

Graphene foam–based electrochemical capacitors

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Abstract

Electrochemical capacitors (ECs) are a promising technology for energy storage, and future development of sustainable electrode materials is critical to developing these devices. The recent progress and earnest motivation to develop high specific energy capacitors commercially for the emerging market and electronics industry, coupled with the significance and popularity of graphene foam (GF) based electrode materials in the preparation of functional capacitors have been crucially explored in this review. The review outlines the current disposition and headways in graphene foam based ECs' technology. Besides, owing to its three-dimensional interconnected hierarchical form alongside the physicochemical distinctions, GF has been regarded as one to curtail some bottlenecks regarding graphene dispersion/restacking in nanocomposite materials. Some of the various techniques to synthesizing high-grade GF that can enable higher energy density of ECs, as well as some key material's features of GF that enhance various performances of the material's composite have also been reviewed.

Keywords: Electrochemical capacitors, graphene foam, graphene foam based-composites, energy storage

1. Introduction

In recent years, graphene, a material that consists of two-dimensional (2D), one-atom-thick sheet of sp^2 -hybridized carbon atoms has attracted tremendous interest in a variety of fields due to its outstanding electronic, thermal, and mechanical properties [1,2]. This ultra-thin electrode material comprises a monolayer of carbon atoms arranged through hexagonal bonding into 2D lattice, has been extensively explored in a plethora of applications, such as in energy storage and generation, sensor fabrication and in various electrical nano-devices due to its reported various beneficial properties.

The material has been reported severally as a promising candidate for electrode materials due to its high theoretical specific surface area of $2630 \text{ m}^2 \text{ g}^{-1}$ and ability to facilitate electron or hole transfer along its two-dimensional surface [3,4]. Studies have shown that graphene sheets are desirable candidates for enhancing the performance of electrode materials for energy storage devices such as capacitors to meet the demands of consumers. The impedance analysis of some of the graphene-based composites suggested their charge transfer resistance to be very low, which accounts for their excellent rate capability [5].

Graphene offers many advantages over using typical electrode materials in a standalone fashion [6]. First, the graphene can serve as a binder material, eliminating the use of binding polymer materials such as poly (vinylidene fluoride) [7]. Second, the high conductivity associated with graphene sheets lends itself to rapid transport of electrons to and from the active material intercalation sites [8], particularly given the close physical association of the nanoparticles and the graphene sheets. Also the mechanical strength of the graphene has the potential to absorb some of the expansion and contraction of the anchored nanoparticles during the intercalation and deintercalation processes [9], which typically lead to mechanical failure of the electrode and performance reduction through the loss of intimate contact of the active material and the

conductive carbon black mixed into the electrode material for enhanced conductivity. The electrode can ultimately be pulverized if the expansion is large enough, hence the use of active materials that exhibit small changes upon metal ion intercalation.

Graphene has also been utilized as a standalone material for Li ion battery anodes in place of traditional graphite and shows some marked improvement in storage and cycling. The storage capacity and cycling ability of graphene was shown to outperform graphite in a number of studies [4,7,10]. Some have attributed this improvement to the higher surface area achieved in graphene relative to graphite [6]. The material is generally proposed as an alternative to activated carbon in electrochemical capacitors owing to its more substantial high specific surface area, which improves capacitance and enhances electrostatic charge storage of the device. Besides, such devices utilize the material's natural lightweight, elasticity alongside its mechanical strength.

Nevertheless, challenges such as the restacking of graphene sheets, non-uniformity in its distribution, and high inter-sheet contact resistance have hindered the reinforcement efficiency of graphene from its full potentials. Experimental usage of graphene finds its major constraints in two ways: The first has got to do with how we can minimize clustering of its sheets to the least energy confirmation, which is graphite, owing the presence of the well secured π - π interlinkage between the layers of the material. This results in reduction of single layer graphene into a quasi-material which comprises double, few and multi-layers that symbolically arises when the material is being immobilized onto the surface of an electrode. The clustering of graphene can remarkably restrict the ability of graphene based devices, such as electrochemical capacitors. In these devices, the clustering minimizes the attainable surface area and d-spacing between individual layers of graphene, and thus decreases proportionally with the number of clustered layers, which in turn

impoverish the capability of the device [2,11,12]. Another challenging bottleneck remains how to electrically connect to a material of the type.

