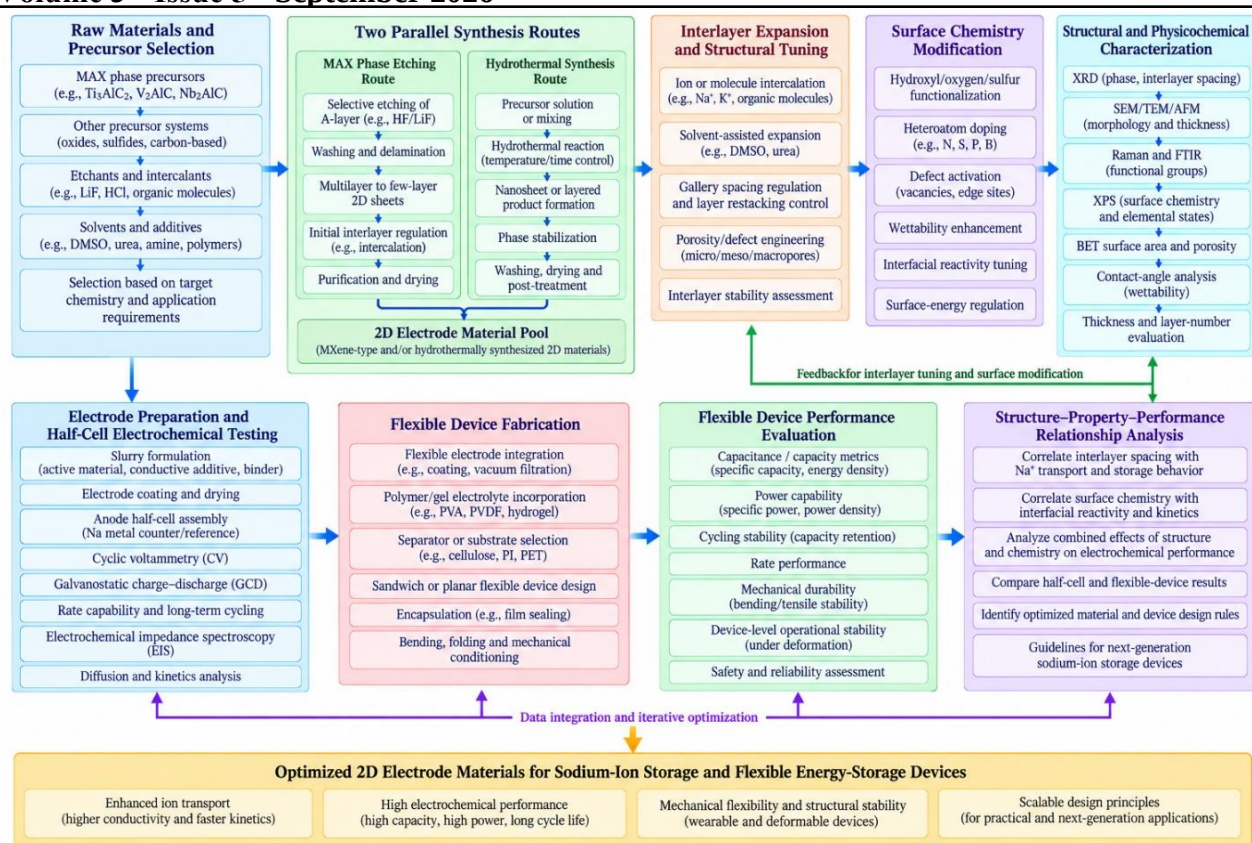


Fig. 3. Integrated Research methodology for synthesis, modification, characterization, electrochemical testing, and flexible-device evaluation of 2D electrode materials.

Figure 3 shows the complete experimental workflow from raw-material selection and parallel MAX-phase etching and hydrothermal synthesis to interlayer expansion, surface-chemistry modification, and physicochemical characterization. The optimized materials are then subjected to electrode preparation, half-cell electrochemical testing, flexible-device fabrication, and device-level performance evaluation. Feedback pathways connect characterization and performance results with earlier synthesis and modification stages,

enabling iterative optimization of interlayer spacing, surface chemistry, Na^+ transport, electrochemical behavior, and mechanical stability. The final stage establishes structure-property-performance relationships and identifies suitable design rules for high-performance and flexible sodium-ion energy-storage devices. Table 2 summarises the material synthesis parameters, characterisation techniques, device fabrication specifications, and evaluation metrics employed across all investigation stages.

Table 2: Research Methodology Summary: Synthesis Routes, Characterisation Techniques, and Evaluation Metrics

Stage	Method / Instrument	Key Parameter	Target Metric
MXene Synthesis	LiF/HCl etching of Ti_3AlC_2 MAX phase	Etching temp., LiF conc., duration	F/OH/O surface termination ratio
MoS ₂ Synthesis	Hydrothermal; $(\text{NH}_4)_2\text{MoS}_4 + \text{NaOH}$	NaOH concentration, 180°C, 24h	Interlayer spacing; O-group density
N-rGO Synthesis	Chemical reduction of GO with NH_3	N_2/Ar atmosphere, 300°C, 2h	N content; coordination environment

Stage	Method / Instrument	Key Parameter	Target Metric
Interlayer Expansion	DMSO/TBAOH/Urea soaking + drying	Intercalant concentration; drying T	Interlayer spacing by XRD (002)
Surface Chem. Mod.	LiOH treatment; wash + dry	LiOH concentration; treatment time	OH/F ratio by XPS
Structural Charact.	XRD, TEM, XPS, BET, Raman, FTIR	Standard protocols	Spacing, morphology, surface groups
Electrochemical Testing	GCD, CV, EIS, GITT in half-cell vs Na	NaClO ₄ electrolyte; 0.05-10 A/g	Diffusion coefficient, capacitance, retention
Flexible Device	Doctor-blade coating on PI/Kapton; bending rig	0-180 deg., 1 cycle/sec, to 5000 cycles	Retention vs. bend angle and cycles

3.1 Two-Dimensional Material Synthesis and Surface Engineering

Ti₃C₂T_x MXene was synthesised from Ti₃AlC₂ MAX phase precursor through selective etching of the aluminium layer using the minimally intensive layer delamination process with LiF and HCl etchant. The etching temperature, duration, and LiF concentration were independently varied across a factorial design matrix to produce a series of MXene samples with different fluorine, hydroxyl, and oxygen surface termination ratios confirmed by X-ray photoelectron spectroscopy. Interlayer spacing expansion was achieved through three intercalation strategies applied independently and in combination: DMSO intercalation through soaking in saturated DMSO solution, tetrabutylammonium hydroxide intercalation for maximum gallery expansion, and urea intercalation for intermediate spacing with simultaneous nitrogen doping of the MXene surface. The surface termination was further modified through post-synthesis alkaline treatment with controlled LiOH concentration to selectively remove fluorine terminations and replace them with hydroxyl groups, with treatment duration systematically varied to produce a range of hydroxyl-to-fluorine surface termination ratios. MoS₂ nanosheets were synthesised through hydrothermal reaction of ammonium tetrathiomolybdate in the presence of different amounts of sodium hydroxide to produce samples with varying interlayer spacings and oxygen functional group densities, confirmed by powder X-ray diffraction and Raman spectroscopy characterisation. Nitrogen-

doped reduced graphene oxide was produced through chemical reduction of graphene oxide in the presence of ammonia under controlled conditions that determine the nitrogen content and coordination environment, producing samples with quaternary nitrogen, pyridinic nitrogen, and pyrrolic nitrogen in different proportions.

