Chapter

Advanced Carbon Functional Materials for Superior Energy Storage

Mujtaba Ikram, Sana Arbab, Huma Anwar, Arsalan Nadeem, Sidra Baber, Abdullah Khan Durrani, Muhammad Ikram, Muhammad Aamir Iqbal, Muhammad Umer Farooq and Asghari Maqsood

Abstract

In the developing world, energy crisis is the main reason for less progress and development. Renewable and sustainable energy may be of bright future for scientific lagging and low-income countries; further, sustainability through smart materials got a huge potential; so, hereby keeping in view the energy crisis which the developing world is facing for many decades, we are proposing to write a chapter project for obtaining energy through cheap, sustainable, and functional advanced carbon materials. Carbon materials are the future of energy storage devices because of their ability to store energy in great capacity. The graphene is a material with amazing properties like no band gap, which turns graphene a wonderful candidate for use in the photovoltaic. Shortly, this chapter will discuss how superior energy storage may be obtained through various routes like using pyrrolic (N5) and pyridinic (N6) doping in advanced carbon functional materials, or superior energy by KOH activation in carbon materials, or through carbonization in organic matter, respectively. Further, for the advanced carbon functional materials, the superior energy storage using pyrrolic (N5) and pyridinic (N6) doping, or KOH activation, or through carbonization will be discussed one by one for lithium ion batteries, supercapacitors, and relevant energy devices, respectively.

Keywords: renewable energy, graphene, physical properties, reduced graphene oxide, superior energy storage, chemical activation, supercapacitors, lithium ion batteries

1. Introduction

In the developing world, energy crisis is the main reason for less progress and development. Renewable and sustainable energy may be of bright future for scientific lagging and low-income countries; further, sustainability through smart materials got a huge potential; so, hereby keeping in view the energy crisis which developing world is facing for many decades, there exists a possibility for obtaining energy through cheap, sustainable, and smart carbon materials. The nanostructures which are made up of sp2-hybridized carbon such as fullerene, carbon nanotubes, and graphene remain pivot point of advanced carbon functional material research [1]. As we look into the reversible electrochemical strength keeping in view of their great electric conductivity, chemical and mechanical durability, and the custom fitted structures that can be developed from advanced carbon functional materials, carbon materials have been the most significant anode material for the Li-ion batteries [2]. Advanced carbon functional materials may include graphene, carbon nanotubes, and fullerenes, respectively. Moreover, CNTs and graphene with high explicit surface territories can store higher charge capacity by the adsorption/desorption of particles at the anode/electrolyte interface. The higher charge capacity is hence incredible subject to the qualities of the carbon material, for example, its pore structure, doping, and defects. In this way, the advancement of electrochemical capacity in carbon needs a judiciously planned structure. One issue identified with the utilization of CNTs and graphene for electrochemical storage is the agglomeration of the nanostructures that prompts diminished efficiency [3, 4]. There has been progressive demand for the electrochemical energy storage with high energy density and remarkable rate performance. Electrical double layer capacitors (EDLCs), additionally known as supercapacitors (SCs), have attracted a worldwide attention because of their long cycle life and high power density but comparatively low energy density of commercially available carbon-based SCs. Graphene has attracted an in-depth attention in energy storage applications relating to its distinctive options of high surface space, flexibility, chemical stability, and remarkable electrical and thermal conduction [5]. Energy storage capacity defines advanced energy technologies. Further, superior energy storage may be obtained through various routes like using pyrrolic (N5) and pyridinic (N6) doping in carbon materials, or superior energy by KOH activation in carbon materials, or through carbonization in organic matter, respectively. Further, energy storage using pyrrolic (N5) and pyridinic (N6) doping, or KOH activation, or through carbonization in organic matter will be discussed one by one.

