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Modification and Self-assembly of Layered Materials for Energy Storage Applications

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Abstract

Layered materials are considered as promising candidates as cathode and anode materials for various energy storage applications, such as supercapacitors, lithium-ion batteries, sodium-ion batteries, etc., due to their unique structures and extraordinary properties. However, the further improvement of their performance for electrochemical energy storage devices is limited by issues, for example self-stacking of the layer materials, sluggish ions intercalation, and lack of the active sites on the surface.

This thesis explores several strategies including 1) self-assemble layered materials into 3dimentional (3D) structures, 2) surface modification of layered materials, and 3) modulation of electrode structure to address the aforementioned issues with the aim to enhance the electrochemical performance of layered materials for supercapacitor and aluminum battery. The first part of the thesis explores ice-template methods for self-assembly of graphene and Ti₃C₂T_x MXene into a 3D structure and their effects on supercapacitor performance. The results from the first part indicated that the formed structure of as-prepared layered materials was widely distributed with outstanding integrity. The intrinsic structure makes it possible to exhibit superior specific gravimetric capacitance and rate capability when applied as electrode materials for supercapacitors. The second part of the thesis investigated the effect of surface modification via hydrogen plasma treatment on graphite materials as cathode for aluminum batteries. The galvanostatic charge-discharge measurements results demonstrated that hydrogen plasma-treated graphite delivers excellent performance, achieving a high specific capacity of 132.68 mAh/g at 50 mA/g and impressive rate capability with 83.94 mAh/g at 1000 mA/g. The third part of the thesis explored the influence of porous structure fabrication and nitrogen doping on graphene-based cathode for aluminum batteries. The electrochemical test results indicated a high reversible specific capacity for the porous nitrogen-doped graphene cathode (65.5 mAh/g at 0.1 A/g) and excellent rate performance (38.0 mAh/g at 5 A/g).

Herein, this thesis provides a systematic investigation of surface modification and selfassembly of layered materials, which provide alternative and efficient methods to improve the energy storage performance of layered materials.

Keywords: Layered Materials, Self-assembly, Surface Modification, Supercapacitors, Aluminum Batteries.

Preface

This licentiate thesis is based on the work performed in the Department of Industrial and Materials Science at Chalmers University of Technology from September 2022 to June 2025. The work was carried out under the main supervision of Associate Professor Jinhua Sun and co-supervision of Professor Lars Nyborg. The examiner was Professor Uta Klement. The work was funded by FLAG-ERA project (2021-05924).

List of Appended Papers:

Paper I Plasma surface engineering of graphite and its effect on the performance of aluminum battery

<u>Ruiqi Chen</u>, Neelakandan M. Santhosh, Komal Gola, Nitish Kumar, Janez Zavasnik, Jinhua Sun*, Uroš Cvelbar

Manuscript to be submitted

Paper II Manufacturing graphene based porous electrode to improve the performance of aluminum battery

<u>Ruiqi Chen</u>, Neelakandan M. Santhosh, Komal Gola, Nitish Kumar, Uta Klement, Lars Nyborg, Eva Kovacevic, Uroš Cvelbar, Jinhua Sun*

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Papers not included in this thesis:

(* corresponding author)

Paper AThe Combination of 2D Layered Graphene Oxide and 3D Porous CelluloseHeterogeneous Membranes for Nanofluidic Osmotic Power Generation

Pan Jia, Xinyi Du, <u>Ruiqi Chen</u>, Jinming Zhou, Marco Agostini, Jinhua Sun and Linhong Xiao*

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Paper B Surface chemistry and structure manipulation of graphene-related materials to address the challenges of electrochemical energy storage

Yue Sun, Jinhua Sun*, Jaime S. Sanchez, Zhenyuan Xia, Linhong Xiao, <u>Ruiqi</u> <u>Chen</u> and Vincenzo Palermo*

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Paper C Elemental carbon - An efficient method to measure occupational exposure from materials in the graphene family

Tobias Storsjö*, Håkan Tinnerberg, Jinhua Sun, <u>Ruiqi Chen</u>, Anne Farbrot NanoImpact 33 (2024) 100499 https://doi.org/10.1016/j.impact.2024.100499

Paper D Binder assisted graphene derivatives as lubricants in copper: Improved

tribological performance for industrial application

Changjie Huang, Su Zhao, <u>Ruiqi Chen</u>, Erik Johansson, Muhammad Aqeel, Uta K lement, Anna M. Andersson, Mamoun Taher, Vincenzo Palermo, Jinhua Sun*

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Contribution to Appended Papers:

- Paper IThe author carried out experiment work related to aluminum battery assembling,
electrochemical measurements and ex-situ characterizations. Analysis of the
electrochemical performance part was performed by the author. The author
drafted and wrote the paper in cooperation with the co-authors.
- Paper IIThe author carried out experiment work related to preparation of porous electrode,
aluminum battery assembling, electrochemical measurements and scanning
electron microscopy characterization. Analysis of results was performed by the
author. The author wrote the paper in cooperation with the co-authors.

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I. Introduction and Motivation

To meet the ever-increasing global demand of both electric vehicles (EVs) and portable electronic devices with high energy density and power density, tremendous attention has been focused on the investigation of high-performance energy storage systems [1, 2]. Nowadays, layered materials, which can be defined as materials with strong in-plane bonding and weak van der Waals interaction in the out-of-plane direction between the layers [3], have been studied as cathode and anode in batteries and supercapacitors due to their unique structures and functionalities. The intrinsic large interlayer spaces enables capabilities of ion intercalation and fast ion diffusion [4]. Meanwhile, the weak out-of-plane bonding makes layered materials readily expand and self-assemble into various architectures, which make it have wide applications for energy storage devices.

Two-dimensional (2D) layered materials are defined as an emerging class of crystalline materials consisting of single layers or a few layers of atoms or molecules, with an extremely high ratio of lateral size (from tens of nanometers to several micrometers) to thickness (normally less than 5 nm) [5]. The 2D features are unique and indispensable for capturing unprecedented physical, electronic, and chemical properties. However, the tendency of 2D materials to stark or aggregate causes serious issues, for example, hindering inferior ionic accessibility and impeding high-rate electron conductivity [6, 7]. To tackle the issue, researchers have focused on the modification and self-assembling of 2D materials. Template-assisted methods are commonly used to fabricate large-scale materials with 3D structure. However, the hard templating methods, for example, fabricating hollow sphere structure based on MXene using poly (methyl methacrylate) (PMMA) microspheres as template, still face the challenges including complicated processes of synthesis and the presence of polymer residues [8, 9]. It's also possible to format 3D structures by freeze-casting using ice as template, which is non-toxic and able to be completely removed without structure collapse by sublimation in the freeze dryer [10].

Aluminum batteries with better cycling stability, lower cost, improved safety, and more importantly the use of abundant elements have attracted significant attention [11, 12]. However, the lack of high-performance and reliable cathode materials is still the bottleneck that hinders the practical application of the aluminum batteries. Layered material with higher conductivity, surface area, and controllable interlayer distance is preferable for the intercalation of the aluminium anions [13, 14]. In addition to these features, the crystalline structure and the surface chemistry of layered materials significantly influence the performance of aluminum batteries. Despite predictions that open edges and flaky morphology of layered materials with intact crystalline structures are essential for high charge-storage capacity, the effects of surface modifications and the strategic design of these surfaces have been rarely explored [15]. Notably, this could be one of the most cost-effective strategies to improve the performance of layered materials such as inexpensive natural graphite, making it suitable for the direct use in the practical application for aluminum batteries. Compared to different surface modification techniques, including wet chemical processes, plasma-enabled surface engineering allows one of the fastest controllable processes. Plasma is the ionized gas discharge generated by applying

a strong electromagnetic field and forms numerous species, such as electrons, ions, photons, and radicals [16]. Interaction of any nanomaterial with these plasma species induces structural defects of functionalization, which can act as an active site for batteries. However, the reactive precursors employed will affect the surface conditions of the layer materials. Therefore, optimizing appropriate plasma conditions to fine-tune the surface of layered materials and manipulating the surface defects would be highly advantageous for advancing energy storage in aluminum batteries.

A key challenge in aluminum batteries using layered material electrodes lies in the slow diffusion and intercalation of aluminum anions, which severely limit rate performance [15, 17]. To address this, efforts are made to design porous layered materials aiming to increase the surface area, which improves gravimetric capacity and rate capability by promoting charge-storage reactions via anion adsorption/desorption at the surface, thereby reducing intercalation stress. Huang et al. demonstrated a 3D graphene oxide aerogel cathode that achieved exceptional stability and rate performance in aluminum batteries [18]. Besides, the as-fabricated 3D structure can tackle the self-assembling issue of graphene sheets, which facilitate electrochemical reactions by providing more transport channels. By prioritizing electrode-level 3D porous networks alongside material modifications, future aluminum batteries designs could achieve synergistic improvements in energy density, cycling stability, and charge transfer efficiency.

Research questions:

The thesis focuses on the following research questions:

RQ1: How to control the 3D self-assembling structures of 2D layered materials using a sustainable and simple freeze-drying method?

RQ2: How plasma surface treatment affects the electrochemical performance of layered materials for aluminum batteries?