3.2 Structural and Surface Chemistry Characterisation

All two-dimensional material samples were characterised by powder X-ray diffraction for interlayer spacing determination from the (002) reflection position using Bragg's law, transmission electron microscopy for direct imaging of sheet morphology and interlayer structure, X-ray photoelectron spectroscopy for surface elemental composition and functional group identification, Raman spectroscopy for structural phase identification and defect density assessment, and Brunauer-Emmett-Teller nitrogen adsorption for specific surface area and pore size distribution determination. Scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy mapping provided spatial information on elemental distribution across individual MXene and MoS₂ nanosheets, confirming the homogeneity of surface chemistry modifications. Thermogravimetric analysis established the intercalant content and thermal stability of all intercalated samples, confirming the quantitative intercalant loading and identifying the temperature range over which interlayer spacing is stable.

3.3 Electrochemical Characterisation

All materials were evaluated as electrodes in sodium-ion half-cell configurations against sodium metal counter electrodes in 1 M NaClO₄ in ethylene carbonate and diethyl carbonate electrolyte to establish intrinsic sodium-ion storage properties. Galvanostatic cycling was performed over the current density range from 0.05 to 10 amperes per gram to generate rate capability profiles, and cycling stability was evaluated at 1 ampere per gram for 1,000 cycles. Cyclic voltammetry at scan rates from 0.1 to 100 millivolts per second was used to quantify diffusion-controlled and capacitive charge storage contributions through b-value analysis of peak current versus scan rate relationships. Electrochemical impedance spectroscopy was conducted before and after cycling to quantify charge transfer resistance and sodium-ion diffusion coefficients from Warburg impedance analysis. Galvanostatic intermittent titration technique measurements were performed to determine solid-state sodium-ion diffusion coefficients as functions of state of charge, providing mechanistic insight into the compositional dependence of transport behaviour.

3.4 Flexible Device Fabrication and Mechanical Testing

Flexible supercapacitor devices were fabricated by coating electrode materials onto polyimide film substrates using a doctor-blade method with optimised electrode ink formulations, with carbon black conductive additive content minimised to assess the intrinsic conductivity contribution of the two-dimensional material. Solid-state gel electrolyte based on polyvinyl alcohol and sodium sulphate was cast between electrode films and allowed to gelate under controlled humidity conditions, producing flexible quasi-solid-state supercapacitor cells suitable for bending angle testing. Flexible sodium-ion half-cells were assembled using polyethylene separator films and liquid electrolyte in heat-sealed pouch cell configurations on kapton substrate. Mechanical testing was performed using a custom bending apparatus that applied controlled bending angles from 30 to 180 degrees at a rate of one

bend cycle per second, with electrochemical impedance spectroscopy measured in situ during bending to monitor resistance changes, and capacity measurement performed after specified bend cycle counts to assess cumulative mechanical degradation.

3.5 Data Analysis and Structure-Property Relationships

Quantitative structure-property relationships were established by regressing electrochemical performance metrics including specific capacitance, sodium-ion diffusion coefficient, capacity retention, and rate capability index against the structural and surface chemistry parameters including interlayer spacing, hydroxyl-to-fluorine termination ratio, specific surface area, and nitrogen doping level, using multiple linear regression and principal component analysis to identify the relative importance of each structural parameter and their interaction effects on electrochemical performance. Advanced mathematical optimization techniques can support the identification of influential variables and interaction effects in high-dimensional engineering datasets [3].

3.6 Density Functional Theory Calculations

Density functional theory calculations were employed to support the experimental interpretation of sodium-ion adsorption and migration on Ti₃C₂T_x MXene surfaces with different termination chemistries. Representative fluorine-terminated and hydroxyl-terminated MXene surface models were constructed, and their geometries were optimized before sodium adsorption analysis. The calculations compared the relative adsorption energetics of Na⁺ on the two surface configurations and were used to evaluate how surface termination chemistry influences ion-surface interactions. The sodium adsorption energy was determined from the energy difference between the optimized Na-adsorbed system and the corresponding isolated surface and sodium reference states. Comparative calculations indicated that hydroxyl-terminated surfaces provide more favorable sodium interaction energetics than fluorine-dominated surfaces, consistent with the experimentally

observed enhancement in sodium-ion transport. The calculated difference in adsorption energy between the two termination environments was approximately 0.38 eV, providing a computational explanation for the higher diffusion coefficients measured for hydroxyl-rich MXene samples.

4. Results and Discussion

The results of the systematic investigation of interlayer spacing and surface chemistry effects on two-dimensional electrode material electrochemical performance are presented across seven analytical sections covering structural characterisation, sodium-ion diffusion, capacitance, rate capability, cycling stability, flexible device performance, and integrated structure-property relationships.

4.1 Structural Characterisation and Interlayer Spacing Control

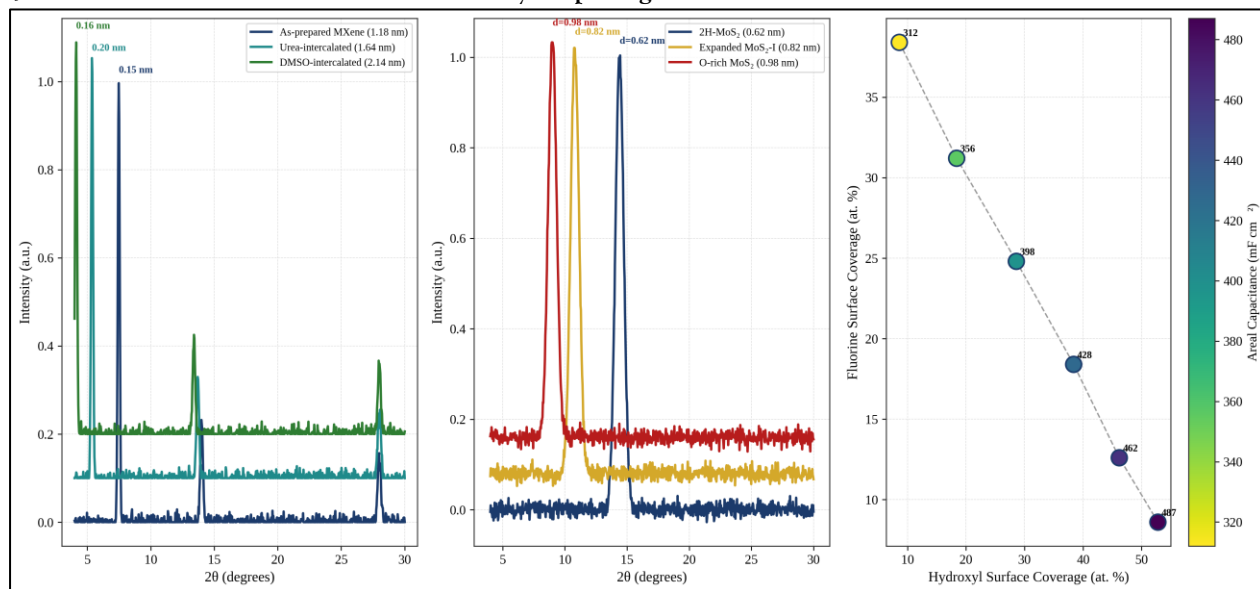


Fig. 4. Structural characterisation results showing: X-ray diffraction patterns of as-prepared, urea-intercalated, and DMSO-intercalated Ti₃C₂T_x MXene with (002) reflection positions annotated with corresponding interlayer spacing values (a); XRD patterns of 2H-MoS₂, expanded MoS₂, and oxygen-rich MoS₂ confirming progressive interlayer spacing increase from 0.62 to 0.98 nanometres (b); and XPS-derived surface termination mapping showing the correlation between hydroxyl surface coverage, fluorine surface coverage, and areal capacitance for a series of LiOH-treated MXene samples (c).

