Carbonaceous Two-Dimensional Electrode Materials for High Performance Electrochemical Double Layer Capacitors

Dhiman Kalita [a, b], B. Sheetal Priyadarshini [a, b], Unnikrishnan Manju [a, b*]

[a] *Materials Chemistry Department, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar, Odisha - 751013, India*

[b] *Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, Uttar Pradesh - 201002, India*

** Corresponding author : manju@immt.res.in*

Abstract

Research dedicated towards improving the efficiency and performance of the Electrochemical Double Layer Supercapacitors (EDLCs) can prove to be pivotal for sustainable energy storage. Selection of proper electrode material is imperative for enhancing the performance as the energy storing mechanism is dependent on the redox reactions occurring on the surface of the electrodes. 2D materials have been extensively studied for fabrication of electrode materials in EDLCs due to their unique layered structure and electrochemical properties. This review offers a holistic overview of the carbon-based 2D electrode materials and also discusses the challenges to be addressed for high performance EDLCs.

Keywords: *Supercapacitors, Energy, 2D materials, Graphene, MXene,*

1.1 Introduction

The depletion of fossil fuel reserves and the increasing energy demand urge us to unplug ourselves from its reliance on fossil fuels and look for development of alternating energy sources from renewable energy, such as solar and wind power. These sources are intermittent in nature and hence require energy storage for the harvested energy, such as batteries and capacitors. Batteries are preferred for applications requiring high energy density but restricted power output; on the other hand, capacitors are favored in those requiring high power. However, for applications requiring high energy as well as power density, neither batteries nor capacitors are sufficient, which prompts to an investigation of new types of energy storage systems known as electrochemical capacitors.

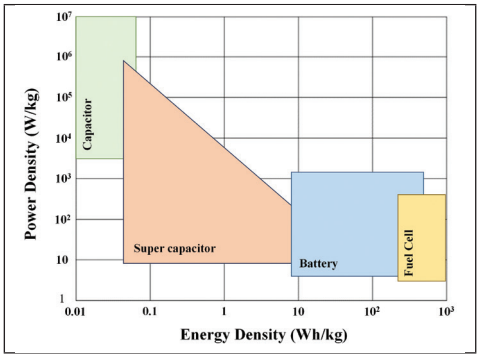


Figure 1: Ragone plot for energy storage devices [1]

Electrochemical capacitors (ECs) are electrical energy storage devices based on the electric double-layer existing at the interface between a solid electrode and an electrolyte. Hermann von Helmholtz proposed the electric double-layer theory that focus on the interfacial electrochemical reactions between a charged electrode and an electrolyte. ECs also known as supercapacitors or ultracapacitors can store larger amounts of energy than that conventional capacitors as depicted in the Ragone plot (Figure 1) [1]. Low capacitance values in the range of microfarad to picofarad of electrostatic capacitors limit their use in low-power applications. Whereas, the need for high-power capabilities due to the rapid growth in mobile electronic gadgets and electrical vehicles led to the development of supercapacitors. Becker at SOHIO in 1957 invented the first supercapacitor with exceptionally high capacitance with carbon material used as electrode [2]. Later, Boos developed the first practical supercapacitor in 1970 [3].

Supercapacitors use electrode materials with a high specific surface area and thinner dielectrics, resulting in very high specific capacitance [4],[5] They are also environment friendly, have a long

service lifetime, can operate in a wide temperature range, and can retain charge even at high applied current; which make them suitable for consumer electronics, transport, and smart meters [4], [5], [6], [7]. Supercapacitors can be divided into three categories on the mechanism on energy storage as shown in Figure 2.

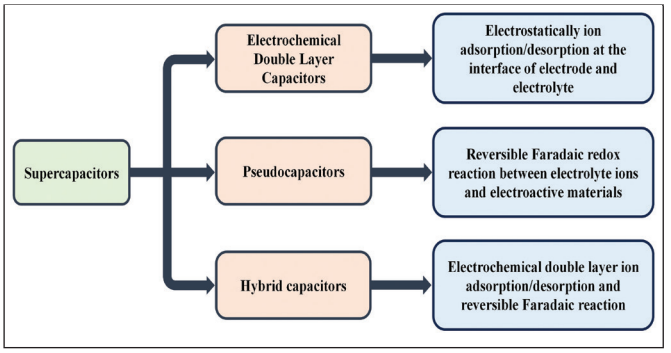


Figure 2: Supercapacitors types based on energy storage mechanism

Mostly, the progress of supercapacitor focuses on the development of electrode materials. Scientist have designed, developed and integrated one-dimensional, two-dimensional and three-dimensional electrode materials into supercapacitors to fabricate high performance electrode materials. In this review we focus on the electric double layer capacitor (EDLC) and concentrate on the electrode materials based on two-dimensional carbon materials.