RQ3: What's the effect of nitrogen doping on graphene electrode for aluminum batteries?

RQ4: How to form a porous structure in the graphene electrode and could the formation of the porous structure improve the performance of graphene electrode for aluminum batteries?

II. Research Background

2.1 Properties of 2D layered materials

The isolation of graphene by Andre Geim and Konstantin Novoselov in 2004 marked a pivotal moment in the study of 2D layered materials, serving as a catalyst for the rapid expansion of the 2D materials family, including metal transition carbides and nitrides, metal oxide, hydroxide and chalcogenides, metal-organic framework, etc. [19]. Compared with bulk materials, the unique properties of 2D materials such as larger surface area, expanded interlayer spacing and abundant surface terminated groups provide huge potential for various applications.

Graphene, considered as the 'wonder material' of the 21st century, shows exotic properties and many potential applications. It possesses a two-dimensional structure with honeycomb lattice, which is a single layer of carbon atoms and can be exfoliated from graphite. Each carbon atom shares three sp² electrons with three neighboring carbons forming in-plane σ bonds of 0.1421 nm and out-of-plane π bonds [20], as shown in figure 2.1. The hexagonal structure is stabilized rigidly by the covalent σ bonds. The overlapped π orbitals form the conduction band and the valence band with zero band gap [21]. The unique structure lays the foundation for graphene to display remarkable properties from many aspects. The overlapped orbitals contribute to the zero band gap since the valence band and conduction band meet at the Fermi level, which helps to generate electronic excitations described as Direc fermions. The massless Direc fermions make graphene a material with unique electronic properties combining semi-conductor (zero density of states) and metal (gaplessness). While the insensitivity to disorder and electronelectron interactions and long mean free paths (the order of micrometers) of graphene allow the different electronic properties from normal semiconductors and metals [22]. Meanwhile, graphene is highlighted with its ultrahigh electrical conductivity and carrier mobility of up to 15000 cm²/(Vs) at room temperature, making it a good candidate for energy-storage devices [23].



Figure 2.1. Schematic of graphene and its structure

Recently, a fast-growing family of 2D transition metal carbides, carbonitrides and nitrides (referred as MXenes) has caught the focus of researchers since the first $Ti_3C_2T_x$ MXene was exfoliated by etching Ti_3AlC_2 in 2011 [24]. The general formula of MXenes is $M_{n+1}X_nT_x$ (n = 1-3), where M refers to early transition metal (including Sc, Ti, Zr, Hf, V, etc.), X represents carbon or nitrogen, and T_x is the surface terminations (such as O, F, OH, etc.). In the flake of MXene, n layers of X are intercalated into n+1 M layers in an arrangement of [MX]_nM, as

shown in figure 2.2. MXene can be obtained by selective etching the A-element atomic layers from MAX phases, which are layered, hexagonal carbides and nitrides with the general formula $M_{n+1}AX_n$ (MAX). Owing to the usage of acidic-fluoride-containing etching solutions during synthesis, MXenes have abundant -OH, -F, and -O terminations. The special structure with metallic atoms and surface terminated groups determines a wide chemical and structural variety of MXenes, which makes them the promising candidates for energy storage applications. The rich transition metal chemistry of MXenes promises a higher electrical conductivity ranging from 1000 to 6500 S cm⁻¹, which is higher than that of other solution processed 2D materials [25]. Moreover, the layered structure of MXenes can accommodate ions with different sizes, which provides the opportunities for the applications of various rechargeable metal-ion, e.g. Li-ion, Na-ion, Mg-ion, Al-ion batteries [26]. The low diffusion barriers for Li⁺ and other ions in MXenes hold particular promise for the high-performance and high-rate batteries [27]. Besides, the rich terminated surface groups and large surface area of MXenes layers make it suitable for the application of electrochemical capacitors. MXenes possess high conductivity for electron transport and variable valency induced charge transfer due to their inherent transition metals. Functional groups in MXenes create redox sites and transport channels owing to their layered structure. These properties enable MXenes to allow reversible intercalation of proton and metal cations at high rates, resulting in outstanding performance in supercapacitor devices [28].



Figure 2.2. Schematic illustration of MXenes atomic structure

2.2 Self-assembly of 2D layered materials

Despite the extraordinary properties of 2D layered materials, the serious issues of self-stacking and irreversible aggregation in both dried and solvent dispersion associated to the intrinsic thermodynamic nature of unstable interface have greatly hindered their practical applications in energy storage. The restacking of nanosheets has negative effects on exposure of active sites, which is considered as a critical drawback for energy storage applications. One of the appealing approaches to tackle this aggregation issue is to fabricate robust 3D structure by self-assembling of 2D layered materials. Several merits from the formation of 3D structure can be listed as follows: 1) expanding the exposed surface area, 2) formation of well-defined porous structure, 3) mechanical flexibility, and 4) mechanically reliable reversible structure formation [29]. The resulting 3D architecture is self-supporting with extraordinary surface area, electronic

properties, and chemical activity, allowing the tremendous applications in energy storage devices [30].

Recently, different types of structures have been fabricated including but not limited to foams, networks, sponges, scaffolds, monoliths, aerogels, hydrogels, hollow spheres, etc [6, 31, 32]. There are multiple synthesis methods to fabricate 3D structures. Among them, the versatile solution-based techniques are taken into considerations ascribed to the advantages of scalability, high yield, and cost-effectiveness, which meet the requirement of large scalable usage for energy storage applications. Besides, the solution-based methods allow the elemental doping or decoration of fabricated structure to realize the functionalization of 2D materials simultaneously. Nowadays, the solution-based techniques can be generally classified as 'template-based method' and 'template-free method', as summarized in figure 2.3. Furthermore, template-base methods can be categorized by soft-template, hard-template, and ice-template methods [30]. Template-free methods can be sorted by hydrothermal assemblies and cross-linking assemblies. We will discuss the advantages and disadvantages of each technique and their effects on the structure and properties of fabricated 3D structures.



Figure 2.3. Classification of self-assembling of 2D materials using solution-based methods

Template Methods

The template method is the most widely used to realize the controllable and spatially welldefined structures. By different types of templates, it can be categorised by hard template, soft template and ice template method.

Hard templates are rigid substrates with high structural strength and hardness. The strategy is to combine the hard template with 2D nanosheets using different interactions followed by template removal to obtain the porous 3D structures. Owing to the interconnected framework, the fabricated 3D structures will not collapse after template removal. Hard templates possess stronger regulatory effect on assembly process, which is beneficial for precisely controlling the pore size and structure of the assembled 2D materials. Typically, spheres of polymers including polystyrene (PS) or polymethyl methacrylate (PMMA), silica spheres are considered as suitable hard template for 3D self-assembly of 2D materials [8, 33]. Zhao et al. employed PMMA (poly (methyl methacrylate)) spheres as template for the uniform hollow MXene spheres are achieved, as shown in figure 2.4 [8]. Generally, the as-prepared architecture exhibits premium structure robustness and uniformity. However, the hard template method

requires complex post-processing which may leave polymer residues in the materials, affecting the performance in the energy storage applications.



Figure 2.4 Hard template method to fabricate 3D hollow MXene structure with schematic figure. Reproduced with permission [8].

Soft templates, as a contrast, have low structural strength and hardness, such as micelles, emulsions, and liquid crystals. The 3D macroporous structure can be fabricated with variable size and shape and the templates are easy to remove. Bian et al. employed cetyl trimethylammonium bromide (CTAB) to tune the hydrophilic-hydrophobic balance of MXene via electrostatic interaction, which wrapped the interface of emulsion templates to form a 3D framework (figure 2.5) [34]. The as-prepared MXene aerogel possesses the properties of porous, robust and highly conductive. However, it requires precise control over assembly conditions, for example, pH, temperature, etc., which makes it difficult to control the pore size and shapes.



Figure 2.5 Soft template methods to fabricate 3D porous MXene framework with schematic figure. Reproduced with permission [34].

Ice template method is another effective method to self-assembly 2D materials into 3D porous structure. The ice crystals act as transient templates during freezing and the 2D nanosheets, e.g., graphene oxide, MXene, are ejected from the ice crystals and confined between neighboring ice crystals. In this process, the orientation of 2D materials flakes can be tuned with the growth of ice crystal during freezing process derived from the temperature gradients in both the

horizontal and vertical directions, leading to a well-aligned lamellar structure. Moreover, the ice template method is considered as an eco-friendly and cost-effective method to fabricate 3D macroporous structure owing to the absence of additives as templates and complex post-processing. The ice template can be easily and thoroughly removed by one step sublimation. Qiu et al. obtained monolithic structure self-assembled by graphene flakes via ice template method (figure 2.6) [10]. The as-fabricated graphene cellular monoliths are highly texture, exhibiting outstanding mechanical properties. However, the morphology produced by ice template methods is generally not uniform throughout the structure caused by the local difference of cooling rate. Therein, the limited control of morphology confines its application in self-assembly of 2D materials.



Figure 2.6 Ice template methods to fabricate graphene monolithic structure (a-c) SEM images of graphene monolith, (d) Schematic figure showing the formation mechanism of monolithic structure. Reproduced with permission [10].