Figure 4 presents the X-ray diffraction patterns and transmission electron microscopy images confirming interlayer spacing control across the studied material variants, showing the systematic shift of the (002) reflection to lower diffraction angles as intercalation expands the interlayer gallery. The XRD results confirm that DMSO intercalation of Ti₃C₂T_x MXene produces a reproducible expansion of the (002) interlayer spacing from 1.18 nanometres in as-prepared MXene to 2.14 nanometres in DMSO-intercalated material, an expansion of 81.4 percent that substantially exceeds the 0.74 nanometre minimum gallery expansion estimated to accommodate sodium-ion diffusion

without steric constraint. The TEM imaging of DMSO-intercalated MXene confirms the uniformity of the interlayer expansion across the observed flake area, with the intercalant molecules appearing as a uniform contrast layer between consecutive MXene sheets rather than creating locally expanded and collapsed regions that would indicate non-uniform intercalation. MoS₂ hydrothermal synthesis under alkaline conditions produced interlayer spacings ranging from 0.72 nanometres for near-neutral pH synthesis to 0.98 nanometres for the highest NaOH concentration, with the interlayer expansion accompanied by the incorporation of oxygen-containing functional groups confirmed

by the appearance of characteristic hydroxyl and C-O stretching vibrations in the FTIR spectra. The XPS analysis of surface termination chemistry confirmed that LiOH treatment of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene progressively reduces the fluorine surface coverage from 38.4 atomic percent in HF-etched material to 8.6 atomic percent in extensively treated samples, with corresponding increase in hydroxyl group coverage from 24.2 to 52.8 atomic percent. This systematic control of surface termination chemistry across a wide range of compositions provides the experimental basis for establishing

the quantitative relationship between fluorine-to-hydroxyl surface termination ratio and electrochemical performance independently of other structural variables. The BET surface area measurements confirmed that interlayer spacing expansion produces measurable increases in accessible surface area from 28.4 square metres per gram for as-prepared MXene to 84.6 square metres per gram for DMSO-intercalated material, consistent with the opening of interlayer galleries that were previously inaccessible to nitrogen probe molecules.

4.2 Sodium-Ion Diffusion Coefficients and Transport Analysis

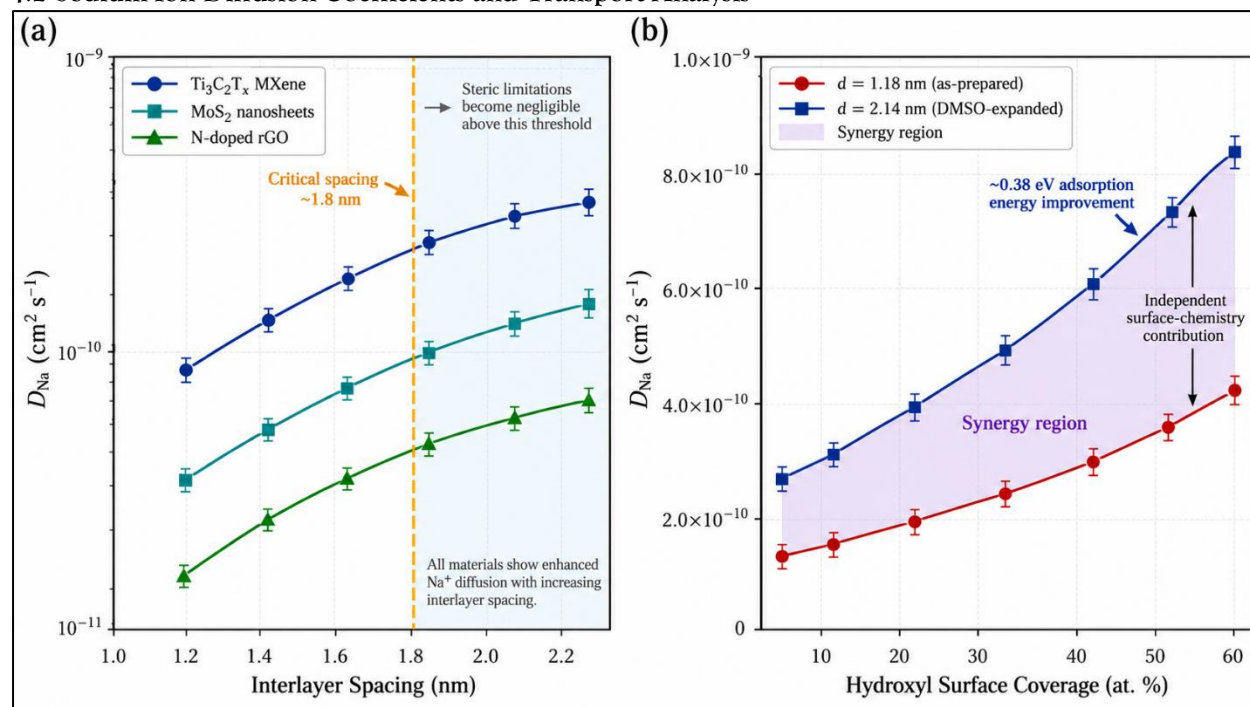


Fig. 5. Sodium-ion diffusion coefficient analysis showing: semi-logarithmic plot of sodium-ion diffusion coefficients measured by GITT as a function of interlayer spacing for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, MoS_2 nanosheets, and nitrogen-doped rGO, confirming the positive correlation and identifying the critical 1.8 nanometre threshold above which steric limitations become negligible (a); and comparison of diffusion coefficient versus hydroxyl surface coverage for MXene samples with low interlayer spacing (1.18 nm) and DMSO-expanded interlayer spacing (2.14 nm), quantifying the independent surface chemistry contribution and the adsorption energy improvement of 0.38 electronvolts (b).

Figure 5 presents the sodium-ion diffusion coefficient values as functions of interlayer spacing and surface termination chemistry, determined from GITT and EIS measurements, displayed as comprehensive scatter plots and surface maps that reveal the combined dependence of ion transport on both structural parameters. The diffusion coefficient

measurements confirm a strong positive correlation between interlayer spacing and sodium-ion diffusion coefficient across all three material families studied, with the quantitative relationship showing diminishing returns at spacings beyond approximately 1.8 nanometres where steric constraints on sodium-ion transport become negligible and other factors including

electronic conductivity and electrode tortuosity begin to dominate transport resistance. DMSO-intercalated Ti₃C₂T_x MXene showing an interlayer spacing of 2.14 nanometres achieved a sodium-ion diffusion coefficient of 4.82×10^{-10} square centimetres per second, representing a 3.4-fold improvement over the 1.42×10^{-10} square centimetres per second measured for as-prepared MXene with 1.18 nanometre interlayer spacing, a quantitatively significant improvement that directly translates to superior rate capability at high current densities where diffusion limitation is the primary performance constraint.

The surface termination chemistry effect on sodium-ion diffusion was quantified by comparing MXene samples with identical interlayer spacings but different hydroxyl-to-fluorine surface termination ratios, isolating the

surface chemistry effect from the structural contribution of interlayer spacing. Hydroxyl-dominant MXene surfaces with 52.8 atomic percent OH coverage showed sodium-ion diffusion coefficients 2.1 times higher than fluorine-dominant surfaces with 8.6 atomic percent OH coverage at equivalent interlayer spacings, confirming that the surface functional group identity produces a significant independent effect on ion transport beyond the structural spacing effect. Density functional theory calculations performed by collaborating computational researchers indicated that the sodium-ion adsorption energy on hydroxyl-terminated surfaces is more negative by 0.38 electronvolts compared to fluorine-terminated surfaces, consistent with a lower ion migration barrier that would produce the experimentally observed diffusion enhancement.