1.2. Electrochemical Double Layer Capacitors

An electrochemical device comprises two electrodes with an electrolyte sandwiched between them. A typical double-layer capacitor is shown in Figure 3. The positive charges that accumulate on the positive electrode attract an equal number of negative charges due to Coulomb's force. However, they possess a net negative charge near the electrode due to the heat fluctuation in the electrolyte. The balance of charges between the electrode and the electrolyte is a representation of an electric double layer. The same phenomena occur across the negative electrode as well, which forms another electric double layer. Therefore, a complete two electric double layers with the positive electrode-electrolyte interface and the negative electrode-electrolyte interface is formed.

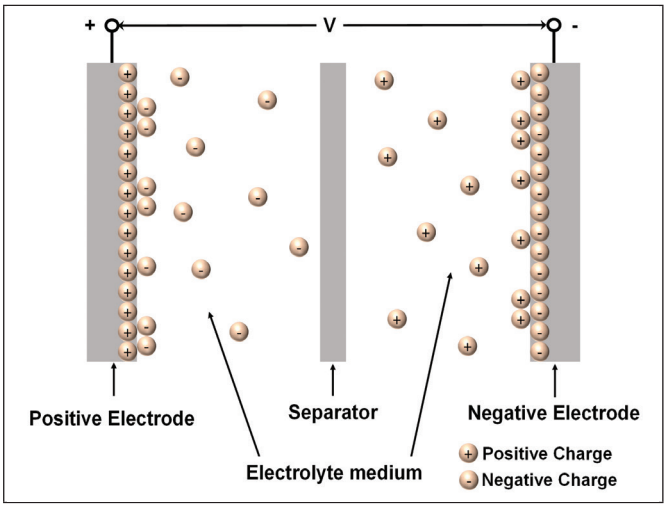


Figure 3: Schematic of electric double-layer capacitor

1.2.1. Working Mechanism

The initial development of the electric double layer model was based on an aqueous electrolyte. Later, non-aqueous as well as ionic liquids electrolytes were also used. The charge generated at the interface between the electrode and the electrolyte solution is balanced by an induced accumulation ions having opposite charges near the electrode surface in the electrolyte through the exertion of Coulomb's force as shown in Figure 4. Heat fluctuation helps scatter net negative charge ions with a higher concentration near the positive electrode surface and vice-versa. This scattered negative charged layer with the electrode positive charge array is termed a "diffuse double-layer" or "diffuse layer". This diffuse layer is also called the "Gouy point charge model" or the "Gouy-Chapman model" (Figure 4a). The diffuse layer thickness is dependent on the temperature, concentration of the electrolyte, number of charges carried by the ions, and the dielectric constant of the electrolyte.

In general, at high temperatures, the diffuse layer thickness increases. Whereas, at higher concentrations, a high number of charges carried by the ions and dielectric constant, the diffuse layer thickness decreases. A model with low temperature

and high electrolytic concentration, charge number carried by the ions, and dielectric constant gives a very thin diffuse layer leading to a compact electric double-layer termed as Helmholtz layer (Figure 4b) [8]. In a working model, these two layers coexist as shown in Figure 4c and it is termed as the Stern-Grahame model.

According to the fundamental relationship of capacitors ($C= (\varepsilon_0 \times \varepsilon_r \times A)/d$), the capacitance of a standard capacitor can be increased by increase in the dielectric constant of the material and surface area and the distance between the interplanar distance. However, such improvement can be achieved by the modification of the materials and the design of the capacitor. The selection of electrode materials and the design of electrodes play an important role in the subsequent electrochemical performance. 2D materials with a larger surface area have been developed as promising materials for electrodes [9],[10] After the discovery of "wonder material" graphene, the development of 2D nanostructured materials drastically increased. In the next section, we have discussed about the various carbon-based materials for the use of electrode material.

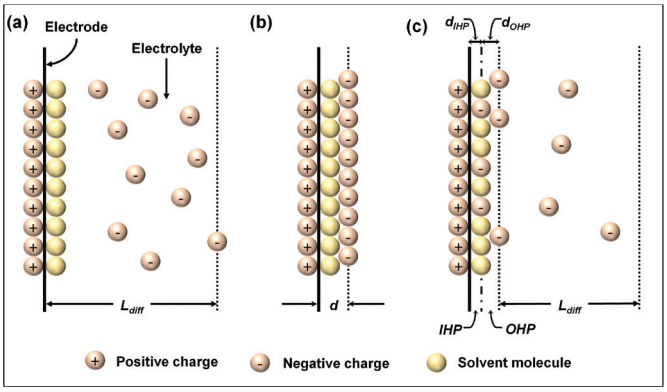


Figure 4: Schematics of the interface of electrode and electrolyte of electric double-layer. (a) Diffuse layer or Gouy-Chapman model, L_{diff} is the length of the diffuse layer. (b) Helmholtz layer, d is the double-layer thickness. (c) Stern-Grahame layer, IHP, and OHP are the inner and outer Helmholtz plane, and d_{IHP} and d_{OHP} are the respective thickness.