2. Energy storage using pyrrolic/pyridinic nitrogen in advanced carbon functional materials

For energy storage, ideal structures may become complex due to agglomeration at nanolevel during carbon reconstruction process. The gathering of sp2-hybridized carbon nanostructures to frame a 3D arrangement can adequately hinder any agglomeration and sustain electrical properties of the building structures. Moreover, the 3D arrangement gives channels for particle relocation. Required carbon structures may be obtained through the freeze drying or aqueous treatment of graphene or CNT suspensions with the help of templates. With increasingly proficient electron move and a progressively powerful structure, a customized 3D carbon will give possible higher electrochemical charge capacity by interfacing the structure squares covalently rather than by van der Waals communications. A graphene with a SSA of ≈850 $m^2.g^{-1}$ has indicated astounding electrical and mechanical attributes for Li-ion batteries. Nitrogen doping may be used to increase electrochemical storage in the advanced functional carbon materials and consequently to increase the capacitance at the anode/electrolyte interface [4, 6]. At the edges of graphene, it is experimentally proved, in the electrolyte, that the nitrogen ions have benefited the wettability of solo carbon layers. Consequently, it would increase the overall capacitance, which may occur due to ideal Faradaic redox responses. For Li-ion storage capacity of the carbon (N-doped), it may provide extra dynamic sites, which helps adsorption (Li-ion), resulting in an enhanced gravimetric limit [6, 7]. Among the N-dopants in graphitic carbon, pyrrolic (N5), pyridinic (N6), and quaternary N, pyrrolic N, and pyridinic N are viewed as additional dynamic for electrochemical storage, while the graphitic structure is the most fragile among them. Also, topological imperfections, for example, di-vacancy and Hurler Stone-Ribs deserts in the graphitic carbon may give additional dynamic destinations to particle adsorption or on the other hand for charge move in electrochemical storage. Furthermore, various works have demonstrated the significant job of full-scale macropores and mesopores in the particle transportation for high power thickness or brilliant rate execution in supercapacitors or Li-ion batteries. Along these lines, a carbon for unrivaled Li-ion capacity would preferably have the accompanying highlights, a 3D arrangement which contains the mesopores for quick particle relocation and a covalently associated structure made of sp2-hybridized carbon for high electrical conductivity [6, 8]. Further, a finely tuned arrangement of dopant molecules and deformities for increasingly dynamic locales is another requirement. To accomplish a carbon with these highlights, scientists picked a high-energy carbon nanostructure, C60, which is more receptive than CNTs and graphene, as the antecedent, and treated it with KOH at temperatures of 500–700°C [6]. The mentioned treatment helps changing the C60 molecules to carbon which contains enhanced nitrogen along with defects. Nitrogen which presents in the doped carbon consists of two types (pyrrolic and pyridinic). With 7.8% nitrogen-doped carbon, porous carbon (when used as anode) has shown 600 mA h g^{-1} (storage capacity), which occurs at 5 A g^{-1} for the Li-ion batteries [6]. A first-standard calculation has proposed that the unrivaled anode execution of the N-doped permeable carbon is intently identified with the bending of the carbon layers (graphenes) and the pyrrolic/pyridinic N-doping in the carbon. FCC structure has been obtained when agglomeration happens in the C60 molecules, which turns C60 into different carbons (permeable carbon) in KOH activation. While in path B, ammonia stream has been act to apply during the tempering, resulting in porous carbon which is highly N-doped. Meanwhile, scientists have proved that nanopores have been prepared in KOH activation, while quantum dots (of carbon) were fabricated without KOH activation [6, 8, 9]. It is believed that enhanced handling time (while keeping proportion of KOH and C60 lower) led to higher interfacial interactions and amends into a progressive structure at certain phase of activation. Likewise, it was discovered that the N-content expanded with activation temperature in the range 500–700°C; yet a further temperature increment to 800°C prompted an extremely low yield of N-aC60 tests. Further, systematic fabrication of nitrogen-doped carbon through activation of C60 molecules (route A indicates normal activation in argon flow, while route B indicates N doping in NH_3 flow) is as shown in **Figure 1** [6].

X-ray diffraction (XRD) analysis of C60, aC60, and N7.5%-aC60 revealed important information regarding structures, which further demonstrates that the C60 molecules have been totally rebuilt by KOH actuation which gave porous