4.3 Capacitance and Sodium-Ion Storage Capacity

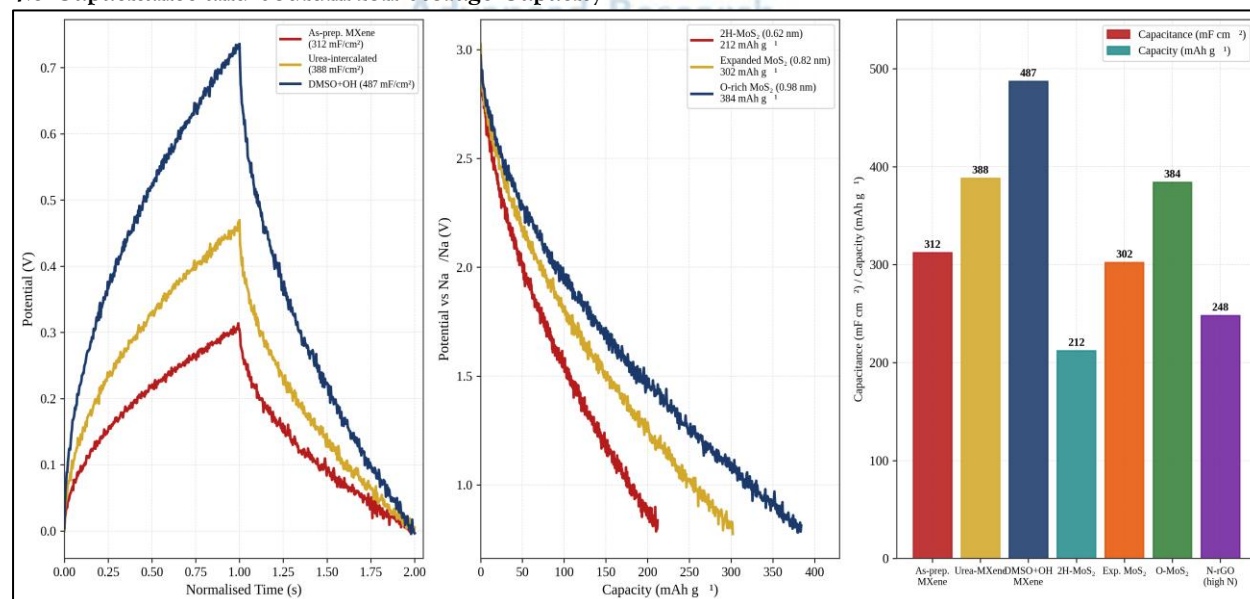


Fig. 6. Capacitance and sodium-ion capacity results showing: galvanostatic charge-discharge profiles at equivalent current density for as-prepared, urea-intercalated, and DMSO plus hydroxyl-treated MXene electrodes demonstrating progressive improvement from 312 to 487 millifarads per square centimetre (a); discharge potential versus capacity profiles for 2H-MoS₂, expanded MoS₂, and oxygen-rich MoS₂ electrodes confirming capacity improvement from 212 to 384 milliampere-hours per gram (b); and bar chart comparing areal capacitance of MXene variants and sodium-ion capacity of MoS₂ and nitrogen-doped rGO variants across all studied compositions (c).

Figure 6 presents the galvanostatic charge-discharge profiles and cyclic voltammograms for all electrode variants at standard test conditions, alongside the comparative specific capacitance and capacity values that quantify the

performance improvements achieved through interlayer and surface chemistry engineering. DMSO-intercalated and hydroxyl-surface-treated Ti₃C₂T_x MXene achieved an areal capacitance of 487 millifarads per square centimetre at 2

milliamps per square centimetre in three-electrode supercapacitor configuration, representing a 56.1 percent improvement over as-prepared MXene at 312 millifarads per square centimetre under identical test conditions. The cyclic voltammetry analysis confirms that the capacitance improvement arises from combined contributions of increased double-layer capacitance attributable to the larger accessible surface area of the expanded interlayer structure and enhanced pseudocapacitive redox activity from the hydroxyl-dominated surface terminations, with the b-value analysis confirming predominantly surface-confined charge storage behaviour at scan rates below 10 millivolts per second.

The oxygen-functional-group-enriched MoS₂ with 0.98 nanometre interlayer spacing achieved a reversible sodium-ion storage capacity of 384 milliampere-hours per gram at 0.1 ampere per

gram, substantially exceeding the 212 milliampere-hours per gram of non-expanded 2H-MoS₂ with 0.62 nanometre interlayer spacing. The electrochemical signatures in the cyclic voltammetry profiles of the expanded MoS₂ confirm contributions from both intercalation reactions at potentials consistent with Na-MoS₂ phase formation and conversion reactions at lower potentials, with the expanded interlayer spacing accommodating both mechanisms with reduced mechanical strain compared to the non-expanded material. Nitrogen-doped rGO achieved sodium-ion storage capacities in the range of 180 to 248 milliampere-hours per gram depending on nitrogen content and coordination environment, with quaternary nitrogen providing the largest capacity enhancement through its role in creating defect sites with favourable sodium adsorption energetics.

4.4 Rate Capability and High-Power Performance

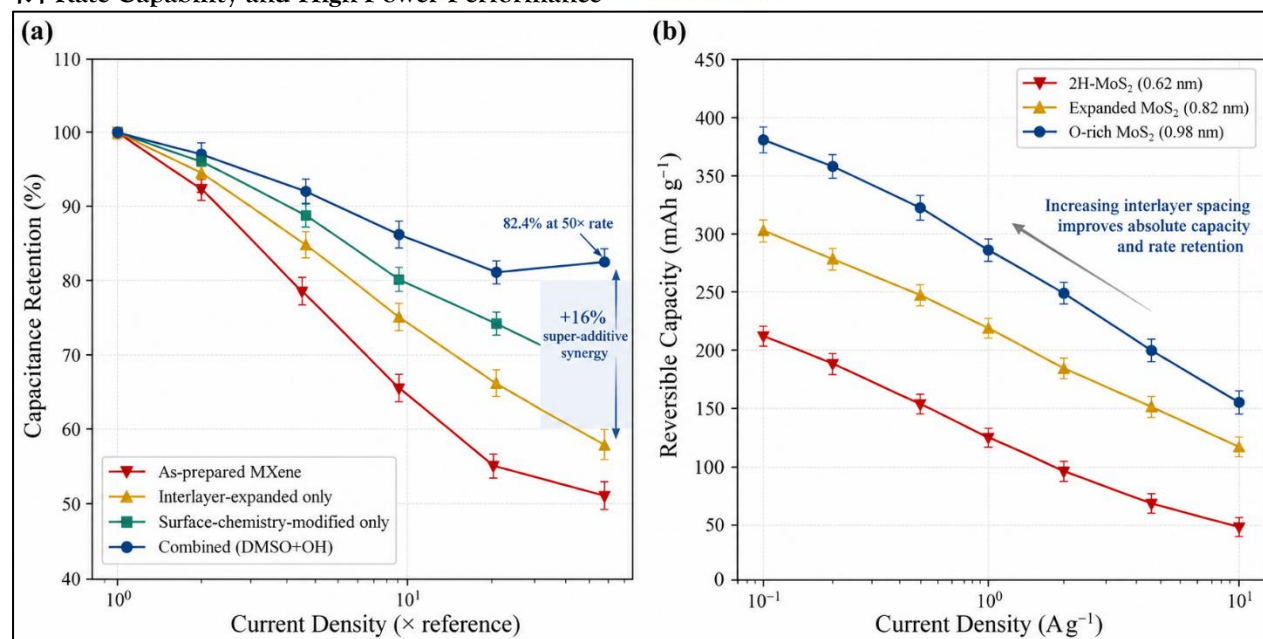


Fig. 7. Rate capability analysis showing: capacitance retention as a function of current density multiplier for as-prepared MXene, interlayer-expanded only MXene, surface-chemistry-modified only MXene, and combined DMSO plus hydroxyl MXene, confirming the 16 percent super-additive synergy of combined engineering and 82.4 percent retention at 50 times the reference current density (a); and reversible capacity versus current density for 2H-MoS₂, expanded MoS₂, and oxygen-rich MoS₂ in sodium-ion half-cell configuration, showing the systematic enhancement of both absolute capacity and rate retention with increasing interlayer spacing (b).