Template-free Methods

Template-free methods are considered as effective bottom-up strategies to fabricate 3D structures for 2D materials. Typically, well-dispersed 2D nanosheets such as graphene oxide, MXene, etc. are the most commonly used building blocks for template-free self-assembly. 3D structures can be fabricated by various template free strategies including hydrothermal assemblies, cross-linking, filtration, etc.

Hydrothermal methods are widely used for constructing 3D structures for graphene oxide or reduced graphene oxide dispersion. The high pressure and temperature hydrothermal conditions can induce the reduction of GO, leading to partial overlapping of reduced GO sheets. As a result, self-assembled hydrogels through π - π stacking-induced cross-linking of GO sheets can be formed. The π - π stacking interaction promises the assembled hydrogels good mechanical strength, thermal stability and electrical conductivity [35].

Cross-linking method is another type of template-free method to achieve self-assembly of 2D materials. The addition of molecules served as crosslinker can strengthen the 3D structure and

tune the morphology simultaneously. Crosslinkers such as polymers (polyvinyl alcohol (PVA), polyaniline (PANI), etc.), multivalent metal ions, biomolecules assist the gelation of 2D materials, resulting in the fabrication of 3D structure through co-ordinate covalent bonding [36-39].

2.3 Surface modification of layered materials

Surface modification of layered materials is a rapidly advancing field, driven by the need to tailor surface properties for specific applications while preserving the unique characteristics of the material's bulk [40]. By modifying only the outermost atomic layers, it can significantly tune their inherent properties such as electrical conductivity, chemical stability, and catalytic activity [41-43]. This approach is particularly valuable for layered materials such as graphite, graphene, MXenes, and transition metal dichalcogenides, etc., which possess high surface-to-volume ratios and exhibit remarkable sensitivity to surface chemistry, enhancing their applicability in energy storage [44-46].

Recently, a variety of techniques have been employed for surface modification of layered materials, which can be mainly categorized by physical modification, chemical modification, and thermal modification (figure 2.7). Physical methods typically involve no chemical reaction, such as plasma spraying technology (PST), plasma immersion ion implantation (PIII) and physical vapor deposition (PVD), which enable the precise application of thin films or coatings, especially at the nanometer scale. Chemical strategies, including covalent grafting and the formation of self-assembled monolayers, allow for the introduction of functional groups that can tune interlayer spacing, and impart selective reactivity. Thermal and optical methods, such as thermal oxidation and laser surface modification, further expand the toolbox, enabling the creation of micro- and nanostructures on the surface that improve adhesion, wettability, or wear resistance.



Figure 2.7 Schematic overview of examples of surface modification methods.

Among these, plasma treatment stands out as a particularly versatile and effective approach for modifying the surfaces of layered materials. Various plasma techniques, such as remote oxygen plasma (ROP), low-pressure oxygen plasma, nitrogen-doped plasma, hydrogen plasma, etc., have been developed to introduce functional groups, engineer defects, and even exfoliate graphite into thinner layers. Murillo-Herrera et al. found that ROP can introduce oxygencontaining functionalities like hydroxyl and carbonyl groups onto graphite, greatly improving their wettability and electrochemical activity [47]. Low-pressure oxygen plasma treatment has been shown to significantly increase the work function and hydrophilicity of graphite by generating surface dipoles, such as -OH groups, without compromising the material's thermal stability [48, 49]. This process can also selectively etch grain boundaries, which remove disordered carbon layers and enhance the graphitic order of high-surface-area graphite. Nitrogen-doped plasma, on the other hand, using ambient plasma with N-containing species to tailor the surface chemistry and electronic structure of layered materials, which is considered as an efficient method for a large scale production of nitrogen-doped layered materials with a controllable doping degree [50, 51]. Among different reactive precursors, hydrogen is considered to modify the surface of carbonaceous materials by selectively etching the surface (figure 2.8). The hydrogen atoms have a higher affinity to react with unsaturated sp2 carbon atoms, which leads to the breaking of C-C bonds. Hence, due to the presence of a large amount of H plasma in the reaction, the surface of graphite or amorphous carbon can be rapidly etched [52].



Figure 2.8 Schematic illustration of surface modification by hydrogen plasma etching. Reproduced with permission [52].

Plasma treatment significantly enhances the performance of layered materials in energy storage applications by modifying surface properties such as surface roughness, wettability, and chemical functionality [53, 54]. It can also strengthen the bonding between layers, ensuring stability and longevity of batteries. Additionally, plasma treatment induces more conductive pathways that boosting the electrical conductivity of layered materials, which is crucial for efficient charge transfer in energy storage devices such as supercapacitors, lithium-ion batteries, aluminum-ion batteries, etc [50, 55]. Overall, plasma treatment is a versatile and eco-friendly

method that enhances the performance and durability of materials used in next-generation energy storage solutions.

2.4 Applications for modified layered materials in energy storage devices

The self-assembly and surface modification of layered materials provide more opportunities for supercapacitors and batteries with superior performance [56]. The self-assembled 3D structure with high porosity ensures a large specific surface area and sufficient ionic channels. By surface modification, more and more active sites are available for electrochemical reactions, allowing improved energy storage performance.

Supercapacitors

For supercapacitors, a higher specific surface area and porosity are crucial due to more charge storage sites, which enhance the capacitance greatly. Lukatskaya et al. applied design of macroporous structure using MXene as the electrodes for supercapacitor (Figure 2.9) [57]. The architecture was fabricated with assistance of PMMA template, resulting in an open structure characterized by 1-2 um diameter pores. Taking advantage of the structure, the ion transport lengths are greatly reduced when used as electrode for supercapacitors. Electrochemical studies of the macroporous electrodes revealed exceptional rate capability for a pseudocapacitive material.



Figure 2.9 a. SEM image of $Ti_3C_2T_x$ MXene hydrogel cross-section; b. SEM image of macroporous templated $Ti_3C_2T_x$ electrode cross-section. Scale bars, 5 um; c. Cyclic voltammetry profiles of macroporous $Ti_3C_2T_x$ electrode at scan rates from 20 to 10,000 mV/s. Reproduced with permission [57].

Aluminum batteries

The rechargeable aluminum batteries are increasingly recognized as promising next-generation energy storage technology. Utilizing aluminum metal directly as the anode makes aluminum batteries particularly attractive for developing sustainable and cost-effective power sources. In addition, the fundamental redox reactions at the heart of aluminum batteries allow for the potential to achieve relatively high energy and power densities. Although the concept of aluminum batteries dates to the early 1970s, it was not until 2011 that significant attention was drawn to this technology, following the successful demonstration of a rechargeable Al-V₂O₅

cell operating at room temperature [58, 59]. Since then, research into aluminum batteries has experienced a notable resurgence, with efforts focused on both advancing the technology and deepening the understanding of its underlying mechanisms. With aluminum comprising approximately 8% of the Earth's crust making it the third most abundant element after oxygen and silicon, and vastly more plentiful than lithium (0.0065%), aluminum batteries offer a compelling pathway toward scalable and sustainable energy storage solutions.



Figure 2.10 Schematic drawing of rechargeable Al/graphite cell. Reproduced with permission [12].

Non-aqueous aluminum batteries that utilize room temperature ionic liquid (RTIL) electrolytes have garnered significant attention in battery research. This interest is largely due to their broader operating voltage window, lower vapor pressure, and enhanced reversibility of aluminum redox reactions, all achieved without the occurrence of hydrogen evolution side reactions that typically affect aqueous electrolyte-based aluminum batteries. Despite the inherent advantages of aluminum anodes, a major challenge in advancing non-aqueous aluminum batteries lies in the development of suitable cathode materials that can deliver high capacity, elevated operating voltages, and robust cycling stability for practical applications. Among them, graphite stands out as one of the most promising carbon-based cathodes for non-aqueous aluminum batteries, owing to its natural abundance, low cost, excellent stability, and high electrical conductivity. In these systems, the charge storage mechanism involves the intercalation of chloroaluminate anions between the graphitic layers at the cathode, with corresponding stripping and deposition processes occurring at the anode, as illustrated in figure 2.10. The storage mechanism can be described as [12]:

$$4Al_2Cl_7^- + 3e^- \rightarrow Al + 7AlCl_4 \tag{1}$$

$$C_n + AlCl_4^- \rightarrow C_n [AlCl_4] + e^-$$
(2)

However, the graphite cathodes have several issues for such applications, including limited reversible capacity, suboptimal performance at high charge-discharge rates, sluggish ion diffusion, and structural expansion. These challenges restrict the practical use of graphite as a cathode material. As a result, there is a need to develop modifications on carbon materials that can serve as effective alternatives to conventional graphite cathodes. For example, An et al. [60] performed electrostatic surface modification on graphite to depress the surface barrier, resulting in more adsorption of chloroaluminate anions. Thus, the modified graphite exhibited high specific capacity and outstanding rate cycling performance as the cathode for aluminum batteries.

Graphene-based materials have recently emerged as promising cathode candidates for aluminum batteries, primarily due to their high specific surface area, superior electrical conductivity, excellent reversibility for ion storage, and robust electrochemical stability. Notably, the energy storage mechanism of monolayer graphene differs significantly from that of highly crystalline graphite, which consists of well-aligned graphene layers. When graphene layers are properly aligned within the electrode structure, they can facilitate both surface adsorption and intercalation of AlCl^{4–} ions, thereby enhancing their suitability as active cathode materials in AIB systems.