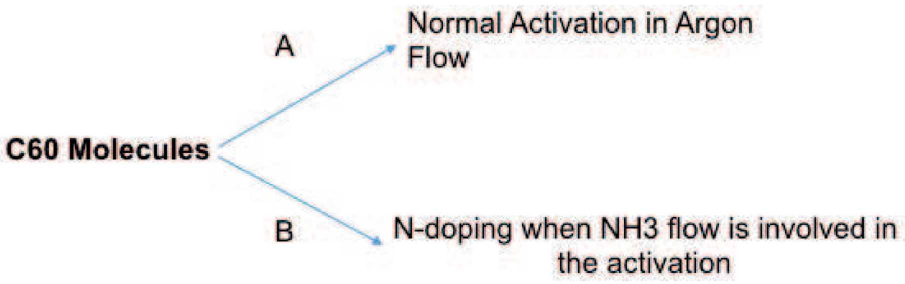

Figure 1.
Systematic fabrication of nitrogen-doped carbon through activation of C60 molecules (route A indicates normal activation in argon flow, while route B indicates N doping in NH_3 *flow) [6].*

carbon [6]. X-ray photoelectron spectroscopy (XPS) has been utilized to reveal significant constituents present in final product. FTIR results show that C─OH and C─O bonds are seen in both aC60 and N7.5%-aC60. Estimations utilizing the XPS information show that oxygen content increments from 1.3 at.% in C60 to 4.2 at.% in aC60 and to 9.5 at.% in N7.5%-aC60 samples, respectively. To additionally comprehend Li-ion battery's capacity, scientists explored the adsorption capacity of Li particles on graphene and C60 sections with and without nitrogen doping through atomic demonstrating. Two potential impacts, i.e., a curvature impact and an N-doping impact, have been thought to be important. For the former one, it has the adsorption capacity of a Li storage on a large portion of a C60 atom with edges immersed by H, i.e., $C_{30}H_{10}$, and a level graphene piece containing the equivalent number of carbon particles, i.e., $C_{30}H_{14}$, respectively [6, 10].

In synopsis, KOH activation has been utilized to totally convert C60 atoms to a 3D permeable carbon. In the porous carbon, the doping (of nitrogen) may additionally bring deformities and a large number of pores. The activation process may increase the doping level that depends upon activation conditions, resulting in a suitable storage capacity for Li-ion batteries [6]. KOH activation gave the bended layer structure also; further, N-doping, particularly pyrrolic nitrogen, has added to the high Li-ion stockpiling limit in the carbon.

3. Energy storage through sponge-templated activation of advanced carbon functional materials

There has been progressive demand for the electrochemical energy storage devices with high energy density and remarkable rate performance. Electrical double layer capacitors (EDLCs), additionally known as supercapacitors (SCs), have attracted a worldwide attention because of their long cycle lifespan and really high power density, but comparatively lower energy density has considerably limited the applications of the carbon-based supercapacitors [11, 12]. Graphene has enormous energy applications relating to distinctive physical properties of chemical stability, flexibility, and remarkable electrical conduction. Scientists have found that during wet chemical techniques, graphene platelets may tend to agglomerate, thus resulting in lower surface areas than the theoretical worth of 2630 m^2g^{-1}. Strategies are developed to assemble graphene-based platelets to 3D structures so as to stop the restacking of platelets for high surface areas while maintaining the intrinsic conduction of platelets [13]. For instance, scientists have demonstrated a graphene film which is 3D having macropores, within which PMMA functions as the main template. Scientists have prepared TiO_2-rGO sheets employing PU sponge (which is porous) as a model for the photoelectrochemical reaction of ethanol. A recent study reported that compressible all-solid-state SCs supported polyaniline-SWCNTs-sponge electrodes, in which sponge provides squeezability and polyaniline offers pseudo capacitance. As an economical model, sponge is ready to act as a wonderful support for the assembly of nanostructures for SC electrodes. It is found that graphene structures obtained using sponge templating may have lower surface area, which leads to lower interfacial interactions and limited SC performance. It is experimentally proved that graphene-based capacitors are of lower cathode thickness even if they possess higher surface areas, which led to lower performance of ultimate devices. Scientists have regenerated graphene colloidal gel films with a high packing density up to 1.33 gcm^{-3} what's more at the same time noticeable capacitive exhibitions (209 Fg^{-1}) and 261 Fcm^{-3} in organic electrolytes. The layer like stacking of graphene platelets may deteriorate the surface because of particle channels within the direction perpendicular to the layers [11, 14].