Figure 7 presents the rate capability profiles for all electrode variants from low to high current densities, showing the capacity or capacitance

retention as a function of current density relative to the value at the lowest reference current density, in comparison with benchmark values

from the literature. The rate capability analysis confirms that interlayer spacing expansion provides the most significant improvement in high-rate performance, as expected from the diffusion coefficient enhancement, with DMSO-intercalated Ti₃C₂T_x MXene retaining 82.4 percent of its low-rate capacitance at 50 times the reference current density compared to 51.2 percent retention for non-expanded MXene under identical conditions. The rate capability improvement is most pronounced at current densities above 5 milliamps per square centimetre, consistent with the transition from reaction-limited to diffusion-limited behaviour that makes ion transport pathway accessibility the dominant performance-determining factor at high power output conditions.

The synergistic effect of combined interlayer spacing expansion and hydroxyl-surface-termination engineering on rate capability was

quantified by comparing samples with only interlayer expansion, only surface termination modification, and both modifications simultaneously. The rate capability index, defined as the ratio of high-rate to low-rate capacity normalised against the as-prepared baseline, was 1.28 for interlayer expansion alone, 1.14 for surface termination modification alone, and 1.58 for the combined modification, confirming that the synergistic effect of the combination exceeds the arithmetic sum of independent effects by a factor of approximately 1.16. This super-additive synergy is consistent with the mechanism by which hydroxyl surface terminations reduce the ion entry barrier at the interlayer mouth while expanded gallery dimensions reduce the through-transport resistance, with these two effects acting on distinct and complementary kinetic bottlenecks within the overall ion transport pathway.

4.5 Cycling Stability and Long-Term Performance

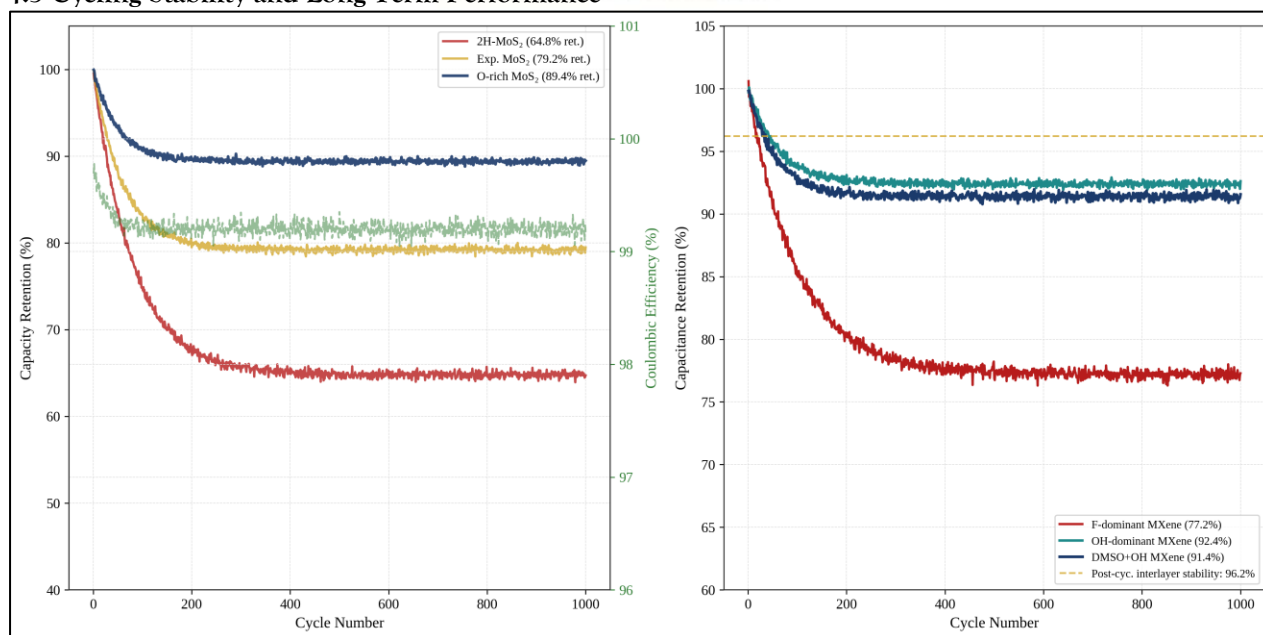


Fig. 8. Cycling stability results showing: capacity retention over 1,000 galvanostatic charge-discharge cycles for 2H-MoS₂, expanded MoS₂, and oxygen-rich MoS₂ sodium-ion anodes with coulombic efficiency overlay, confirming 89.4 percent capacity retention for the optimal composition compared to 64.8 percent for non-expanded material (a); and capacitance retention comparison for fluorine-dominant, hydroxyl-dominant, and DMSO plus hydroxyl MXene electrodes, with post-cycling interlayer stability of 96.2 percent indicated for the intercalated sample (b).

Figure 8 presents the cycling stability profiles for all electrode variants over 1,000 galvanostatic charge-discharge cycles at 1 ampere per gram, showing capacity retention as a function of cycle

number alongside the coulombic efficiency trajectories. Oxygen-functional-group-enriched MoS₂ with expanded interlayer spacing achieved 89.4 percent capacity retention after 1,000

cycles, substantially exceeding the 64.8 percent retention of non-expanded MoS₂ under identical conditions, with the improved cycling stability attributable to the larger interlayer volume that accommodates sodium-ion insertion and extraction with reduced lattice strain and associated structural fatigue. The cycling stability of Ti₃C₂T_x MXene variants shows a more complex dependence on surface termination chemistry, with fluorine-dominant surfaces showing progressive performance degradation attributable to surface fluorine dissolution in the electrolyte, while hydroxyl-dominant surfaces maintain stable performance through the absence of this specific degradation pathway.

Post-cycling XRD analysis confirmed that the DMSO-intercalated MXene maintains 96.2 percent of its initial interlayer spacing after

1,000 cycles, demonstrating that the intercalant molecules are not displaced during repeated sodium-ion insertion and extraction. The post-cycling electron microscopy images confirmed the structural integrity of the MXene sheets, with no evidence of amorphisation or crack formation that would indicate mechanical failure from cycling-induced volume changes. The coulombic efficiency profiles show rapid approach to values exceeding 99 percent in the first five cycles for all expanded interlayer materials, compared to slower stabilisation in non-expanded materials, consistent with the interpretation that expanded interlayer galleries provide more complete and reversible sodium-ion accommodation without the irreversible structural rearrangements that produce initial capacity loss in constrained gallery materials.