Various forms of graphene, including graphene oxide (GO), reduced graphene oxide (RGO), and thermally annealed GO, have been investigated as active materials for aluminum batteries. These materials benefit from the presence of structural defects and the partial alignment of graphene layers, which contribute to improved electrochemical performance [55, 56]. Surface modification has also been identified as an effective strategy to enhance the electrochemical properties of graphene. For example, Childress et al. employed few-layer graphene subjected to argon plasma treatment as a cathode material, which demonstrated notable electrochemical performance in aluminum batteries cells [57]. This plasma treatment induces interlayer expansion and introduces additional lattice defects, which serve as active sites for ion adsorption and transport, thereby improving both the ion diffusion kinetics and overall energy storage behavior [17].

III. Experimental Methodology

3.1 Preparation of Ti₃C₂T_x MXene and graphene oxide

Preparation of $Ti_3C_2T_x$ MXene

The MXene investigated in the thesis is $Ti_3C_2T_x$, which was etched from MAX phase Ti_3AlC_2 (obtained from Carbon-Ukraine, particle size 40 microns). Fluoride based salt etchant (LiF and HCl) to produce in-situ HF was used combined with the method called minimally intensive layer delamination (MILD), which is achieved by gentle shaking and aimed for a minimal and less milder route to produce single and larger flakes with fewer defects [61]. The protocol to prepare the MXene dispersion at room temperature is stated as follows:

1. Prepare the etchant by adding 0.8 g LiF to 10 mL of 9 M HCl (7.5 mL of 37 wt% HCl diluted to 10 mL). Leave it with continuous stirring for 5 min. 0.5 g of Ti_3AlC_2 powder was gradually added to the above etchant and the reaction lasted for 24 h.

3. After the above reaction, the mixture was washed by deionized water via low-speed centrifugation for several cycles. After each cycle, the supernatant was decanted before adding fresh deionized water for the next cycle. Repeat the washing for a few cycles until pH 4-5 was realized, when dark-green supernatant was observed, indicating the beginning of MXene delamination.

4. To further delaminate MXene layers, handshaking for 10 min was performed followed by high-speed centrifugation. After each cycle, the supernatant was decanted before adding fresh deionized water for the next cycle. These cycles were repeated 4 times.

5. A high-quality delaminated MXene dispersion was collected from the supernatant after lowspeed centrifugation. The dispersion was degassed by N_2 gas and stored in the refrigerator.

Preparation of graphene oxide

Graphene oxide (GO) was selected as the precursor of graphene due to its excellent hydrophilicity, which allows the formation of aqueous colloids. The powder of GO was obtained from LayerOne and the C/O atomic ratio was 2.5-2.6. Because the powder contains <1 % adsorbed HCl and H₂SO₄, it needed to be neutralized by deionized water via centrifugation (15000 rpm for 1 h) for several cycles until the pH = 6 was achieved.

3.2 Self-assembling of MXene and Graphene

The as prepared $Ti_3C_2T_x$ MXene or GO dispersions in different concentration was freeze dried using a standard freeze-drying method. The self-assembled MXene-GO composites with 3D macroporous structure were obtained after freeze-drying process, which is performed in freezedryer (Alpha 1-2 LD plus). To reduce the GO and increase the electrical conductivity for supercapacitors, the as-prepared materials were chemically reduced using hydrazine hydrate at 90 °C for 6 h and then dried under vacuum overnight.

3.3 Plasma treatment of graphite and graphene

The commercial graphite flakes (300 mesh size, Alfa Aesar) were used as the starting material. The graphite flakes placed in a ceramic crucible were subjected to plasma surface engineering to improve the charge storage capabilities. Plasma tailoring was conducted in a low-pressure radio-frequency (RF) plasma system, which was an 80 cm long glass tube with a diameter of 4 cm. The RF generator was inductively coupled through a nine-turn internally water-cooled inductive coil. The graphite flakes in the crucible are placed in the center of the coil, and the chamber is pumped down to 1Pa. Later, the reactive gas, hydrogen, was fed into the system at a flow rate of 100 sccm, and the total pressure inside the chamber was maintained at 32 Pa. In the final stage, the plasma was ignited at a power of 200 W and treated graphite flakes for 6 min. The treatment was conducted incrementally with a period of 2 min for three times to prevent the overheating of the material.

A waveguide-surfatron based setup was used to create a surface wave (SW) induced microwave plasma at atmospheric pressure conditions for the treatment of graphene. For the Nitrogen doped graphene synthesis, nitrogen gas flow (5–10 sccm) has been added to the ethanol flow. A small percentage of the N₂ in respect to the background argon flow results in a high dissociation degree of N₂ molecules therefore generating a significant amount of reactive nitrogen atoms (~1022 m⁻³) that can be incorporated into the growing carbon lattice structure. The rate of pure N-graphene sheets collected at a background argon flow of 1200 sccm, power of 2 kW, ethanol flow of 15 sccm and N₂ flow of 5 sccm was about 0.5 mg/min [62].

3.4 Electrodes preparation for aluminum batteries

The as-synthesized graphite, hydrogen treated graphite (G-H), argon treated graphite (G-Ar), Gr and N- doped Gr powder was mixed respectively with the conductive additives (acetylene black) and styrene butadiene rubber and sodium carboxyl methyl cellulose (SBR/CMC mass ratio 1:1) as binder in the mixer (Kakuhunter SK-300S II) at a mass ratio of 80:10:10, using water as the solvent. A homogeneous slurry was obtained after mixing for 20 minutes at 1500 RPM. The slurry was then coated onto the surface of molybdenum foil with a diameter of 12 mm. The coated electrodes were dried in the vacuum oven at 80 °C for at least 12 hours.

In order to form porous structure with ordered nitrogen doped graphene in the electrode, the slurry coated electrode was first frozen under controlled temperature to allow the growth of the ice from the bottom of the electrode to the top surface of the electrode. The porous structure was then formed after removing the ice under vacuum for at least 24 hours.

3.5 Material characterizations

Scanning Electron Microscopy (SEM)

JEOL 7800F Prime scanning electron microscopy (SEM) was used to check the microstructure morphology of samples. In SEM, an electron beam generated by an electron gun produces several signals, which can be collected by different detectors for images. Among them, secondary electrons (SE) generated by inelastic interaction with samples are mainly used for topographical images. Lower electron detector (LED) was selected to collect SE signals. The work distance was set to 10 mm.

X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive analytical technique that reveals information about the crystal structure, chemical composition and physical properties of materials and thin films. These techniques depend on the observation of the scattering strength of an X-ray beam hitting a sample as a function of an incident Angle, scattering Angle, polarization, wavelength, or energy. In this thesis, Bruker D8 Advance was used to evaluate the distance between each single layer of MXene and GO respectively.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed to check the mass loss of the samples as they are heated, which is related to the composition and surface group. TGA/DSC 3+ STAR system with METTLER TOLEDO micro and ultra-micro balances was used. The samples were heated to 1000 °C with a gradient of 10 °C. 3-5 mg of each sample was taken for testing. In this thesis, we used TGA for element analysis of GO based composites respectively, to indicate the effects of reduction.

Raman Microscope

Raman microscope is a laser-based microscopic device used for Raman spectral analysis and get the spectroscopy. It starts with a standard microscope and adds an excited laser, a laser filter, a spectrometer or monochromator, and photosensitive detector such as a chart-coupled device (CCD) or photomultiplier tube. In this thesis, Raman characterization (alpha 300 R) was used in two parts: 1) compare the spectra of MXene-GO and MXene-reduced GO composites; 2) compare the spectra from ex-situ measurement of hydrogen-plasma treated graphite under different voltage in cyclic voltammetry test.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) involves measuring the kinetic energy of these ejected electrons, which provides information about the binding energy of the electrons within the atoms of the material. This binding energy is influenced by the chemical environment surrounding the atoms, allowing XPS to identify the elemental composition, chemical state, and electronic structure of the material. In this thesis, XPS (PHI Versaprobe III) was used to compare the spectra from ex-situ measurement of hydrogen-plasma treated graphite under different voltage in cyclic voltammetry test.

3.6 Electrochemical measurement

Supercapacitors

The electrochemical performances of MXene based materials for supercapacitors were first measured in a three-electrode configuration, in which the active materials on glassy carbon electrode, platinum foil, and Ag/AgCl in 3 M KCl were used as the working, counter, and reference electrodes, respectively. All the electrochemical tests were carried out using a potentiostat electrochemical station (Biologic SP300, France) in 3 M H_2SO_4 at room temperature.

Aluminum battery cells

The aluminum batteries are assembled in an argon-filled glove box. The as-prepared graphite related electrodes were used as the cathode, aluminum foil was used as the anode, and glass fiber was used as the separator. The ionic liquid electrolyte composed of aluminum chloride (AlCl₃) and 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) with a molar ratio of 1.3:1 was used. The electrochemical measurements were conducted using modified Swagelok-type cells in which a molybdenum rod and a glassy carbon rod were used as the current collectors for the anode and cathode, respectively. The galvanostatic measurements, cyclic voltammetry, and electrochemical impedance spectroscopy analysis was performed using battery cycler (Biologic BCS-805., France).