1.3. 2D Carbon based Electrode Material

Energy stored in EDLCs is primarily governed by the surface-controlled electrochemical phenomenon occurring on the electrodes. The choice of the electrode material is essential as they provide sites for charge separation at the electrode-electrolyte interface, i.e., Helmholtz double layer. The electric double layers formed at the interface between both the electrodes with the electrolyte influence the differential capacitance which decides the performance of the EDLC. Hence, it is imperative to enlarge the overall surface area of the electrode materials which renders more readily available active sites for energy carriers for efficient energy storage.

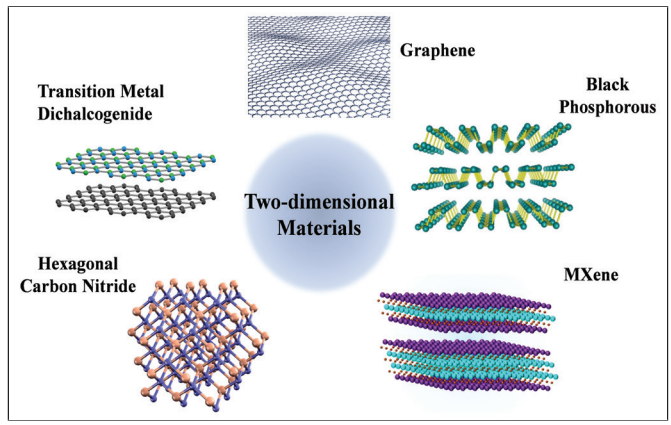


Figure 5: Some commonly explored two-dimensional materials as electrode materials for supercapacitor applications.

Ideally, the electrodes should be characterized by high surface area, good stability, superior mechanical properties, and excellent electrical conductivity [11]. Various nanostructured materials have been investigated for supercapacitor applications as electrode materials owing to the higher surface area than their bulk counterpart. 2D materials, possessing typical ultrathin and nanolayered structures, are considered promising electrode materials in EDLCs due to their large surface area and unique morphology (Figure 5) [12],[13] In recent years, many fabrication methods have been implemented to develop 2D electrode materials. To fabricate high-performance EDLC, both positive and negative electrode plays a critical role. However, very less importance has been given to the negative electrode materials. Different negative electrode materials have diverse operating voltage ranges, which drastically affect their performance. Usually, 2D materials show much better performance as negative electrodes than the positive electrodes [14].

1.4.1 Graphene

Owing to its peculiar two-dimensional honeycomb structure with sp^2 hybridized carbon sheets in hexagonal lattice conformation, graphene has been studied intensely for supercapacitor applications among other carbon-based materials [15]. The exceptionally high specific surface area of about 2630 $m^2 g^{-1}$, coupled with high electrical conductivity of about 10^6 S cm^{-1}, makes them an excellent choice as electrode materials in double-layer capacitors. Further, the added advantages of being corrosion resistant in aqueous electrolytes, superior cycle stability, high optical transmittance (97.7 %), higher Young's modulus (~1TPa), good thermal conductivity (~5000 W m^{-1} K^{-1}), and excellent carrier mobility (2 x 10^5 cm^2 V^{-1} s^{-1}) favor its usage in platforms for energy storage [16]. Commercial synthesis of graphene is also made scalable and economical by its facile and low-cost fabrication process using Hummer's method (Figure 6a).

The high carrier mobility of the graphene sheets enhances charge transfer during the charging and discharging process, however individual nanosheets are aggregated during fabrication due to interplanar π- π interaction and van der Waals forces. This drastically reduces the surface area and inhibits the diffusion of electrolyte ions which affects the performance of the EDLC. This is resolved by heteroatom doping and chemical bonding with highly conductive polymers or metal oxides. The composite of graphene with these materials synergistically enhances the ion transport and reduces sheet aggregation in graphene, thus increasing the overall capacitance of the EDLC.

Liu et al. synthesized a novel graphene-polypyrrole composite by hybridizing polypyrrole nanotubes with chemically reduced graphene sheets that combined the advantage of an electric double layer and pseudocapacitor. At a current density of 0.3 A g^{-1}, the hybrid composite electrode offered a very high specific capacitance of 400 F g^{-1}, which was significantly higher than previously reported values [17]. In another study reported by Tai et al., a unique bi-layered graphene/ shape-memory polyurethane (SMPU) electrode was synthesized via a simple bonding method. A graphene paper was closely bonded with SMPU and owing to the flexibility