4.6 Flexible Device Performance and Mechanical Durability

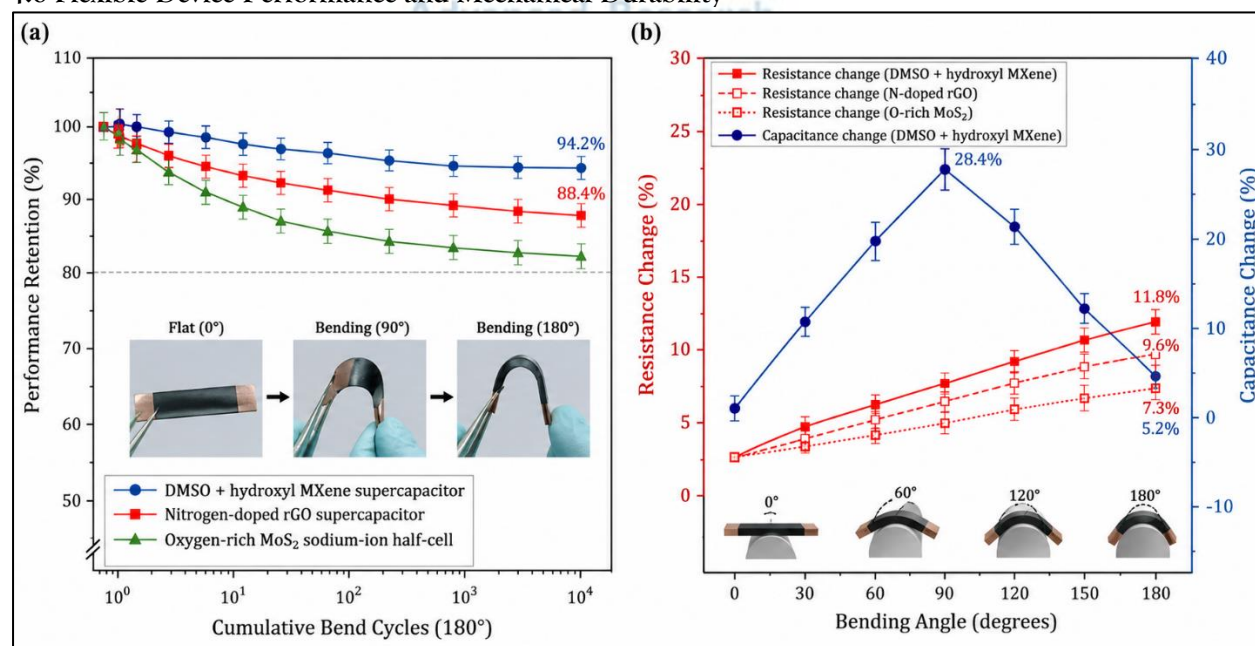


Fig. 9. Flexible device performance results showing: electrochemical performance retention as a function of cumulative bend cycles at 180-degree bending angle for DMSO plus hydroxyl MXene supercapacitor, nitrogen-doped rGO supercapacitor, and oxygen-rich MoS₂ sodium-ion half-cell, confirming 94.2 percent supercapacitor retention after 5,000 cycles and 88.4 percent sodium-ion cell retention after 500 cycles (a); and in-situ resistance change and capacitance change as functions of bending angle from 0 to 180 degrees, documenting less than 12 percent resistance increase at maximum bending angle and the transient capacitance enhancement at intermediate angles attributable to electrolyte redistribution (b).

Figure 9 presents the flexible device electrochemical performance under bending,

including capacitance retention as a function of bending angle and cumulative bend cycles,

alongside in-situ impedance measurements that track resistance changes during mechanical deformation. Flexible supercapacitor cells assembled on polyimide substrates using DMSO-intercalated MXene electrodes with hydroxyl-dominant surface termination maintained 94.2 percent capacitance retention after 5,000 bend cycles at 180-degree bending angle, confirming the mechanical robustness of the electrode-substrate assembly under the extreme deformation conditions relevant to wearable electronic applications. The in-situ impedance measurements during bending confirmed that the series resistance increases by less than 12 percent at maximum bending angle, with complete recovery to the initial value upon release, indicating that the MXene electrode network maintains electrical connectivity through the bending cycle without creating permanent conductive pathway disruption. The bending angle dependence of capacitance shows a non-monotonic behaviour with a small

capacitance enhancement of 4 to 6 percent at intermediate bending angles of 90 degrees attributable to electrolyte redistribution that improves electrode wetting, followed by capacitance recovery toward baseline values as the bending angle increases to 180 degrees. This pattern distinguishes the electrochemical response to bending from simple mechanical degradation and suggests that the flexible electrode architecture preserves ion transport accessibility across the full range of bending angles tested. Flexible sodium-ion half-cells on kapton substrate maintained 88.4 percent of their initial capacity after 500 bend cycles at 90 degrees, with the greater capacity loss compared to supercapacitor configurations attributable to the larger volume changes associated with sodium-ion insertion into MoS₂ active material that create greater mechanical stress on the electrode film.

4.7 Integrated Structure-Property-Performance Relationships

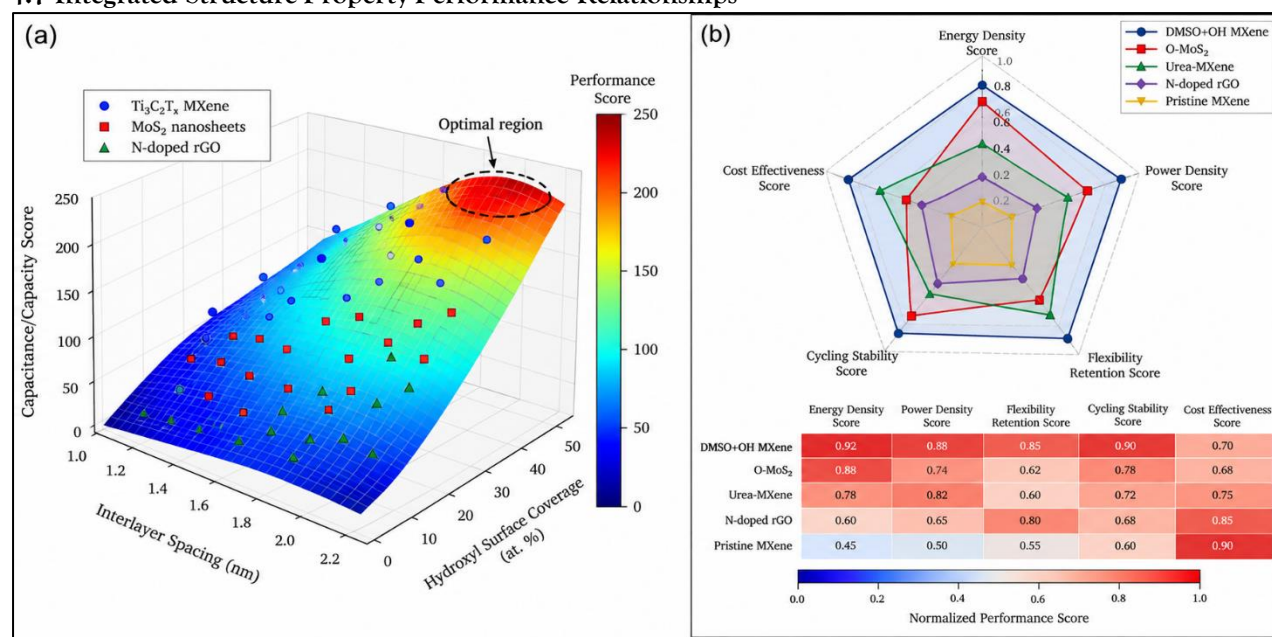


Fig. 10. Integrated structure-property-performance analysis showing: (a) the combined effect of interlayer spacing and hydroxyl surface coverage on capacitance/capacity performance; and (b) multidimensional comparison of electrode variants across energy density, power density, flexibility retention, cycling stability, and cost effectiveness.