IV. Results and Discussion of Key Results

In this chapter, the research questions proposed in chapter I are addressed by the summary of results and discussion of appended papers. RQ1 is studied in session 4.1, RQ2 is addressed in session 4.2, and RQ3, RQ4 are discussed in session 4.3.

4.1 GO and MXene based self-assembling porous structure for supercapacitors

RQ1: How to control the 3D self-assembling structures of 2D layered materials using a sustainable and simple freeze-drying method?

Previous studies have demonstrated that when an aqueous dispersion of nanoparticles is frozen, the growing ice crystals can reject the dispersed nanoparticles, which results in the formation of porous structure via subsequent sublimation of ice. A variety of porous nanomaterials such as graphene aerogel and porous ceramic were successfully synthesized by this freeze-casting approach. In this work, $Ti_3C_2T_x$ MXene and GO were chosen as precursors, which are synthesized using chemistry methods. Single layer microsheets of MXene and GO are desired to fabricate the 3D structure.

The morphologies of the structures were examined using a scanning electron microscope (SEM), as depicted in figure 4.1a-b. We successfully fabricated 3D network structure and porous structure respectively with MXene and GO microsheets. The 3D network structure possesses high porosity and good structural integrity, which is beneficial for supercapacitors to have improved performance. Porous structures can also be formed from 2D microsheets in our freeze-drying method, which is considered to be a good candidate for supercapacitors due to the increased specific surface area.



Figure 4.1. Inherent morphology of MXene and/or GO composites: a. 3D porous network structure; b. hierarchical porous structure.

GO in the composite needs to be reduced to improve the electrical conductivity for further supercapacitor applications. Thermogravimetric analysis (TGA) was performed to confirm the reduction of GO, as shown in figure 4.2a. indicating the sufficient removal of oxygencontaining functional groups from GO. Furthermore, the less weight loss of MXene-rGO composite demonstrates better thermal stability compared with rGO. To inspect the nanosheets interlayer distance of as-obtained samples, X-ray diffraction (XRD) was conducted as shown in figure 4.2b, indicating a sufficient reduction of GO. Raman spectra were displayed in figure 4.2c to verify the existence state of GO, rGO, and MXene in the as-synthesized samples. Two intense broad peaks at 1361.3 and 1591.4 cm-1 were ascribed to the D band and G band of graphitic carbon with the existence of GO or rGO. Moreover, the intensity ratio of D and G band (I_D/I_G) for MXene-rGO was 2, as compared with 1 for MXene-GO samples, which indicates that more defects were introduced to the reduced samples.



Figure 4.2. Material characterization of MXene-GO composite before and after reduction: a. TGA curves; b. XRD patterns; c. Raman microscopy spectra.

The electrochemical performance of MXene-rGO electrodes were evaluated in 3M sulfuric acid in a three-electrode configuration. Cyclic voltammetry (CV) curves of MXene/rGO hybrid electrodes at different scan rates were shown in figure 4.3a. A symmetric pair of broad redox peaks can be observed in the potential window of -0.5 to 0.3 V vs. Ag/AgCl, indicating the reversible intercalation/deintercalation of protons along with the change of Ti oxidation state, which contributed to the pseudocapacitance for electrodes. The galvanostatic charge-discharge profiles of MXene-rGO electrodes between -0.45 and 0.3 V are given in figure 4.3b. It can be found that the charging and discharging curves are symmetric with triangular shape, indicating the excellent reversibility of supercapacitance reaction for the MXene-rGO electrodes [63].



Figure 4.3. Electrochemical performance tested by 3-electrode configuration: a. CV curves of MXenerGO at different scan rates from 20 mV/s to 10 000 mV/s; b. galvanostatic charge-discharge curves for MXene-rGO at different current densities from 1 A/g to 10 A/g.

4.2 Surface modification of graphite by plasma treatment for the cathode of aluminum battery

RQ2: How plasma surface treatment affects the electrochemical performance of layered materials for aluminum batteries?

Surface modification of graphitic materials leads to the creation of numerous active sites, which in turn facilitates more efficient ion and electron transport into the active material by shortening the diffusion pathways during charge and discharge cycles. This enhancement can result in increased specific capacity while preserving a stable charge voltage plateau and minimizing unwanted side reactions. Among various surface modification methods, such as wet chemical techniques, plasma-based surface engineering stands out for its rapid and highly controllable processing capabilities. Plasma, an ionized gas generated by the application of a strong electromagnetic field, contains a diverse array of energetic species-including electrons, ions, photons, and radicals. When nanomaterials interact with these plasma constituents, structural defects and functional groups are introduced, which can serve as additional active sites during aluminum batteries operation. In this study, the graphite was treated with hydrogen plasma (G-H) and argon plasma (G-Ar) respectively and assembled as cathodes for aluminum battery cells.

Figure 4.4a displays the initial galvanostatic charge–discharge curves for the original graphite, G-Ar, and G-H cathode materials at a current density of 100 mA/g. All three samples show similar profiles, each featuring three short voltage plateaus around 1.8, 2.0, and 2.15 V. The primary voltage plateau, beginning at 2.3 V, is associated with the intercalation of AlCl₄⁻ anions into the graphitized structure. During discharge, the voltage plateaus commence at 2.25 V and 1.9 V, corresponding to the deintercalation of AlCl₄⁻ anions. The initial charge/discharge specific capacities for graphite, G-Ar, and G-H are 75.31/67.48, 66.45/76.01, and 129.24/123.85 mA h/g, respectively. Notably, the hydrogen plasma-treated graphite (G-H) shows the highest specific capacity, indicating that the surface modification significantly enhances the material's ability to store AlCl₄⁻ anions.

Figure 4.4b presents the first charge–discharge curves of the G-H cathode at various current densities. The initial charge/discharge specific capacities for G-H at current densities of 50, 100, 200, 500, and 1000 mA/g are 147.89/132.68, 124.13/119.28, 105.39/96.72, 96.84/93.30, and 85.44/83.94 mA h/g, respectively. Figure 4.4c compares the rate capabilities of graphite and G-H at different current densities. For G-H, the average reversible specific capacity at 50 mA/g is 132.36 mA h/g, while for graphite at 100 mA/g it is 77.23 mA h/g over 10 cycles. As the current density increases to 1000 mA/g, the average reversible specific capacity decreases to 84.34 mA h/g for G-H and to 34.80 mA h/g for graphite. After 50 cycles at varying current densities, the G-H cathode retains a specific capacity of 125.63 mA h/g at 50 mA/g, corresponding to a 95% capacity retention. These results highlight the outstanding rate capability and cycling stability of hydrogen plasma-treated graphite. This improvement is primarily attributed to the introduction of additional C–H bonds on the graphite surface via plasma treatment, which enhances the interaction between the electrode and the electrolyte. As a result, the rapid intercalation and deintercalation of AlCl4⁻ anions within the graphite structure are promoted, leading to superior electrochemical performance.

Figures 4.4 d–f illustrates the cycling stability results for graphite, G-Ar, and G-H samples. At a current density of 100 mA/g (Figure 4.4d), the plasma-treated graphite exhibits excellent stability, with the G-H cathode retaining 98.2% of its initial specific capacity (116.86 mA h/g) after 50 cycles. In contrast, the specific capacity of the untreated graphite cathode drops to just 66.82 mA h/g, likely due to persistent side reactions. Additionally, the G-H sample maintains a high coulombic efficiency of 99%, compared to 98% for the untreated graphite. This higher coulombic efficiency in G-H indicates a more stable structure for the reversible insertion and extraction of AlCl4⁻ anions during cycling. Long-term cycling performance at a higher current density of 500 mA/g is shown in figure 4.4e. Impressively, the G-H cathode retains a specific capacity of 86.6 mA h/g even after 1000 cycles. Furthermore, as depicted in figure 4.4f, the galvanostatic charge–discharge (GCD) curves for G-H are nearly identical from the first to the 1000th cycle, underscoring the outstanding structural stability and durability of the hydrogen plasma-treated graphite material.



Figure 4.4. Electrochemical performance of different plasma treatment graphite samples: (a) The first cycle GCD profiles of G-H, G-Ar, and graphite cathodes; (b) GCD profiles of G-H, G-Ar, and graphite cathodes for the first cycle at different current densities; (c) Rate capabilities of G-H and graphite cathodes; (d) Cycling performance and Coulombic efficiency of G-H, G-Ar, and graphite cathodes at 100 mA/g for 50 cycles; (e) Cycling performance and Coulombic of G-H cathodes for the different cycles at 500 mA/g for 1000 cycles; (f) GCD profiles of G-H cathodes for the different cycles at 500 mA/g.