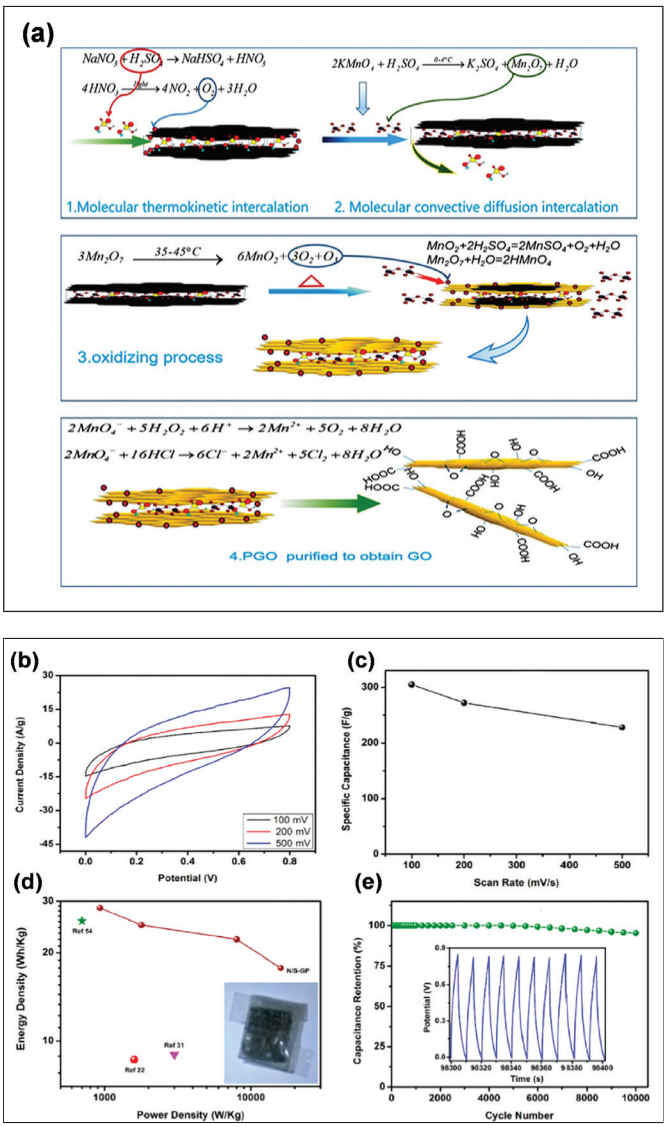


Figure 6: (a)Mechanism of oxidation of flake graphite to graphene oxide (GO) by Hummer's method. The figure encapsulates the oxidative chemical reactions that convert graphene to GO. Reproduced with permission from Ref. [19], Copyright 2022, American Chemical Society. (b) Cyclic voltammograms of supercapacitor device using free-standing dual doped graphene electrode in 6M KOH electrolyte at different scans and (c) the specific capacitance obtained. (d) Ragone plot of the fabricated symmetric supercapacitor as compared with graphene-based supercapacitor devices in ionic and aqueous electrolyte (inset shows the image of the assembled supercapacitor) (e) cyclic stability of the fabricated device at a current density of 5 A g^{-1} (inset shows magnified data of the last 10 cycles) Reproduced with permission from Ref. [20], Copyright 2016, American Chemical Society.

of the graphene paper, the composite film could adapt to different shapes and exhibited exceptional shape-recovering ability. The film shows a superior capacitive performance of 218 F g-1 at a current density of 0.75 A g-1 which is relatively stable up to 2000 charging-discharging cycles [18].

The electrochemical performance of graphene-based electrodes is closely related to the morphology of the material. Akhter et al. developed a flexible 3D architecture of graphene paper doped with nitrogen and sulfur through a one-pot thermal treatment of liquid crystalline graphene oxide and dopant composite followed by a soft assembly approach. This approach ensures layer-by-layer deposition of graphene oxide between which the dopant is trapped resulting in a composite electrode that exhibits a high specific capacitance of 305 F g^{-1} (Figure 6b, c), superior energy density (Figure 6d) and excellent capacitance retention up to 95.4% after 10,000 cycles (Figure 6e). The lightweight framework and binder-free synthesis make it apt for electronics and modern technology due to its economical scalability [20]. Zhang et al. followed a facile one-step synthesis procedure for rGO@NiO composite electrodes for supercapacitor electrode application via the electrode-assisted plasma electrolysis method. The fabrication process is mediated through electrochemical polarization which significantly reduces the deposition time, thus ensuring faster and more efficient synthesis than conventional methods. The hybrid composite delivers a superior specific capacitance of 1093 F g^{-1} at a current density of 1 A g^{-1}. The capacitance retention (87%) and Coulombic efficiency (90.6%) are well maintained over 5000 cycles, thus promising making it a robust electrode material in supercapacitors [21].