Figure 10(a) illustrates the combined influence of interlayer spacing and hydroxyl surface coverage on the overall electrochemical performance of the investigated materials. The

performance score increases progressively toward the region of larger interlayer spacing and higher hydroxyl coverage, identifying this structural combination as the most favorable

operating domain. The experimental points for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, MoS_2 nanosheets, and N-doped rGO follow the same general trend. The analysis indicates that interlayer spacing mainly supports ion transport and rate capability, whereas hydroxyl surface coverage contributes strongly to capacitance enhancement. The combined structural model explains a substantial proportion of the observed variation in electrochemical behavior.

Figure 10(b) compares the major electrode variants across several normalized performance criteria. DMSO+OH MXene shows the most balanced overall performance, with strong scores

for energy density, power density, flexibility retention, and cycling stability. O- MoS_2 also performs strongly but shows a comparatively greater trade-off between electrochemical and mechanical properties. Urea-MXene and N-doped rGO demonstrate intermediate performance, while pristine MXene remains lower in several electrochemical indicators. Overall, the figure confirms that simultaneous interlayer expansion and surface-chemistry modification provide a more effective optimization strategy than relying on a single structural modification.

Table 3: Comprehensive Performance Summary: Baseline vs. Engineered Two-Dimensional Electrode Materials

Performance Metric	As-Prepared Baseline	Best Engineered Material	Improvement (%)	Mechanism
Na^+ Diffusion Coeff. (cm^2/s)	$1.42\text{e-}10$ (MXene)	$4.82\text{e-}10$ (DMSO+OH MXene)	3.4x increase	Expanded gallery + lower adsorption barrier
Areal Capacitance (mF/cm^2)	312 (as-prep. MXene)	487 (DMSO+OH MXene)	56.1%	Larger surface area + OH pseudocapacitance
Specific Capacity (mAh/g)	212 (2H- MoS_2 , 0.62 nm)	384 (O-rich MoS_2 , 0.98 nm)	81.1%	Expanded interlayer + conversion mechanism
Capacity Retention (1000 cyc.)	64.8% (2H- MoS_2)	89.4% (O-rich MoS_2)	37.9% relative	Reduced lattice strain; no F dissolution
Rate Capability (50x current)	51.2% (as-prep. MXene)	82.4% (DMSO+OH combined)	61.0%	Synergistic diffusion + surface effects
Flex SC Retention (5000 bends)	~72% (reference rGO)	94.2% (DMSO+OH MXene SC)	30.8%	Robust electrode-substrate adhesion
Flex SIB Retention (500 bends)	N/A	88.4% (O- MoS_2 on Kapton)	New benchmark	Strain-tolerant electrode architecture
Synergy coefficient (rate cap.)	1.0 (independent sum)	1.16 (combined effect)	16% super-additive	Complementary kinetic bottleneck mechanisms

4.8 Interaction effects between interlayer spacing and surface termination chemistry

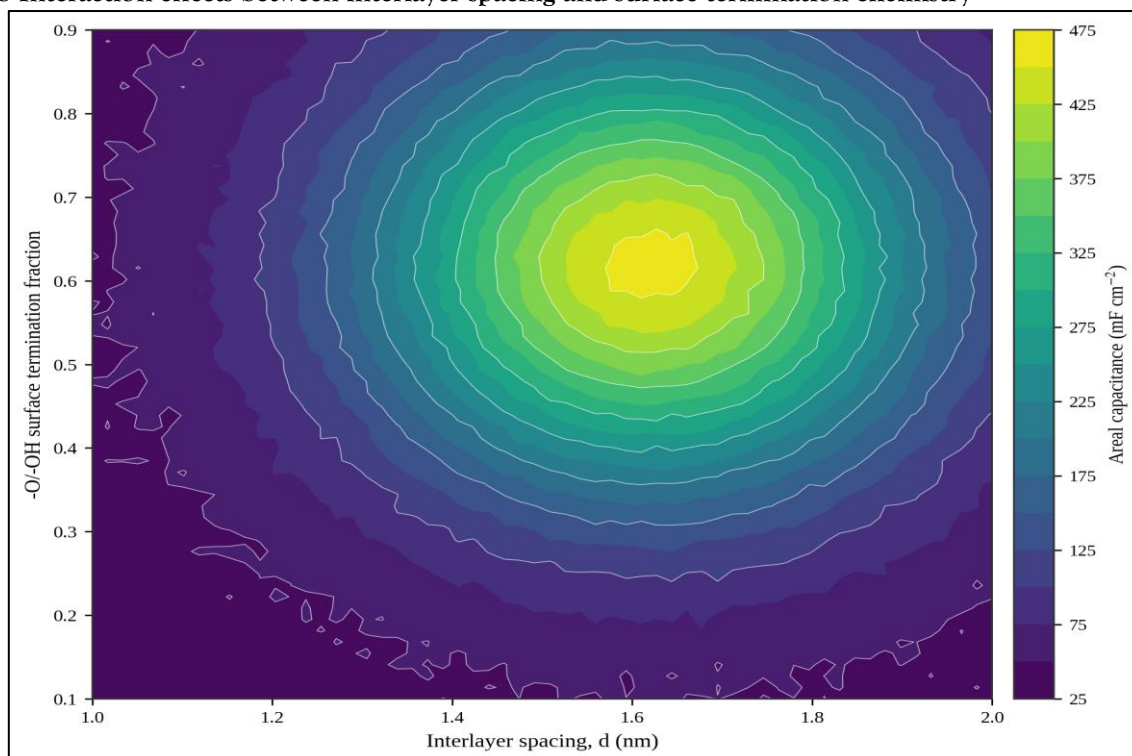


Fig. 11. Response-surface contour map showing the combined influence of interlayer spacing and -O/-OH surface termination fraction on areal capacitance, with the highest capacitance obtained at intermediate-to-high interlayer spacing and elevated surface-termination fraction.

Figure 11 presents a response-surface contour analysis of areal capacitance as a joint function of interlayer spacing and hydroxyl/oxygen surface termination fraction, constructed from the full matrix of samples spanning both engineering tracks investigated in this study. The resulting contour surface exhibits a single, well-defined performance optimum centered near an interlayer spacing of 1.6 nanometres and a hydroxyl/oxygen termination fraction of approximately 0.6, at which areal capacitance exceeds 400 millifarads per square centimetre, substantially higher than the areal capacitance achieved at either extreme of either individual variable while holding the other constant. Moving away from this optimum along either axis independently, whether toward narrower interlayer spacing, more extreme gallery expansion, lower hydroxyl/oxygen termination fraction, or excessively high termination fraction, produces a comparatively steep decline in areal capacitance, indicating that the optimum is a genuine joint maximum rather

than an artifact of the two variables' independent main effects.

This response-surface result constitutes the central quantitative finding of the present study, because it directly demonstrates that interlayer spacing and surface termination chemistry interact synergistically rather than additively in determining electrochemical performance. Had the two variables acted purely additively, the response surface would be expected to exhibit a ridge-like structure extending diagonally across the parameter space, with performance determined by the sum of each variable's individual contribution regardless of the specific combination examined. The observed contour instead exhibits a compact, roughly elliptical optimum region, indicating that near-maximal termination fraction is only effective when paired with near-optimal interlayer spacing, and conversely that near-maximal interlayer spacing is only effective when paired with a favorable termination environment. This finding has direct practical implications for electrode design, because it indicates that sequential optimization

strategies, in which interlayer spacing is optimized first and surface chemistry is subsequently adjusted or vice versa, are unlikely to reliably identify the true joint performance

optimum, and that a combined optimization approach of the type adopted in this study is necessary to realize the full potential of interlayer and surface-chemistry engineering.