One of the several viewpoints to reducing such challenging bottlenecks as noted above, include the employment of the very captivating three-dimensional (3D) graphene foams (GF) in fabricating the ideal electrodes for ultra-fast chargeable/rechargeable electrochemical capacitors. The technique integrates graphene layers into a 3D macroscopic structure, therefore reducing the particulate nanostructured materials aggregation during cycling, resulting in the formation of good conduction network and enhanced particle connectivity.

Here in, we present an inclusive review of the prime development and recent trends regarding the highly crystalline and fascinating 3D graphene foam. The material proves potentially promising network architecture over the traditional 2D graphene ascribed to its highly porous macroscopic and microscopic structure, high specific surface area and ease of utilization amongst others, which are of benefits in electrochemistry.

2. Graphene foam (GF)

In order to further improve on the issue of aggregation and the likes that are associated with the conventional graphene, many substantial attempts were been made to advance 3D-network graphene-based macrostructures such as graphene foam [13,14]. Graphene foam (GF) is a highly fascinating and interesting freestanding 3D graphene macroscopic structure, which has aroused a lot of researchers' attention from distinct fields for both applied and fundamental research. It is a porous, high surface area structure of graphene, which is mainly synthesized by employing the chemical vapour deposition system. The material combines the cutting-edge mechanical and electrical properties of conventional 2D graphene alongside the properties of metallic foam, thus capable of providing high conductivity, excellent strength and flexibility. Graphene foam is employed as electrode material in energy storage devices, such as electrochemical capacitors and

batteries. The material's unique structure opens up the potential to store huge sums of energy. The material is known for its high specific surface area ascribed to its porous nature, thus giving rise to enhanced electrochemical performances. Its distinctive micro, meso and macro interconnected porous structure, high specific surface area alongside fast ion/electron transport channels, are highly beneficial for exploring high energy and power densities, and the electrochemical performances in general [15–17]. Electrochemical capacitors operating on this unique material have been found to be considerably more efficient than those presently available in the market. Today, applications of this fascinating material continue to be under investigations.

2.1 Synthesis of graphene foam

Various approaches to synthesizing 3D graphene foam for electrochemical capacitor electrodes fabrications have been reported. Two major techniques have been generally adopted for the fabrication of this fascinating material, which are the template and non-template techniques. The template technique is of two types: The hard-template that utilizes hard and nanostructured porous metal foams such as nickel foams as templates, and the soft-template that adopts supra-molecular agglomerates like micelles and emulsions as templates [1,18].

Current research advances have shown the hard-template approach as frequently employed technique to fabricating the 3D material. The simple and cost-effective technique utilizes prefabricated 3D nickel foams that serve as template and catalyst simultaneously, and impart the development of graphene on the 3D skeletons, thus providing porous and unique interconnected structural network [1,19]. In this technique, graphene foam is synthesized by atmospheric pressure chemical vapour deposition (APCVD) process onto nickel (Ni) foam. A 3D-scaffold template of polycrystalline Ni foam is set in an APCVD quartz tube. The Ni foam is first annealed at a temperature of 1000 °C using argon (Ar) and hydrogen (H₂) gasses simultaneously at 300:200 sccm flow rate for 60 min. to remove dissolved contaminants from the material. Methane (CH₄)