The influence of anionic surfactant sodiumlaurylsulphate (SLS) on the electrochemical performance of polyaniline (PANI) wrapped reduced graphene oxide hybrid composites (SPGO) for electrochemical energy storage was explored by Athira et al. The composite was prepared at sub-zero temperatures by oxidative polymerization of PANI on SLS-activated rGO layers that increase the overall surface area and provide ample surface-active sites allowing easy intercalation of electrolyte ions by reducing the diffusion time. The symmetric supercapacitor made up of SPGO electrodes showed a high capacitance of 531 F g^{-1} at a current density of 0.2 A g^{-1}. The prototype device also achieved an excellent working potential of 1.2 V with a specific energy of 26.5 Wh kg^{-1}. Owing to the scaffolding effect of SLS-modified rGO which establishes synergy with PANI and the corresponding Faradaic and double-layer interactions, the SPGO achieved 98% Coulombic efficiency after 5000 cycles which makes it a perfect candidate for electrochemical energy storing applications [22].

Graphene has been combined with a variety of polymers to yield composites with varying morphologies and conformations that have a significant influence on the capacitive properties. The composite of graphene with polypyrrole-based materials is less porous than graphene/PANI due to the larger size of the former. This renders enhanced cyclic stability to the graphene/PANI composites which makes them a better choice for electrode materials. The surfactants are known to improve the porosity of a composite and enhance its surface area. The SLS surfactant is widely used for cleaning and emulsifying purposes by reducing the surface tension of the medium. Its incorporation into GO improved its wettability and contributed to enhancing the specific capacitance of the hybrid composite by decreasing the agglomeration of GO layers which helped in the easy integration of PANI between the rGO layers.

4.2 Carbon-based MXenes

The fascinating structure of MXenes, a new class of 2D materials, has drawn the interest of researchers due to its unique morphology, large interlayer spacing, high electrical conductivity and melting point, exceptional hardness, large surface area, and superior thermal stability and hydrophilic nature. MXenes are transition metal carbides or nitrides having the general formula $M_{n+1}X_nT_x$ where M is a transition metal like Ti, V, Cr, Mo, W and Nb, X is either carbon or nitrogen or both and T is the surface termination groups like -OH, -F or -O. MAX phases, the precursors of MXenes, are a family of layered transition metal carbides or nitrides with the general formula $M_{n+1}AX_n$ where A is a group 13 or 14 element. The selective etching of the highly reactive "A" layers of MAX phases and their replacement with -OH, -F, or -O results in separated 2D-MXene sheets [23].

MXene is characterized by a layered hexagonal structure belonging to the space group $P6_3/mmc$. In addition to the inherent conformation of MXenes that renders more surface-active sites for electrochemical reaction, complete electron transport channels, metallic conductivity and ceramics nature of carbon/nitrogen contribute to enhancing the electrochemical performance that makes them a lucrative electrode material for supercapacitor applications. Further, the tunability of the surface groups endows them with exceptional thermal stability, good mechanical stability, superior optical properties, good hydrophilicity, and corrosion resistance which is an added advantage for usage in supercapacitors [24].

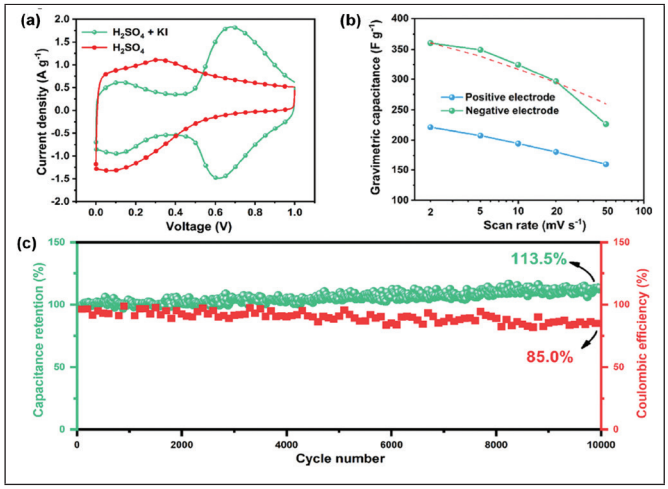


Figure 7: (a) CV curve of the symmetric supercapacitor with MXene electrodes in 3M H_2SO_4 and mixed electrolyte (3M H_2SO_4 and 0.2 M KI) at 5mV/s (b) Gravimetric capacitance of the positive and negative electrode in 3M H_2SO_4 at different scan rates. The difference in capacitances of the electrode occurring due to redox reactions of Ti is evident from the graph. (c) Cyclic stability of the MXene-based electrode in mixed electrolyte over 10,000 cycles at 10 A g^{-1}. Reproduced with permission from Ref. [25], Copyright 2020, American Chemical Society.

Delamination of MXenes involves the exfoliation of the layered MXene by intercalating with organic moieties which increases the interlayer distance, thus reducing the attractive forces between the MXene layers. Studies have shown that the delamination of layered MXenes into flakes enhances the electrochemical energy storing capacity. Dall'Agnese et al. demonstrated that delamination of MXenes resulted in a significant increase in the electrochemical capacitance to 325 F g^{-1} at a current density of 5 A g^{-1} with excellent stability up to 10,000 cycles. The intercalation with dimethyl sulfoxide (DMSO) increased the surface area and modified the surface chemistry which resulted in the enhancement of electrochemical capacitance [26].