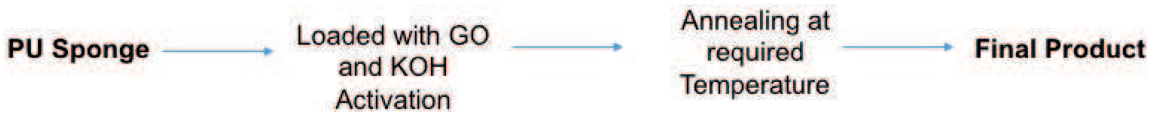

Figure 2.
Preparation of 3D carbon through sponge KOH activation via GO loading [11].

Chemical activation is an efficient methodology to make pores, e.g., within the preparation of activated carbons (ACs). Among various chemical activation strategies, KOH activation has been considered as an accustomed method. Recently, scientists have fabricated a porous carbon through chemical activation of GO; it is found that the selected capacitance of 166 Fg^{-1} has been demonstrated. Transforming low-thickness carbons to templates to get valuable thickness but yet with a moderately high porosity and high electrical conductivity is required for high-performance SCs [11, 13, 14].

Scientists have developed a carbon which was obtained using sponge templating followed by chemical activation (KOH activation) of GO. It is demonstrated that the GO platelets gather around the sponge's backbone. Meanwhile, KOH activation goes within the PU sponge which helps to create pores using temperature treatments, which may result in a conductive carbon. Using fabricated carbon for energy storage in two-electrode and three-electrode configurations, it has shown nearly perfect energy storage behavior, which may lead to acceptable superior power density [11, 15].

Preparation of the 3D carbon (aPG-10) is shortly illustrated within the **Figure 2** as shown [11].

After chemical activation of PU/GO mixture, the dried PU/GO/KOH mixture was toughened at 9000°C for 2 hours in inert gas flow, and hence subjected to drying, resulting in a final sample named as aPG-10 (final product) [11, 14].

The exhibition of the aPG-10 as an anode material for supercapacitors was evaluated using cycle voltammetry (CV) and galvanostatic charge-discharge (GCD) curves, respectively. In a three-electrode configuration, the execution of aPG-10 anode coated on a shiny carbon has been designed with 1.0 MH_2SO_4 as electrolyte. The particular capacitance determined from the charge/discharge curves at a current thickness of 5 Ag^{-1} is 401 Fg^{-1}, which stays 349 Fg^{-1} at a current density of 100 Ag^{-1}. Once aPG-10 was tried in two-electrode configuration, a particular capacitance of 227 Fg^{-1} at 5 Ag^{-1} was acquired [11].

In summary, a graded porous carbon was obtained through sponge KOH activation via GO loading [11, 14, 15]. The sponge has filled in as a proficient layout to pull KOH into its backbone, which helps to create large number of pores, in order to give highly porous carbon. Meanwhile, low sheet obstruction, high BET surface region, and much acceptable conductor density are accomplished based on the carbon activation through KOH which introduces sort of nitrogen which covers defects from graphitic lattice. Every one of these benefits leads to the great electrochemical execution of carbon terminals [11, 13, 15].

4. Energy storage through functional porous carbon obtained from frozen tofu (organic matter)

Frozen tofu is a source of carbon and nitrogen [16]. By using one-step carbonization activation method, it can be converted into oxygen-doped carbon and nitrogen-doped carbon, respectively. By one-step carbonization, sponge-like carbon (co-doped) has a maximum surface area of 3134 m^2g^{-1}. High volumes of mesopores (1.11 cm^3 g^{-1}) and micropores (0.71 cm^3 g^{-1}) are present in this hierarchical (graded) porous carbon [16, 17]. Scientists have discovered that this acquired carbon is used to make supercapacitors which acts as electrodes, in 1 M aqueous electrolyte sulfuric acid; it has a remarkable capacitance of 243 Fg^{-1} (evaluated at 0.1 Ag^{-1}); after 10,000 cycles, it has a capacitance retentiveness of 93% at 10 Ag^{-1}. In BMIMBF4 (1-butyl-3-methylimidazolium tetra fluoroborate) liquid ion electrolyte, the said carbon shows a precise capacity of 170 Fg^{-1} (assessed in 1 Ag^{-1}) along with a valuable effectiveness (135 F g^{-1} at 20 Ag^{-1}) ensuring the power density of 72 W h kg^{-1} (at 889 W kg^{-1}). A carbon supercapacitor (derived from frozen tofu) can comfortably drive 25 light-transmitting diodes in excess of 2 minutes [16]. The fabrication flow chart for porous carbon through one-step carbonization is as shown in **Figure 3** [16].