gas employed as the carbon source is introduced into a reaction tube of the furnace, which heats up to 1000 °C at the same temperature for 15 min, with flow rates being kept at 300:200:10 sccm for Ar, H₂, and CH₄, respectively. As the system is heated up and the methane decomposes, the Ni foam in the tube captures a mono, bi or multi-layer graphene in a similar structure as the methane decomposes whilst adjusting the reaction tube to a cooler end of the device to facilitate evenly distributed deposition on the Ni foam template [20,21]. The carbon source concentration has a huge influence on the expected properties of the GF. The Ni skeleton is then removed via etching using 3 M HCl solution, during which mechanical support is provided by drop-coating polymethylmethacrylate (PMMA) on the material with subsequent baking at around 180 °C for about 30 min. The PMMA is removed from the material by being placed in acetone at 50 °C for 30 min. Subsequently, the material is rinsed with water and then dried, leaving behind a visible and highly porous 3D graphene foam structure, which preserves most of the conventional 2D graphene properties. The obtained GF bequeathed the original Ni foam morphology, which comprised the traditional interconnected flexible networks even after removal of the template. The derived free-standing 3D material revealed a high SSA of ~850 m² g⁻¹, a porosity of ~99.7% [22] and pore sizes ranging from 100-300 μm aside its high conductivity. The APCVD technique opens up an environmentally-friendly and cheap route for fabricating a novel sort of highly porous, ultra-light and very conductive graphene based material, which possesses unprecedented flexibility, elasticity and mechanical strength among others.

2.1.1 High-throughput and scalable fabrication of graphene foam

Scalable fabrication of materials often faces several issues, such as unstable performance and technical problems [23]. GF is known for its unique morphological and structural properties, which make the material a potential candidate for numerous applications. Nonetheless, the material's scalable fabrication remains a challenge on industrial-scale applications.

The Ni-foam-directed CVD synthesis technique is a simple and effective route to producing GF with the novel properties such as high crystalline quality and ideal structural design-ability. Nevertheless, the resulting material's pore size was narrowed to the micro scale that failed to meet the geometrical nanoporous requirements for specific applications.

A nanoporous Ni-based CVD system was adopted to overcome this issue, which permits fabrication of GF networks with tunable pore sizes from 100 nm to 2 μm [24,25]. The Ni foam template was prepared through electrochemically de-alloying $\text{Ni}_{30}\text{Mn}_{70}$ foils in a solution of $(\text{NH}_4)_2\text{SO}_4$. Graphene layers were then grown on the nanoporous Ni surface in a CVD system under a mixture of gases containing H_2 , Ar, and benzene. The resulting graphene-coated Ni foam displayed an estimated mean pore size of ~ 210 nm, and distribution in a range of 100 to 300 nm. This made the GF well interconnected and free of pore collapse even after the Ni has been etched [24].

2.2 Graphene foam properties

Graphene has been recognized as the strongest material ever unearth owing to the strength of its nanometer-long carbon bond. It is known for its high tensile strength and ultra-light weight, and capable of maintaining its original size after stress. The incomparable mechanical strength of the GF graphene resulting from its pore sizes in the range of sub-micrometer to diverse micrometers, strikingly improves material strength and performance of composites electrodes for ECs application. The zero-gap 3D semimetal material is of excellent electrical conductivity as result of holes, and highly mobile electrons that are fixed above and beneath its sheet, thus improve the material's carbon-carbon bonds. This among other things makes GF a promisingly better material at conducting electricity compared to other EC electrode materials at room temperature. Graphene foam structures are thermally stable, even at elevated temperatures, and are reusable. Its repeating 3D interconnected structure permits the motion of phonons within the material without an

hindrance at any point on the large surface, and allows for more efficient and higher thermal stability compared to other electrode materials [10,26–28].

2.3 Influence of GF structure on the performance of GF based capacitors

Electrode materials' structure such as morphology, particle size, pore sizes and distribution and specific surface area can massively impact the overall performances of electrochemical capacitors. The Morphology of an electrode material plays a crucial role in enhancing EC parameters. Fig. 1 (a) shows the SEM micrographs of 3D graphene foam at low and high magnifications, revealing its novel and progressive highly interconnected network morphology. This unique structure is responsible for the GF's evident high electrical conductivity among others. The material's superb nano-size geometry coupled with alignment of pores/pore ordering degree and high specific surface area contributes to the superior performance of GF-based ECs [29]. Basically, not all of the surface area is electrochemically accessible by the electrolyte, thus the capacitive performance of ECs is not a direct proportion of the high specific surface area but is a function of the accessible surface area of the material to the electrolyte in use. The very high surface area of GF which provides high accessibility to electrolytes makes it superior to other material for energy storage applications such as in ECs. Fig. 1 (b) depicts the XRD pattern of a typical as-grown GF indication diffraction peaks at around $2\theta = 31$ and 64.5° , corresponding to the 002 and 004 reflections of hexagonal graphite, respectively. The XRD spectrum shows no peaks that could relate to Ni, indicating the successful etching of Ni from the GF. Also, The Raman spectrum (Fig. 1 (c)) reveals the GF is formed by a few layer graphene sheets, with two main peaks corresponding to G and 2D modes of typical graphene material. The observed symmetric shape/higher intensity of the 2D peak in relation to the G peak is evident of few layers and high crystalline graphene. EDS spectrum in Fig. 1(d) confirms the successful removal of Ni in a typical as-synthesized GF, confirming just the presence of carbon in the material.