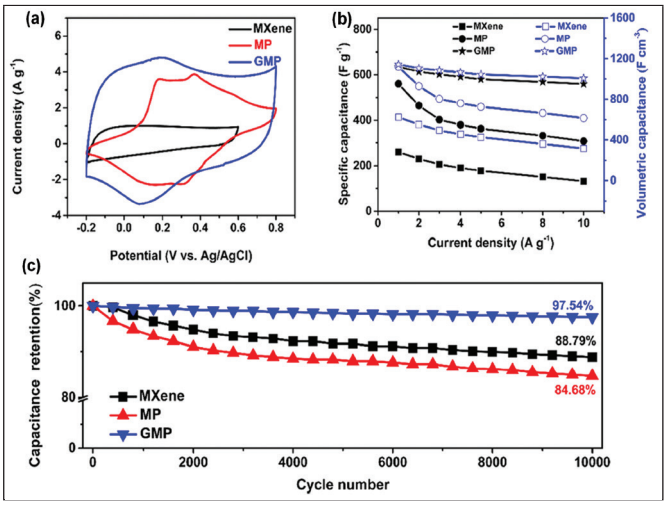


Figure 8: (a) CV curves of MXene, MXene Ti_2CT_x@ polyaniline (MP), and graphene-encapsulated MXene Ti_2CT_x@polyaniline composite (GMP) composite at 5mV s^{-1} showing the highest capacitance of the GMP electrode, indicating fast charge transfer. (b) The specific capacitance of the electrodes at different current densities with GMP showing a maximum specific capacitance of 635 F g^{-1}. (c)Higher stability of capacitance in GMP after 10,000 cycles with a 97.54 % retention at 10 A g^{-1}. Reproduced with permission from Ref. [27], Copyright 2018, American Chemical Society.

In an interesting study, Tian et al. demonstrated that $Ti_3C_2T_x$ based supercapacitors showed an asymmetric voltage splitting between the electrodes in H_2SO_4 electrolyte. They reported that the redox reactions of Ti concerning the bonding/de-bonding of Ti-O with the hydronium ions occur at the negative electrode raising its specific capacitance (361 F g^{-1}) with respect to the positive electrode (221 F g^{-1}) (Figure 7b). They proposed a novel strategy of including a redox electrolyte into the existing H_2SO_4 electrolyte to balance the unequal capacitances. In this study, they used potassium iodide (KI) as the redox electrolyte that is known to take part in reactions taking place at the cathode. They observed that with the addition of the redox

electrolyte the storage mechanism changed from capacitive to battery type (Figure 7a) which ensured higher energy density and displayed excellent cycle stability by retaining ~113% of the capacitance after 10,000 cycles (Figure 7c) [25].

In another study reported by Fu et al., they studied a robust three-component system for supercapacitor applications. The three-component system consisted of accordion-like MXene Ti_3CT_x, ionic-interactive PANI attached to MXene, and a chemically converted graphene sheet (CCG) that encapsulated the whole system into a single composite (GMP). At a pH of 9, the CCG exhibited a negative charge while the MXene-PANI nanocomposite showed a slight positive charge that facilitated the encapsulation of the graphene sheets onto the intercalated MXene system. The conductive PANI was successfully intercalated between MXene sheets, increasing the surface area that resulted in higher current density (Figure 8a) and electrochemical capacitance of 635 F g^{-1} at a current density of 1 A g^{-1} (Figure 8b). Additionally, the GMP electrode also exhibited excellent stability of the capacitance (97.54 %) after 10,000 cycles (Figure 8c). The GMP/graphene pouch-like asymmetric supercapacitor exhibited an exceptional energy density was also 42.3 Wh kg^{-1} at a power density of 950 W kg^{-1} with a cycle stability of up to 94.25 % after 10,000 cycles. This shows that the GMP electrode holds promise in the field of 2D-electrode material for high-performance supercapacitors [27].

MXenes can also be assembled into micro supercapacitors (MSC) that have higher power and energy densities as compared to supercapacitors and can efficiently power up microsensors, micromechanical systems, and smart electronics that require less energy to operate. Peng et al. demonstrated an all-MXene ($Ti_3C_2T_x$) solid-state interdigitated electrodes using spray coating technique as a prospective design for an on-chip energy storage module. The novelty of the MSC lies in the integration of noble-metal-free, all-MXene heterostructures for both electrodes, where the larger MXene flakes constituted the current collector and the smaller flakes formed the active layer. As compared to MSCs with platinum current collectors, the all-MXene MSC displayed excellent stability, lower contact resistance, and higher capacitances. The areal and volumetric capacitances of the all-MXene MSC were found to be ~27 mF cm^{-2} and 357 F cm^{-3}, respectively. The device exhibited a capacitance retention of 100% at a scan rate of 50 mV s^{-1} after 10,000 cycles which vouches for its robust nature. This unique study opens doors for a myriad of designs that can be incorporated into MSC using MXenes to enhance the volumetric and areal capacitances for increasing their electrochemical energy storing abilities [28].