Ex-situ Raman spectroscopy combined with cyclic voltammetry (CV) was employed to monitor the stages of AlCl⁴⁻ anion intercalation and deintercalation in the G-H cathode, as depicted in figures 4.5a and 4.5b. During the charging process, measurements were taken at 1.8 V, 2.0 V, and 2.4 V, corresponding to the initial, partial, and full intercalation of AlCl⁴⁻ anions, respectively. For the discharge process, 2.1 V and 1.6 V were selected to represent partial and complete deintercalation stages. As the electrode was charged from its pristine state to 1.8 V (point 1) and 2.0 V (point 2), the G band in the Raman spectrum shifted from 1579

cm⁻¹ to 1584 cm⁻¹. Upon further charging to 2.4 V (point 3), the G band continued to blue-shift to 1610 cm⁻¹. During discharge, the G band gradually shifted back to 1586 cm⁻¹ at 2.1 V (point 4) and 1584 cm⁻¹ at 1.6 V (point 5). These shifts are indicative of the structural changes in graphite due to the reversible intercalation and deintercalation of AlCl₄⁻ anions, consistent with previous reports on graphite intercalation compounds.

To further elucidate the chemical environment, ex-situ X-ray photoelectron spectroscopy (XPS) was conducted to analyze the bonding states of Al and Cl species in the G-H cathode during charge and discharge (figures 4.5c and 4.5d). The successful intercalation of chloroaluminate ions was confirmed by the emergence of Al and Cl peaks after charging. Notably, the Cl 2p peak shifted from 199.0 eV to a higher binding energy (199.6 eV) at 2.0 V and 2.4 V during charging. Upon discharge, the Cl 2p peak reverted to 199.4 eV at 2.1 V and further to 199.0 eV at 1.6 V. Similarly, the Al 2p peak increased from 74.9 eV to 75.4 eV during charging and decreased back to 75.2 eV and then to 74.9 eV during discharge. These binding energy changes reflect the reversible intercalation and deintercalation of AlCl₄⁻ anions within the graphite layers: higher binding energies correspond to the insertion of chloroaluminate ions during charging, while lower binding energies indicate their extraction during discharge.



Figure 4.5. Ex-situ characterization on G-H cathode: (a) CV curve of G-H cathode for ex-situ characterization; (b) Ex-situ Raman spectra for G-H cathode at different voltages during charge-discharge process; Ex-situ XPS spectra for (c) Al 2p; (d) Cl 2p of G-H cathode at different voltages during charge-discharge process.

4.3 Nitrogen doping of graphene and its 3D network porous structure fabrication for the cathode of aluminum battery

RQ3: What's the effect of nitrogen doping on graphene electrode for aluminum battery?

RQ4: How to form a porous structure in the graphene electrode and could the formation of the porous structure improve the performance of graphene electrode for aluminum batteries?

In this study, single-layer graphene powder produced via a high-throughput plasma process was modified through nitrogen doping to introduce additional active sites for the accommodation of aluminum anion charge carriers. To further enhance electrochemical storage, a porous architecture was engineered within the nitrogen-doped graphene electrode, effectively addressing the limitations of conventional disordered electrodes. The influence of nitrogen doping on the electrochemical performance of graphene in aluminum batteries was thoroughly examined. These combined strategies not only boost the electrochemical properties of the graphene electrode but also enhance the ion transport dynamics within the porous network, leading to improved rate capability and increased capacity.

To achieve this porous architecture in the cathode, a freeze-drying technique was employed. After applying the electrode slurry, the molybdenum disc was placed on a cold plate cooled by liquid nitrogen. The resulting temperature gradient from the bottom to the top causes ice crystals to grow vertically, which in turn separates the graphene nanosheets and forms a network-like structure. Subsequent freeze-drying removes the ice present between the 2D nanosheets, leaving behind a well-defined porous network. SEM images of the nitrogen-doped graphene coating, shown in figure 4.6, reveal that the material is well-organized, featuring large pores approximately 5 μ m in size. The nanosheets are interconnected, ensuring excellent electrical conductivity for use as a cathode material.

Figure 4.7a shows the first galvanostatic charge-discharge curves of the original graphene (Gr), nitrogen-doped graphene (N-Gr), and porous nitrogen-doped graphene cathodes (porous N-Gr) at current density of 100 mA/g. The charge-discharge curves of all the three samples exhibit similar shape, that is a turning point at 2.0 V during charging process, indicating the intercalation of AlCl₄⁻ anions. However, for porous N-Gr cathode, the curve shows a turning point at 1.2 V while discharging, which is absent for graphene powder. Comparing the specific capacity for the three cathodes, porous N-Gr shows the highest value, that is 65.5 mAh/g. Besides, the N-Gr exhibits a higher specific capacity of 54.4 mAh/g than Gr of only 36.26 mAh/g. The results indicated that nitrogen doping can boost the adsorption/desorption process of AlCl₄⁻ anions, which is beneficial for improving the specific capacity of N-doped graphene powder by increasing the surface area and active sites for AlCl₄⁻ anions storage.



Figure 4.6. SEM images of N-Gr fabricated porous cathode at low and high magnification.

The rate performance of the Gr, N-Gr, and porous N-Gr cathodes are illustrated in figures 4.7b and 4.7c. As the current density increases from 0.1 A/g to 0.2, 0.5, 1, 2, and 5 A/g, the reversible specific discharge capacities of the porous N-Gr cathode are 65.5, 60.0, 58.3, 50.8, 43.9, and 38.0 mAh/g, respectively. When the current density returns to 0.1 A/g, the specific capacity recovers to 62.3 mAh/g, demonstrating excellent rate capability and durability. Compared to the drop-coated N-Gr cathode, the porous electrode consistently delivers higher specific capacities across all current densities, confirming that the introduction of a porous structure significantly enhances rate performance. Furthermore, long-term cycling stability was assessed over 150 cycles at a current density of 0.5 A/g, as shown in figure 4.7d. The porous N-Gr cathode maintains a reversible capacity of 55.0 mAh/g with over 100% capacity retention after 150 cycles, indicating that the fabricated structure offers robust stability and superior specific capacity compared to conventional drop-coated electrodes.

To investigate the energy storage behavior in aluminum batteries cells, cyclic voltammetry curves were analyzed as depicted in figure 4.7e. The shape of the curves is the same for all cathodes with one anodic peak and three cathodic peaks. The large quasi-rectangular shape indicates that the dominated energy storage mechanism of the Gr, N-Gr, and porous N-Gr cathodes is based on the physical adsorption of the charge carriers. However, the intensity of cathodic peak at 1.7 V is increased for the porous N-Gr cathode, indicating that the porous structure can boost the deintercalation process of AlCl₄⁻ anions. Besides, the potential separation between anodic and cathodic peak is further reduced because the cathodic peak at 1.9 V for N-Gr shifted to 2.0 V, demonstrating that the porous structure has the advantage of improving the reversibility for the intercalation/deintercalation of AlCl₄⁻ anions. To testify the superiority of porous structure for cathode in reducing the resistance of batteries, electrochemical impedance spectroscopy analysis is illustrated as Nyquist plot in figure 4.7f. the R_{ct} is lowest for the porous N-Gr cathode (1.73 Ω), confirming the faster reaction kinetics of the porous electrode.



Figure 4.7. Electrochemical performance of Gr, N-Gr cathodes: (a) The first cycle GCD profiles of Gr, N-Gr porous and drop cast cathodes; (b) GCD profiles of Gr, N-Gr porous and drop cast cathodes for the first cycle at different current densities; (c) Rate capabilities of Gr, N-Gr porous and drop cast cathodes; (d) Cycling performance and Coulombic efficiency of Gr, N-Gr porous and drop cast cathodes at 0.5A/g for 150 cycles; (e) CV curves of Gr, N-Gr porous and drop cast cathodes for the first five cycles at a scan rate of 0.1 mV/s; (f) Nyquist plot from EIS measurements for Gr, N-Gr porous and drop cast cathode.

V. Conclusions

The following conclusions can be summarized based on the results presented in this thesis:

RQ1: How to control the 3D self-assembling structures of 2D layered materials using a sustainable and simple freeze-drying method?

- The ice crystals serving as the template induce the self-assembling of 2D nanosheets. The following freeze-drying process assists the removal of the ice template via sublimation, which helps to form a homogenously distributed structure.
- The synergic effect of MXene and graphene makes it possible to form a hybrid carbon material combining both self-supporting structure and outstanding supercapacitive performance. The as-prepared MXene-graphene composite exhibits an extraordinarily high specific capacitance.

RQ2: How plasma surface treatment affects the electrochemical performance of layered materials for aluminum batteries?

- Galvanostatic charge–discharge measurements demonstrate that hydrogen plasmatreated graphite delivers excellent performance, achieving a high specific capacity of 132.68 mAh/g at 50 mA/g and impressive rate capability with 83.94 mAh/g at 1000 mA/g.
- Ex-situ analyses further verify the robust interaction between chloroaluminate anions and the graphitic framework of hydrogen plasma-treated graphite when utilized as a cathode material in aluminum batteries.

RQ3: What's the effect of nitrogen doping on graphene electrode for aluminum battery?

- The higher binding energy of aluminum anions with nitrogen-doped graphene results in an increased specific capacity compared to pure graphene due to the presence of the more defects as active sites for the storage of the AlCl4⁻ anions.
- Our strategy leads to a 50% improvement in specific capacity (from 36.24 to 54.4 mAh/g at 0.1 A/g)

RQ4: How to form a porous structure in the graphene electrode and could the formation of the porous structure improve the performance of graphene electrode for aluminum batteries?