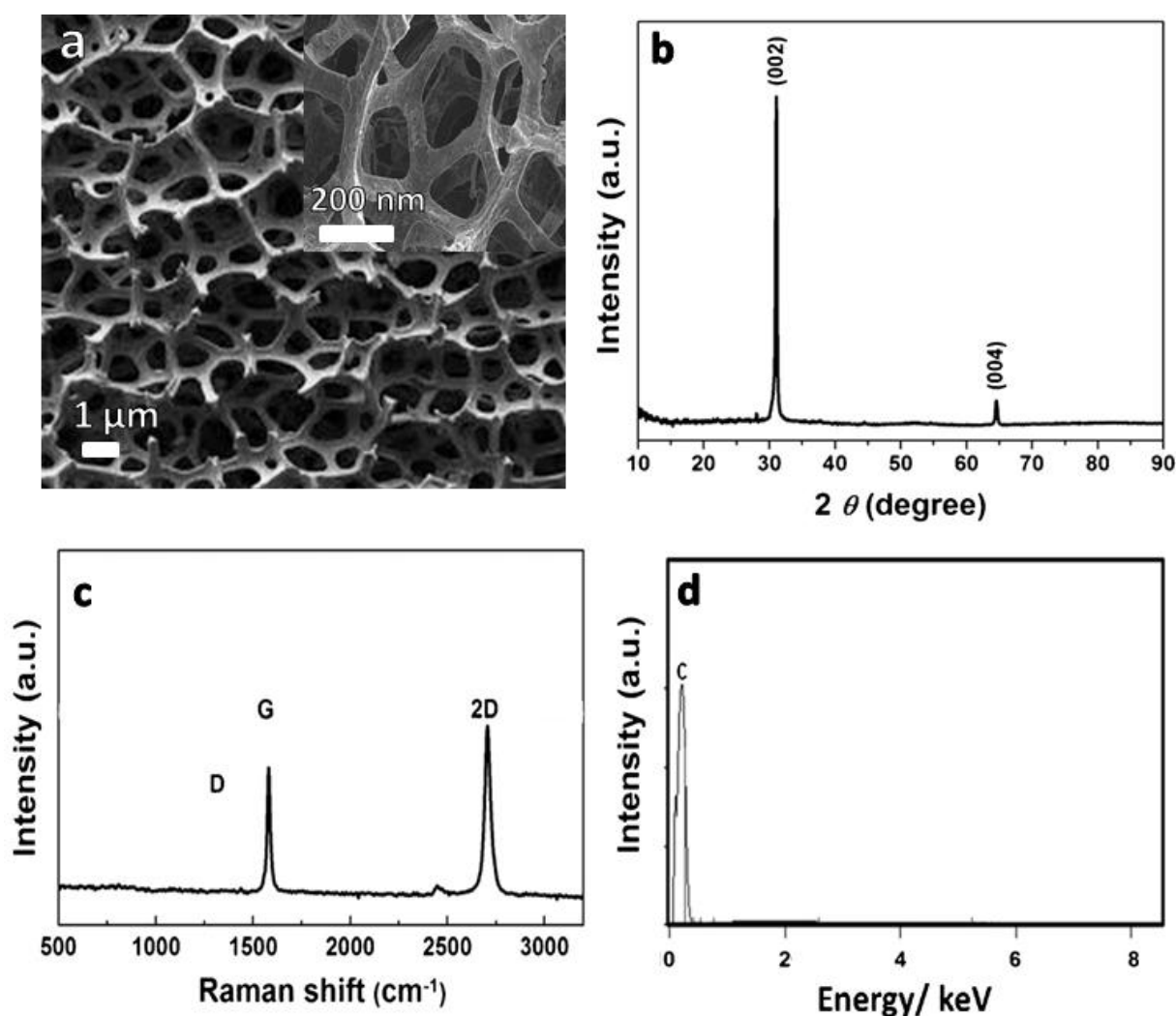


Fig. 1: (a) SEM images, (b) XRD pattern, (c) Raman spectrum and (d) EDX analysis of a typical as-synthesize GF, with b, c and d adapted from [21].

3. Graphene foam based electrochemical capacitors

Recently, GF has been incorporated into material as composite to provide the prevailing EC electrode materials with required strength, further lightweight, higher surface area and chemical stability, which further enhance the capability of ECs. GF-based composites have got a massive prospect to becoming an extensively employed alternative to many materials currently adopted in EC technology. Thus, a 3D free-standing GF architecture has been developed to serve as pathways

to providing high thermal and electrical conduction capability among other fascinating properties, in EC material composites. Table 1 shows a summary of the electrochemical performance of some recently published results concerning GF based electrochemical capacitors.

Table 1: Electrochemical performances of some recently published results on GF-based ECs.

Electrode materials	Electrolyte	Potential (V)	Maximum Specific capacitance (capacity)	Efficiency (% , cycles)	Energy density (Whkg ⁻¹)	Power density (Wkg ⁻¹)	Ref.
NiCo ₂ O ₄ nanowire core and MnO ₂ nanosheet shell on GF	6M KOH	1.5	2577 F g ⁻¹	94.3, 5000	55.1	187.5	[30]
GF/ZnO Superbat	LiPF ₆	2.0	448 F g ⁻¹	N/A	35.0	270	[31]