MXenes are attractive candidates for electrode materials owing to their metallic conductivity, low ion diffusion barrier, higher surface area, and tuneable surface properties but pristine MXene possesses the inherent drawbacks of restacking of MXene layers, easy oxidation on coming in contact with water and mechanical flexibility. However, these can be reduced by forming composites of MXenes with organic moieties that act as spacers and increase the interlayer distance between the successive MXene layers, and prevents the restacking of the layers. It also increases the surface area of the MXenes which enhances the overall electrochemical performance.

4.3 Carbon Nitride

Carbon nitride (CN) is a two-dimensional graphene-like structure with high nitrogen content, unique optical properties, attractive electronic structure, and superior chemical and thermal stability. It exists in seven phases namely, α-C_3N_4, β-C_3N_4, cubic-C_3N_4, pseudocubic-C_3N_4, g-h-triazine, g-o-triazine, and g-h-heptazine (Figure 9). However, the graphitic carbon nitride (g-C_3N_4) phase has attracted the attention of researchers due to its inherent stability at ambient conditions. The g-C_3N_4 structure constitutes a nitrogen-substituted graphene network with sp^2 hybridized carbon and nitrogen, forming a π-conjugated structure. The nitrogen-rich structure results in higher electrons in the π-conjugated bond thus improving the electrical conductivity. Further, g-C_3N_4 is stable to harsh chemicals and resists degradation on being exposed to acids, alkalis, or other organic solvents, making them favorable to be used as electrode materials [29].

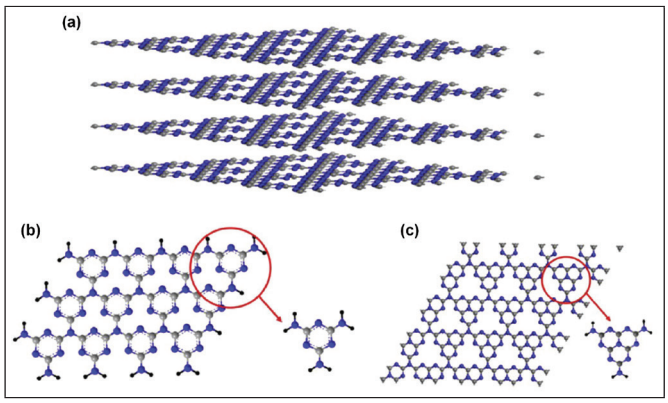


Figure 9: Chemical structure of the widely researched phases of carbon nitride: (a) g-C_3N_4 layered 2D stacked structure, (b) s-triazine and, (c) heptazine structure. Reproduced with permission from Ref. [30], Copyright 2020, American Chemical Society.

Nanostructures of g-C_3N_4 like nanotubes, nanorods, nanosheets, etc, are proven to be more efficient than their bulk counterparts. Tahir et al. explored tubular g-C_3N_4, fabricated using melamine and nitric acid, for supercapacitor applications due to the distinct morphology and high surface area of 182.61 m^2/g. It displayed a good specific capacitance of 233 F g^{-1} at a current density of 0.2 A g^{-1} in a 6 M KOH electrolyte.

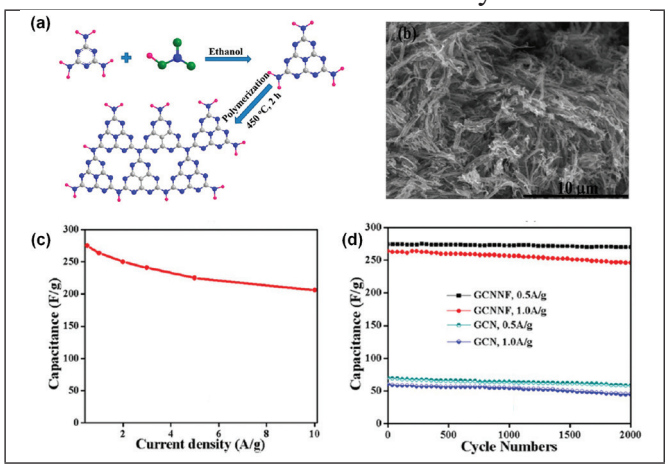


Figure 10: (a) Schematic of the fabrication procedure of GCNNF (b) Scanning electron micrograph of GCNNF (c) Variation of the capacitance of GCNNF with respect to the current density (d) Cyclic stability of GCNNF and graphitic carbon nitride (GCN) at 0.5 and 1 A g^{-1} for over 2000 cycles. Reproduced with permission from Ref. [32], Copyright 2013, American Chemical Society.