Further, systematic steps involved to get porous carbon through carbonization are freeze drying, KOH activation, temperature treatment, and carbonization, respectively, as are shown in flow chart diagram (**Figure 3**). Many energy storage devices are available worldwide but because of potential applications, electrochemical appliances such as lithium-ion batteries (LIBs) and supercapacitors have an appreciable fascination [16, 17]. On the one hand, supercapacitors have active charging/discharge performance and also a fine power density greater than 10 k W kg^{-1}; on the other hand, LIBs have a great energy density (usually 100–200 W h kg^{-1}), yet it has a longer charging time. Two mechanisms mainly used by supercapacitors in order to store energy are as follows [17, 18]:

- Pseudocapacitive electrodes store ions established at the electrode-electrolyte interface for immediate Faradaic reactions.

- Dual layer electrodes with capacitive electricity preserve energy through the desorption and adsorption of ions on a large field of spongy (porous) materials.

The lithium ions in LIBs are moved between anode and cathode, which results in lithium ions storage or discharge through distinct means according to the materials of the electrode. Because of many properties such as chemical stability, pattern porosity, and high electrical conductivity, for both commercial LIBs (e.g., graphite) and supercapacitors (e.g., activated carbon), carbon materials were selected as effective materials [16, 19]. It has been determined that macropores act as ion-buffering storage in porous carbon materials in supercapacitors and mesopores contribute channels for the transport of ions to micropores, where they were ultimately deposited. In the LIB (graphite) anodes, the intercalated LiC compound is the result of the complete intercalation of lithium ions that limits the reversible Li-ion storage potential for graphite (approximately 372 mA hg^{-1}) [16]. In addition,

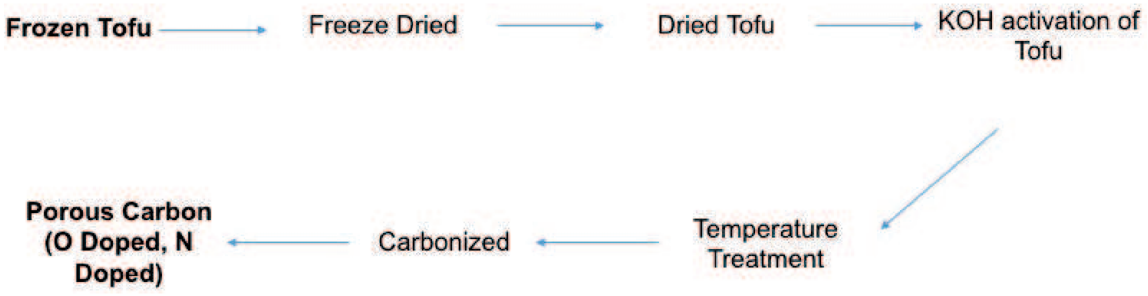

Figure 3.
The fabrication flow chart for porous carbon through one-step carbonization [16].

permeable carbon was too employed in the form of an electromagnetic scaffold or including the electrode in the LIBs, since the spongy (porous) arrangement is known to increase the contact areas of the electrode-electrolyte and decrease the length of the path for ions/electrons transport, which leads to an improvement in the transit kinetics and accordingly the energy density [16, 20].