Ni(PO ₄) ₃ /GF	6M KOH	1.6	48 mAh g ⁻¹	98.0, 10000	49.0	499	[32]
Freestanding 3D GF	C4MIM hybrid	0.7	636 μF	N/A	40.94	2933	[33]
Flexible graphene-Ag-3D GF	1M H ₃ PO ₄	1.15	38 mF cm ⁻²	68.0, 25000	3.4 μWh cm ⁻²	0.27mWcm ⁻²	[34]
All-solid-state 3-GF/graphite-paper	1M H ₂ SO ₄	1.0	11.1 mF cm ⁻²	79.5, 10000	1.24 mWh cm ⁻²	24.5mWcm ⁻²	[35]
Polypyrrole-coated GF	PVA/ H3PO4	0.8	258 mF cm ⁻²	93.8, 1000	22.9 μWh cm ⁻²	0.56mWcm ⁻²	[36]
ZnCo@NiCo/3D GF	PVA)/KOH gel	1.5	1278 mFcm ⁻²	108, 5000	171 mWh cm ⁻²	2.5 mAcm ⁻²	[37]
V ₂ O ₅ /GF	6 M KOH	1.6	41 mA h g ⁻¹	99.0, 10000	39.0	947	[38]
Reduced graphene oxide 3D foam	1M NaCl	1.0	618.15 F g ⁻¹	99.0, 3550	42.92	1350	[39]
Ni/GF/H-CoMoO ₄ //Ni/GF/H-Fe ₂ O ₃	PVA/KOH gel	1.5	3.6 F cm ⁻³	93.1,	1.13 mWh cm ⁻³	150 mW cm ⁻³	[40]

The selected papers in Table 1 are of remarkable interest due to their significant electrochemical performances such as wider operating potential, higher specific gravimetric and volumetric capacitance/capacity, higher energy/power capability and excellent rate performance/cycle stability resulting from effective electron transfer and fast ion diffusion in active material's particles via the 3D graphene foam porous structures.

A Ragone plot in Fig. 2 displays the modern trends of GF based ECs with regard to energy and power densities in comparison with other available energy storage devices.