The superior performance of the tubular g-C_3N_4 is attributed to the high nitrogen content that renders higher surface area and consequently higher active sites. This novel electrode also shows exceptional cycle stability with about 90% capacitance retention after 1000 cycles. The authors also reported that tubular g-C_3N_4 possesses excellent photocatalytic properties and can prove to be an efficient material for energy storage and photocatalysis [31].

Tahir et al. also studied pure carbon nitride and developed a facile and environment-friendly chemical route to synthesize graphitic carbon nitride nanofibers (GCNNF) (Figure 10a, b). The synthesized GCNNF were investigated for their potential applications as electrode materials in supercapacitors due to high surface area and enhanced nitrogen content as compared to bulk C_3N_4, which improved the electrical conductivity. The GCNNF exhibited superior capacitance of 263.75 F g^{-1} at 1 A g^{-1} in a 0.1 M Na_2SO_4 electrolyte (Figure 10c) and capacitance retention of 96.3% after 2000 cycles (Figure 10d) [32]. Gonçalves et al. studied pristine carbon nitride obtained from pyrolysis of urea followed by exfoliation. The synthesized material exhibited high capacitance of 113.7 F g^{-1} at a current density of 0.2 A g^{-1} which displayed a retention of 89.2 % of its initial value after 5000 cycles [33]. Dong et al. designed an electrode from a sandwich-like composite of g-C_3N_4 with polypyrrole fabricated via a chemical oxidation method. The composite yielded a capacitance of 471 F g^{-1} specific capacitance at a current density of 1 A g^{-1} with about 80% retention ability up to 1000 cycles [34].

Carbon nitride is an attractive choice for electrodes in supercapacitors owing to the higher nitrogen content that enriches them with active sites for reaction. However, g-C_3N_4 is characterized by low electrical conductivity and a smaller surface area that severely affects the electrochemical performance in supercapacitor applications. Additionally, a higher concentration of non-graphitic nitrogen and a large bandgap of ~ 2.7 eV mandates different approaches like altering the morphology and doping with other conductive materials to make it suitable for supercapacitor applications. The interlayer van der

Waals interaction in g-C_3N_4 results in restacking of the single layers that diminish its power and energy density. Strategies like hybridization with materials having higher conductivity and downsizing them to the nanoscale have yielded optimistic results which pave the way for a brighter future of g-C_3N_4 in the field of electrochemical energy storage.

5. Future Challenges

Supercapacitors have acquired a niche position in the field of electrochemical energy harvesting due to the high-power density that gives them an edge over the slow kinetics of secondary batteries. The energy density of the supercapacitors is governed by its electrodes which are the sites of electrochemical reactions. 2D materials have been widely explored for electrode applications in supercapacitors due to the unique morphology that endows them with exceptionally high surface area. However, challenges remain in the practical application of 2D-based hybrid electrode materials. Most of the 2D materials are synthesized through a complex chemical process which is energy and time intensive. One-pot synthesis is a more favorable approach to fabricating 2D materials which does not require an exfoliation process but only a few members of the 2D family can be prepared via a single step. Research should be aimed at designing and developing economically feasible and industrially scalable procedures of 2D materials fabrication. Additionally, surfactant contamination and intercalation residues also result in impurities that affect the electrochemical performances. Further, a hybrid of 2D materials with other conductive materials for asymmetric devices can also boost the device's performance. Cycle stability is an important parameter that gauges the performance of the supercapacitors and about 1000 to 10,000 cycles are carried out at lab-scale to check the device's stability. Rigorous cycling is known to induce corrosion in the supercapacitor components and reduces the capacitance and increases the ESR. Stability data from extensive cycling of the electrodes should be included to test the device's potential for real-life application. A major drawback in the performance of the supercapacitors lies in the self-discharging phenomenon, a thermodynamic instability triggered by the redistribution of ions within the pores. The usage of organic electrolytes has been reported to overcome this difficulty. However. much understanding is yet to be acquired on the performance of supercapacitors in organic electrolytes. There is a scarcity of DFT (density functional theory) studies that can support experimental evidence and further provide innovative designs for enhancing the efficiency of supercapacitors. Structural and electronic parameters like bond length, bond angle, lattice energy, density of states, and charge transfer can be easily predicted by DFT studies that will prove to be helpful for developing efficient models. This can also help in integrating the supercapacitor in electronic devices into a single component that is beneficial while developing efficient models for practical applications.

6. Conclusion

2D materials have the potential to perform adeptly as electrode materials due to high exposed surface area, atomic layer thickness, large surface area to volume ratio, and tunable surface properties. The most commonly used carbon-based electrode materials like graphene, MXene, and carbon nitride towards the electrochemical performances of supercapacitors proves their efficiency over other nanomaterials. However, much research needs to be focused on polishing the shortcomings by developing efficient synthesis procedures, designing newer hybrid structures, and integrating them in electronic devices. This will enable the production of new generation, efficient and high-performance supercapacitors that will be the eco-friendly alternative to existing conventional energy storage devices.

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