Power density of industrial supercapacitors is usually lower than 6 W h kg^{-1} and that is beyond from long-term electronic equipment requirements [20]. However, the efficiency and performance of the LIB anodes must also be further enhanced. With regard to the two applications, spongy carbon of great electrical drivability and a customized 3D design is required. In the previous couple of centuries, by using different strategies like self-assembly, activation, and templating, several porous carbon materials have been researched [16, 18, 20]. Among available methods, an efficient method is activation, to increase the surface area of carbon by making several micropores. In supercapacitors, activated carbon is commercially employed due to its great specific surface area (greater than 2000 m^2g^{-1}). Activation will make effective manufacturing possible through treating of precursors of nanostructured carbon in order to get novel carbon compounds [21]. For instance, platelets of graphene may be entirely transformed to a three-dimensional porous (spongy) carbon with a SSA of up to 3100 m^2 g^{-1} and distribution of pore size is 0.6–5 nm by microwave-exfoliated graphite oxide activation of KOH [16, 21]. By KOH activation of C micro tubes, scientists have documented a porous (sponge-like) carbon made up of macropores (numerous microns in size) and micropores (0.47 nm in size). The conductivity and wettability of carbon compounds can be enhanced by adequate heteroatom doping. Additionally, nitrogen is a donor molecule of electrons, as well as in a graphite matrix, they have the ability to promote conductivity of the n-type. As the LIB anode, carbon N-doping has proved itself to support the Li injection because of the hybridization of the long pair of nitrogen electrons with carbon π electrons. In recent times, by activation of C with KOH in an ammonia environment, scientists have achieved porous N-doped carbon (7.5 wt %); the carbon was found to have a reversible power of 1900 mA h g^{-1} at 0.1 Ag^{-1}; furthermore, after 800 cycles (at 2 Ag^{-1}), the capacity is 600 mA hg^{-1}, respectively.

Porous carbon content obtained from renewables can be more environmentally sustainable relative to porous carbon products acquired from wood, polymer blends, tar, and other resources. Researchers have demonstrated that porous carbons can be obtained from various biomass sources such as rice husks, fungi, water bamboo, and rice straw for energy storage applications. For instance, researchers have informed that the willow catkin could be transformed into a cross-linked polymer carbon laminate co-doped with sulfur (S) and N by one-step pyrolysis-activation synthesis. In 1 M Na_2SO_4, the carbon demonstrated a remarkable electrochemical efficiency with a specific capacitance of 298 F g^{-1} at 0.5 A g^{-1} and magnificent cycling endurance at 5 A g^{-1} after 10,000 cycles with only 2% capacitance loss. Tofu consists of moisture, carbohydrates, proteins, and trace concentration of minerals; it is an available resource and is considered as a renewable fuel for nitrogen and carbon [16, 22]. Not long ago, scientists have stated the molten salt synthesis of strongly (N-doped) porous carbon which may be obtained from tofu, in which LiCl/KCl (45/55 in weight) is a eutectic mixture (which functioned as the activator) was used as the solvent to dilute $LiNO_3$. The collected carbon (N-content: 4.72 wt%, density: 0.84 g cm^{-3}, SSA: 1202 m^2 g^{-1}) in a 1 M Na_2SO_4 symmetric supercapacitor, showed 73.2 F g^{-1} capacitance (at 0.2 A g^{-1}). The porous carbon (obtained from frozen tofu) is known to be suitable anode specimens for LIBs, because of their bigger surface areas, porous hierarchical structures, and heteroatom doping. In short, we can easily obtain doped N porous hierarchical carbon from frozen tofu, using single-step carbonization activation. Frozen tofu is environment-friendly, cheap, and extendable biomaterial precursor. It has showed significant SSA of 3134 m^2 g^{-1} and significant pore diameter of 1.82 m^3 g^{-1} on the activation conditions, and this is better than traditional biomass-originated active carbon products. In 1 M H_2SO_4, supercapacitors based on porous carbon (from frozen tofu) revealed 243 F g^{-1} specific capacitance, and in BMIMBF4/AN, it showed an extraordinary power density of about 72 W h kg^{-1} at an ordinary 889 W kg^{-1} energy density. Such carbonization procedure offers a potentially helpful strategy from abundant supportable resources to design carbon electrode materials with supreme execution for supercapacitors and LIBs, respectively [6, 11, 16, 22].

5. Conclusions

In synopsis, this chapter has explained how KOH activation has been utilized to convert C60 molecules to a 3D carbon, while at the same time, doping with pyridinic and pyrrolic nitrogen has huge impact in energy storage capacity. Meanwhile, a graded porous carbon was obtained through sponge KOH activation via GO loading. Further, physical properties such as low sheet obstruction, high BET surface, and higher conductivities are accomplished based on the carbon activation through KOH, which introduces sort of nitrogen which covers defects from graphitic lattice eventually. Every one of these benefits leads to the great electrochemical execution of carbon terminals. Further, carbonization procedure offers a potentially helpful strategy from abundant supportable resources to design carbon electrode materials with supreme storage for supercapacitors and LIBs, respectively.

Conflict of interest

The authors have declared no “conflict of interest.”

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