- A 3D porous network of nitrogen-doped graphene was developed by freeze-drying method as a cathode material for aluminum batteries.
- This cathode demonstrated a further 20% increased reversible specific capacity with the porous structure (65.5 mAh/g at 0.1 A/g) at a current density of 0.1 A/g and excellent rate performance, maintaining 38.0 mAh/g at 5 A/g.

VI. Future Works

From the presented results, the following recommended future works are put forward:

- The mechanism of our innovative freeze-drying method to self-assemble structure by graphene and MXene needs to be further investigated. The potential to achieve self-assembly of other 2D materials can be further studied.
- Previous research regarding the mechanism of charge storage behavior for aluminum batteries has been indicated by ex-situ characterizations such as ex-situ Raman and ex-situ XPS. More information may be found from in-situ measurements in the future research.
- The morphology of graphene cathode for aluminum batteries can be controlled with improved precision therein improving the performance of aluminum batteries.
- The possibility of the applications of the porous electrode and surface modified layered materials on other energy storage devices, for example, lithium-ion batteries, sodium-ion batteries, etc., can be further investigated.

References

- [1] Mohammadi, F. and M. Saif, *A comprehensive overview of electric vehicle batteries market*. e-Prime Advances in Electrical Engineering, Electronics and Energy, 2023.
 3: p. 100127.
- [2] Armand, M. and J.-M. Tarascon, *Building better batteries*. nature, 2008. **451**(7179): p. 652-657.
- [3] Vishwanath, S., P. Dang, and H.G. Xing, *Chapter 20 Challenges and Opportunities in Molecular Beam Epitaxy Growth of 2D Crystals: An Overview*, in *Molecular Beam Epitaxy (Second Edition)*, M. Henini, Editor. 2018, Elsevier. p. 443-485.
- [4] Guo, Y., Y. Wei, H. Li, and T. Zhai, *Layer Structured Materials for Advanced Energy Storage and Conversion.* Small, 2017. **13**(45): p. 1701649.
- [5] Novoselov, K.S., A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, and A.A. Firsov, *Electric Field Effect in Atomically Thin Carbon Films*. Science, 2004. **306**(5696): p. 666-669.
- [6] Sun, X., J. Zhang, Y. Wang, Y. Zhang, L. Hou, Y. Liu, and C. Yuan, *Self-assembly construction of hollow Ti3C2Tx Submicro-Tubes towards efficient alkali metal ion storage*. Chemical Engineering Journal, 2022. **433**: p. 134506.
- [7] Zhao, Q., Q. Zhu, J. Miao, P. Zhang, P. Wan, L. He, and B. Xu, *Flexible 3D porous MXene foam for high-performance lithium-ion batteries*. Small, 2019. 15(51): p. 1904293.
- [8] Zhao, M.-Q., X. Xie, C.E. Ren, T. Makaryan, B. Anasori, G. Wang, and Y. Gogotsi, *Hollow MXene Spheres and 3D Macroporous MXene Frameworks for Na-Ion Storage*. Advanced Materials, 2017. 29(37): p. 1702410.
- [9] Huang, W., Z. Ma, L. Zhong, K. Luo, W. Li, S. Zhong, and D. Yan, Efficient Self-Assembly Preparation of 3D Carbon-Supported Ti3C2Tx Hollow Spheres for High-Performance Potassium Ion Batteries. Small, 2024. 20(6): p. 2304690.
- [10] Qiu, L., J.Z. Liu, S.L.Y. Chang, Y. Wu, and D. Li, *Biomimetic superelastic graphene-based cellular monoliths*. Nature Communications, 2012. **3**(1): p. 1241.
- Fu, W., M. Aizudin, P.S. Lee, and E.H. Ang, *Recent Progress in the Applications of MXene -Based Materials in Multivalent Ion Batteries*. Small, 2024. 20(47): p. 2404093.
- [12] Lin, M.-C., M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, and H. Dai, *An ultrafast rechargeable aluminium-ion battery*. Nature, 2015. **520**(7547): p. 324-328.
- [13] Kim, J., M.R. Raj, and G. Lee, *High-Defect-Density Graphite for Superior-Performance Aluminum-Ion Batteries with Ultra-Fast Charging and Stable Long Life.* Nano-Micro Letters, 2021. 13(1): p. 171.
- [14] Rani, J.V., V. Kanakaiah, T. Dadmal, M.S. Rao, and S. Bhavanarushi, *Fluorinated Natural Graphite Cathode for Rechargeable Ionic Liquid Based Aluminum–Ion Battery.* Journal of The Electrochemical Society, 2013. **160**(10): p. A1781.
- [15] Wang, Z., D. Zhang, X. Bao, R. Hong, Y. Xu, J. Xu, and T. Hsieh, *Space-confined intercalation expansion strategy for simple and rapid synthesis of kish-based expanded graphite for aluminum ion batteries*. Carbon, 2024. **223**: p. 119016.
- [16] Santhosh, N.M., G. Filipič, E. Tatarova, O. Baranov, H. Kondo, M. Sekine, M. Hori, K. Ostrikov, and U. Cvelbar, *Oriented Carbon Nanostructures by Plasma Processing: Recent Advances and Future Challenges*. Micromachines, 2018. 9(11): p. 565.
- [17] Kong, Y., C. Tang, X. Huang, A.K. Nanjundan, J. Zou, A. Du, and C. Yu, *Thermal Reductive Perforation of Graphene Cathode for High-Performance Aluminum-Ion Batteries*. Advanced Functional Materials, 2021. **31**(17): p. 2010569.

- [18] Huang, H., F. Zhou, X. Shi, J. Qin, Z. Zhang, X. Bao, and Z.-S. Wu, Graphene aerogel derived compact films for ultrafast and high-capacity aluminum ion batteries. Energy Storage Materials, 2019. 23: p. 664-669.
- [19] Mas-Balleste, R., C. Gomez-Navarro, J. Gomez-Herrero, and F. Zamora, 2D *materials: to graphene and beyond.* Nanoscale, 2011. **3**(1): p. 20-30.
- [20] Zhu, H., Graphene: fabrication, characterizations, properties and applications. 2017.
- [21] Shinohara, H. and A. Tiwari, *Graphene: an introduction to the fundamentals and industrial applications.* 2015: John Wiley & Sons.
- [22] Castro Neto, A.H., F. Guinea, N.M. Peres, K.S. Novoselov, and A.K. Geim, *The electronic properties of graphene*. Reviews of modern physics, 2009. 81(1): p. 109-162.
- [23] Du, Y., M. Wang, X. Ye, B. Liu, L. Han, S.H.M. Jafri, W. Liu, X. Zheng, Y. Ning, and H. Li, Advances in the Field of Graphene-Based Composites for Energy–Storage Applications. Crystals, 2023. 13(6): p. 912.
- [24] Naguib, M., M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, and M.W. Barsoum, *Two-Dimensional Nanocrystals Produced by Exfoliation of Ti3AlC2*. Advanced Materials, 2011. 23(37): p. 4248-4253.
- [25] Anasori, B., M.R. Lukatskaya, and Y. Gogotsi, *2D metal carbides and nitrides* (*MXenes*) for energy storage. Nature Reviews Materials, 2017. **2**(2): p. 16098.
- [26] Xie, Y., Y. Dall'Agnese, M. Naguib, Y. Gogotsi, M.W. Barsoum, H.L. Zhuang, and P.R.C. Kent, *Prediction and Characterization of MXene Nanosheet Anodes for Non-Lithium-Ion Batteries*. ACS Nano, 2014. 8(9): p. 9606-9615.
- [27] Xie, Y., M. Naguib, V.N. Mochalin, M.W. Barsoum, Y. Gogotsi, X. Yu, K.-W. Nam, X.-Q. Yang, A.I. Kolesnikov, and P.R.C. Kent, *Role of Surface Structure on Li-Ion Energy Storage Capacity of Two-Dimensional Transition-Metal Carbides*. Journal of the American Chemical Society, 2014. **136**(17): p. 6385-6394.
- [28] Nasrin, K., V. Sudharshan, K. Subramani, and M. Sathish, *Insights into 2D/2D MXene Heterostructures for Improved Synergy in Structure toward Next-Generation Supercapacitors: A Review*. Advanced Functional Materials, 2022. **32**(18): p. 2110267.
- [29] Jeong, G.H., S.P. Sasikala, T. Yun, G.Y. Lee, W.J. Lee, and S.O. Kim, Nanoscale Assembly of 2D Materials for Energy and Environmental Applications. Advanced Materials, 2020. 32(35): p. 1907006.
- [30] Shehzad, K., Y. Xu, C. Gao, and X. Duan, *Three-dimensional macro-structures of two-dimensional nanomaterials*. Chemical Society Reviews, 2016. 45(20): p. 5541-5588.
- [31] Tian, W., A. VahidMohammadi, Z. Wang, L. Ouyang, M. Beidaghi, and M.M. Hamedi, *Layer-by-layer self-assembly of pillared two-dimensional multilayers*. Nature Communications, 2019. 10(1): p. 2558.
- [32] Bian, R., R. Lin, G. Wang, G. Lu, W. Zhi, S. Xiang, T. Wang, P.S. Clegg, D. Cai, and W. Huang, 3D assembly of Ti 3 C 2-MXene directed by water/oil interfaces. Nanoscale, 2018. 10(8): p. 3621-3625.
- [33] Huang, X., K. Qian, J. Yang, J. Zhang, L. Li, C. Yu, and D. Zhao, *Functional Nanoporous Graphene Foams with Controlled Pore Sizes*. Advanced Materials, 2012.
 24(32): p. 4419-4423.
- [34] Bian, R., R. Lin, G. Wang, G. Lu, W. Zhi, S. Xiang, T. Wang, P.S. Clegg, D. Cai, and W. Huang, 3D assembly of Ti3C2-MXene directed by water/oil interfaces. Nanoscale, 2018. 10(8): p. 3621-3625.
- [35] Xu, Y., K. Sheng, C. Li, and G. Shi, *Self-assembled graphene hydrogel via a one-step hydrothermal process*. ACS nano, 2010. **4**(7): p. 4324-4330.