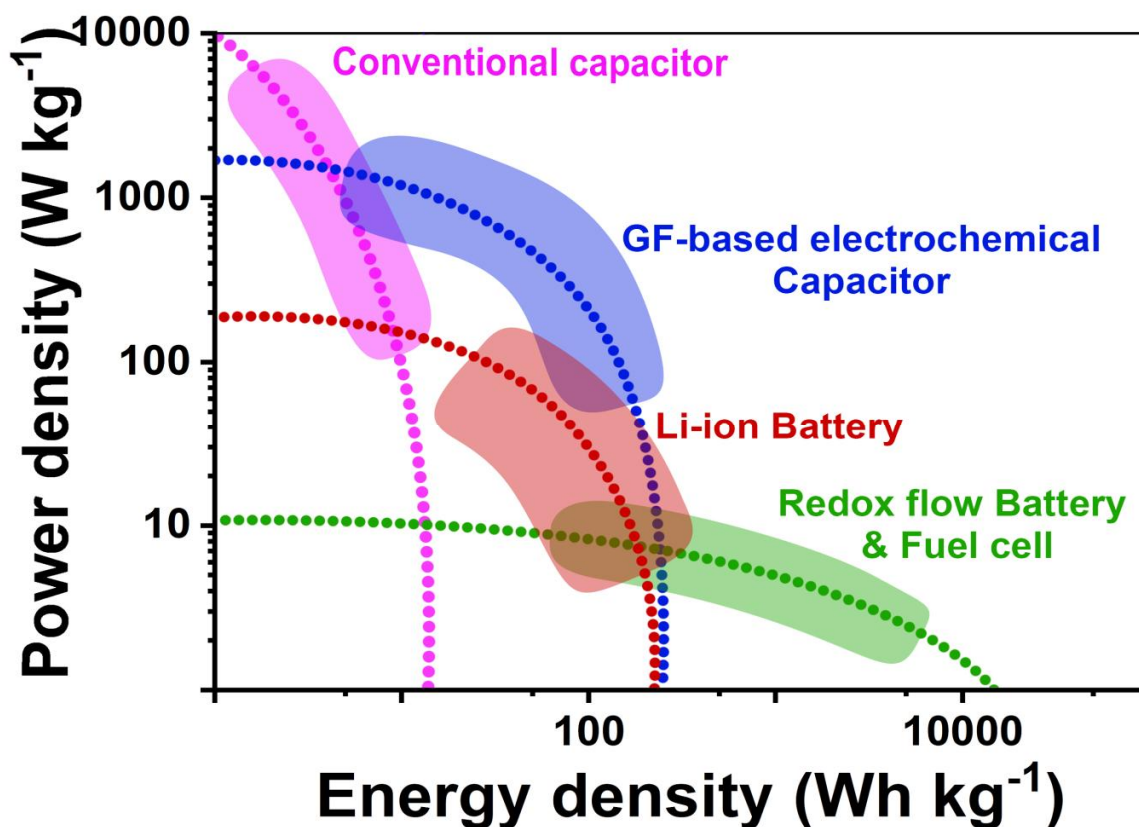


Fig. 2: A comparison of energy and power densities of GF-based EC electrode materials and other currently available energy storage devices.

4. Conclusion and recommendations

Here in, the progress and current trends with regard to 3D graphene foam/-based electrochemical capacitors is being comprehensively reviewed. The influence of GF structures such as morphology, size, geometry, surface area as well as pore sizes and distributions on the GF based capacitors improved electrochemical performances, which include high specific capacitance/capacity, excellent cycle stability, high energy/power density and large operating potential among others have been reviewed. The call for enhanced electrochemical capacitors for herculean energy storage applications supplies both challenges and opportunities for resolved researchers in the field of materials science. Further endeavors have to be put into the research to get the best of the material and to advance the commercialization of GF based ECs for enhanced energy storage device applications. The consistently interconnected networks of graphene and harmoniously porous structure in diverse scales that are obtainable in the 3D graphene foam can result into an improved command over the issue of restacking in graphene sheets. The unique structure of GF can further be exploited for higher internal surface area that could lead to better ion and electron diffusions, and thus enhanced device performances.

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