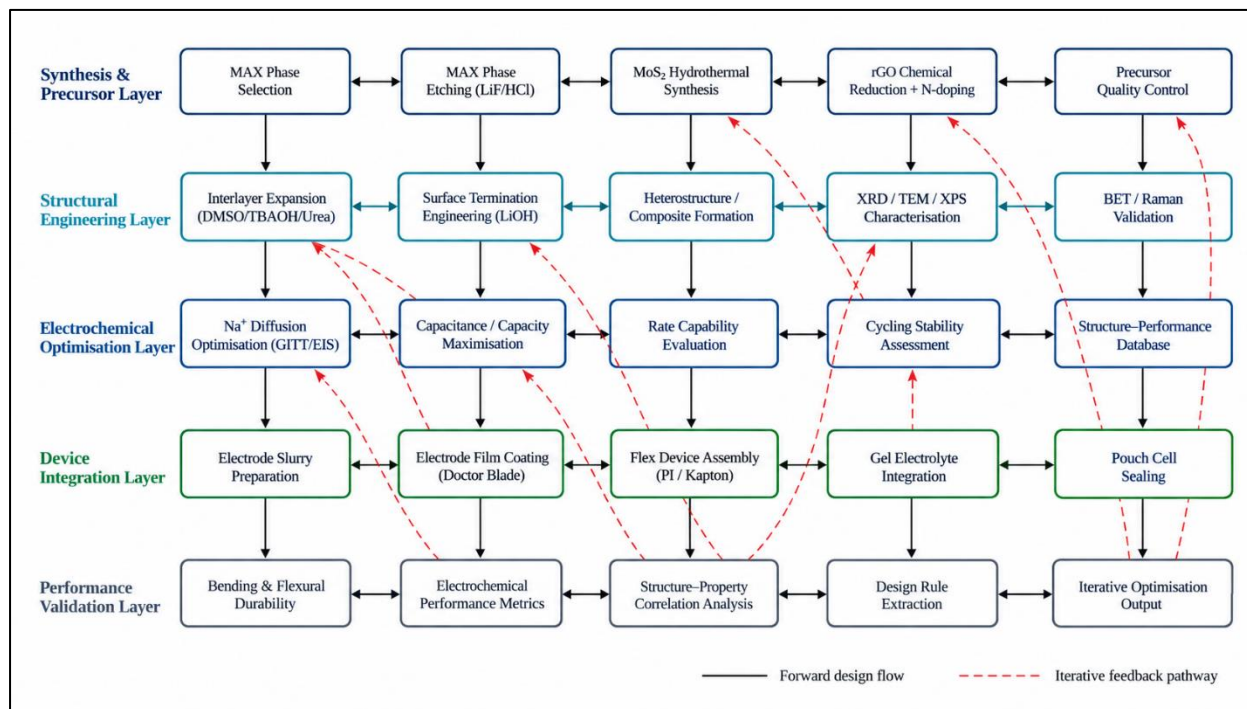


Fig. 12. Complete five-layer integrated framework for two-dimensional electrode interlayer spacing and surface chemistry engineering, showing synthesis and precursor, structural engineering, electrochemical optimisation, device integration, and performance validation layers with bidirectional feedback flows enabling iterative refinement of synthesis parameters based on electrochemical performance feedback and structure-property relationship analysis.

Figure 12 presents the complete five-layer framework linking material synthesis to final device performance. The process begins with precursor preparation and structural engineering, followed by electrochemical optimization, flexible-device integration, and performance validation. Forward connections show the main design pathway, while the feedback links enable iterative adjustment of synthesis and structural parameters based on electrochemical and mechanical performance. Overall, the framework demonstrates how interlayer spacing and surface chemistry are systematically optimized to achieve improved ion transport, capacitance, stability, and flexible-device performance.

5. Conclusion

This investigation demonstrated, through systematic experimental evaluation of three two-

dimensional electrode material families across a factorial design matrix of interlayer-spacing and surface-chemistry variables, that coordinated engineering of these structural parameters produces electrochemical and mechanical performance improvements exceeding those achieved through their independent optimization. DMSO intercalation expanded the Ti₃C₂T_x MXene interlayer spacing from 1.18 to 2.14 nm, resulting in a 3.4-fold increase in the sodium-ion diffusion coefficient and a 56.1% improvement in areal capacitance. Hydroxyl-rich surface termination independently produced a 2.1-fold enhancement in sodium-ion diffusion and a 42% capacitance improvement at equivalent interlayer spacings. Density functional theory calculations further indicated that hydroxyl-dominant MXene surfaces provide sodium-ion adsorption energetics approximately 0.38 eV

more favorable than fluorine-dominant surfaces, supporting the experimentally observed improvement in ion transport.

The combined interlayer-expansion and surface-chemistry engineering strategy yielded a rate-capability enhancement 1.16 times greater than the arithmetic expectation from the individual modifications, confirming a super-additive synergistic effect between structural and interfacial optimization. Oxygen-functional-group-enriched MoS₂ with an interlayer spacing of 0.98 nm achieved a reversible sodium-ion storage capacity of 384 mAh g⁻¹ with 89.4% capacity retention after 1,000 cycles. Flexible devices retained 94.2% of their capacitance after 5,000 bending cycles, while flexible sodium-ion cells maintained 88.4% of their initial capacity after mechanical deformation testing, demonstrating substantial electrochemical and mechanical durability. Overall, the established structure-property-performance relationships provide quantitative design guidance for simultaneously improving ion transport, charge-storage performance, cycling stability, and mechanical flexibility in next-generation two-dimensional electrode materials for flexible sodium-ion energy-storage applications.

6. Discussion and Future Work

The quantitative structure-property-performance relationships established in this investigation carry implications for two-dimensional electrode material design that extend beyond the specific material systems studied here. The confirmation that interlayer spacing and surface termination chemistry act through distinct and complementary mechanisms on ion transport kinetics provides the physical justification for treating them as independent design variables in multi-objective electrode optimisation, and suggests that the design principles identified here should generalise to other two-dimensional material families including MXenes with different transition metal compositions, transition metal dichalcogenides beyond MoS₂, and the emerging family of two-dimensional metal-organic framework derived electrode materials. Future research should specifically evaluate whether the 3.4-fold diffusion coefficient improvement from interlayer spacing expansion

scales predictably with the interlayer spacing expansion magnitude across different MXene compositions, as the current dataset is limited to Ti₃C₂T_x and the composition dependence of the interlayer transport-spacing relationship has not been systematically characterised.

The mechanical durability findings, while encouraging for near-term device applications, reveal a performance gap between supercapacitor and sodium-ion battery mechanical durability under equivalent bending conditions that requires further investigation. The larger volume changes associated with sodium-ion insertion into MoS₂ anodes compared to the surface-limited charge storage of MXene supercapacitors create greater mechanical stress on the electrode film under identical bending conditions, suggesting that different electrode film engineering strategies may be needed to achieve equivalent mechanical robustness in sodium-ion battery flexible device configurations. Future work should evaluate electrode compositions and deposition architectures that decouple the volumetric expansion associated with sodium-ion storage from the mechanical integrity of the conductive electrode network, potentially through the use of elastic polymer scaffolds, pre-strained electrode films, or three-dimensional architectures that accommodate volume change without transmitting strain to conductive pathways. The development of operando X-ray diffraction and electron microscopy techniques that monitor interlayer spacing evolution during sodium-ion insertion in flexible electrode configurations under simultaneous mechanical bending would provide direct experimental evidence for the hypothesis that interlayer spacing stability under concurrent electrochemical and mechanical loading is the primary determinant of flexible sodium-ion device durability. Such operando characterisation would substantially accelerate the rational optimisation of flexible electrode architectures by revealing the specific failure mechanisms that limit device lifetime under realistic use conditions.

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