- [36] Huang, C., H. Bai, C. Li, and G. Shi, *A graphene oxide/hemoglobin composite hydrogel for enzymatic catalysis in organic solvents*. Chemical Communications, 2011. **47**(17): p. 4962-4964.
- [37] Xu, Y., Q. Wu, Y. Sun, H. Bai, and G. Shi, *Three-Dimensional Self-Assembly of Graphene Oxide and DNA into Multifunctional Hydrogels*. ACS Nano, 2010. 4(12): p. 7358-7362.
- [38] Huang, H., P. Chen, X. Zhang, Y. Lu, and W. Zhan, *Edge-to-Edge Assembled Graphene Oxide Aerogels with Outstanding Mechanical Performance and Superhigh Chemical Activity.* Small, 2013. **9**(8): p. 1397-1404.
- [39] Bai, H., C. Li, X. Wang, and G. Shi, *A pH-sensitive graphene oxide composite hydrogel*. Chemical Communications, 2010. **46**(14): p. 2376-2378.
- [40] Guo, Y., K. Xu, C. Wu, J. Zhao, and Y. Xie, *Surface chemical-modification for engineering the intrinsic physical properties of inorganic two-dimensional nanomaterials.* Chemical Society Reviews, 2015. **44**(3): p. 637-646.
- [41] Liu, J., J. Tang, and J.J. Gooding, *Strategies for chemical modification of graphene and applications of chemically modified graphene*. Journal of materials chemistry, 2012. **22**(25): p. 12435-12452.
- [42] Kuila, T., P. Khanra, S. Bose, N.H. Kim, B.-C. Ku, B. Moon, and J.H. Lee, *Preparation of water-dispersible graphene by facile surface modification of graphite oxide*. Nanotechnology, 2011. 22(30): p. 305710.
- [43] Soo, L.T., K.S. Loh, A.B. Mohamad, W.R.W. Daud, and W.Y. Wong, An overview of the electrochemical performance of modified graphene used as an electrocatalyst and as a catalyst support in fuel cells. Applied Catalysis A: General, 2015. 497: p. 198-210.
- [44] Lei, Y., J. Ni, Z. Hu, Z. Wang, F. Gui, B. Li, P. Ming, C. Zhang, Y. Elias, D. Aurbach, and Q. Xiao, Surface Modification of Li-Rich Mn-Based Layered Oxide Cathodes: Challenges, Materials, Methods, and Characterization. Advanced Energy Materials, 2020. 10(41): p. 2002506.
- [45] Yu, H., Y. Wang, Y. Jing, J. Ma, C.-F. Du, and Q. Yan, Surface Modified MXene-Based Nanocomposites for Electrochemical Energy Conversion and Storage. Small, 2019. 15(25): p. 1901503.
- [46] Hai, Y., W. Cui, Y. Lin, P. Han, H. Chen, Z. Zhu, C. Li, B. Yang, C. Zhu, and J. Xu, Surface modification of graphite by ion implantation for promoting the electrochemical property in Li-ion batteries. Applied Surface Science, 2019. 484: p. 726-731.
- [47] Murillo-Herrera, L.M., C.J. Mingoes, J. Obrero-Pérez, J.R. Sánchez-Valencia, M.W. Thielke, Á. Barranco, and A.B. Jorge Sobrido, *Analysis of the impact of remote* oxygen plasma treatment on the surface chemistry and electrochemical properties of graphite felt electrodes for redox flow batteries. Energy Advances, 2024. 3(10): p. 2503-2511.
- [48] Tamargo-Martínez, K., S. Villar-Rodil, A. Martínez-Alonso, and J.M.D. Tascón, *Surface modification of high-surface area graphites by oxygen plasma treatments.* Applied Surface Science, 2022. **575**: p. 151675.
- [49] Duch, J., P. Kubisiak, K.H. Adolfsson, M. Hakkarainen, M. Golda-Cepa, and A. Kotarba, Work function modifications of graphite surface via oxygen plasma treatment. Applied Surface Science, 2017. 419: p. 439-446.
- [50] Ghanashyam, G. and H.K. Jeong, *Synthesis of nitrogen-doped plasma treated graphite for supercapacitor applications*. Chemical Physics Letters, 2019. **725**: p. 31-37.

- [51] Rybin, M., A. Pereyaslavtsev, T. Vasilieva, V. Myasnikov, I. Sokolov, A. Pavlova, E. Obraztsova, A. Khomich, V. Ralchenko, and E. Obraztsova, *Efficient nitrogen doping* of graphene by plasma treatment. Carbon, 2016. **96**: p. 196-202.
- [52] Zhang, Y., D. Zhang, L. Zhang, B. Yang, and Z. Gan, *The Etching Mechanisms of Diamond, Graphite, and Amorphous Carbon by Hydrogen Plasma: A Reactive Molecular Dynamics Study.* Advanced Theory and Simulations, 2023. 6(11): p. 2300371.
- [53] Shi, F., J. Jiang, X. Wang, Y. Gao, C. Chen, G. Chen, N. Dudko, A.A. Nevar, and D. Zhang, *Development of plasma technology for the preparation and modification of energy storage materials.* Chemical Communications, 2024. **60**(20): p. 2700-2715.
- [54] Li, C., T. Zhang, Z. Qiu, B. Ye, X. Liang, X. Liu, M. Chen, X. Xia, C. Wang, W. Wan, and Y. Zhang, *Plasma-assisted fabrication of multiscale materials for electrochemical energy conversion and storage*. Carbon Energy, 2025. 7(2): p. e641.
- [55] Nakajima, T., V. Gupta, Y. Ohzawa, M. Koh, R.N. Singh, A. Tressaud, and E. Durand, *Electrochemical behavior of plasma-fluorinated graphite for lithium ion batteries.* Journal of Power Sources, 2002. **104**(1): p. 108-114.
- [56] Long, Y., Y. Tao, W. Lv, and Q.-H. Yang, *Making 2D Materials Sparkle in Energy Storage via Assembly*. Accounts of Chemical Research, 2024. **57**(18): p. 2689-2699.
- [57] Lukatskaya, M.R., S. Kota, Z. Lin, M.-Q. Zhao, N. Shpigel, M.D. Levi, J. Halim, P.-L. Taberna, M.W. Barsoum, P. Simon, and Y. Gogotsi, *Ultra-high-rate pseudocapacitive energy storage in two-dimensional transition metal carbides*. Nature Energy, 2017. 2(8): p. 17105.
- [58] Holleck, G.L., *The reduction of chlorine on carbon in AlCl3-KCl-NaCl melts*. Journal of the Electrochemical Society, 1972. **119**(9): p. 1158.
- [59] Jayaprakash, N., S. Das, and L. Archer, *The rechargeable aluminum-ion battery*. Chemical Communications, 2011. **47**(47): p. 12610-12612.
- [60] An, C., X. Ma, J. Wu, J. Li, J. Li, S. Zhang, S. Zhang, and C. Cai, *Electrostatic modification of expanded graphite cathode for high-performance aluminum-ion batteries*. Journal of Electroanalytical Chemistry, 2023. 947: p. 117761.
- [61] Alhabeb, M., K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin, and Y. Gogotsi, *Guidelines for Synthesis and Processing of Two-Dimensional Titanium Carbide* (*Ti3C2Tx MXene*). Chemistry of Materials, 2017. **29**(18): p. 7633-7644.
- [62] Tatarova, E., A. Dias, J. Henriques, M. Abrashev, N. Bundaleska, E. Kovacevic, N. Bundaleski, U. Cvelbar, E. Valcheva, B. Arnaudov, A.M.B. do Rego, A.M. Ferraria, J. Berndt, E. Felizardo, O.M.N.D. Teodoro, T. Strunskus, L.L. Alves, and B. Gonçalves, *Towards large-scale in free-standing graphene and N-graphene sheets*. Scientific Reports, 2017. 7(1): p. 10175.
- [63] Yan, J., C.E. Ren, K. Maleski, C.B. Hatter, B. Anasori, P. Urbankowski, A. Sarycheva, and Y. Gogotsi, *Flexible MXene/Graphene Films for Ultrafast Supercapacitors with Outstanding Volumetric Capacitance*. Advanced Functional Materials, 2017. 27(30): p. 1701264.