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Aerogels Utilization in Electrochemical Capacitors

Ranganatha Sudhakar

Abstract

Supercapacitors are the integral part of electrochemical energy conversion and storage media. Energy storage mechanism is different in supercapacitors compared to batteries and results in exhibition of excellent power density. The supercapacitor performance is sensitive to material used as electrode, nature of electrolyte, etc. and the very significant is electrode surface nature. Based on the type of energy storage mechanism, supercapacitors are divided as electrochemical double-layer capacitors and pseudocapacitors. There is a practice to have both kind of these materials as electrode materials to achieve high electrochemical performance. Aerogels with inherent characteristics such as large pores, very high surface area, and superior mechanical stability make them superior candidates for electrode materials for high performance electrochemical supercapacitors. In this chapter, aerogels derived from different sources, their suitability and performance in view of electrochemical supercapacitors are discussed.

Keywords: supercapacitors, porous, mesoporous, specific capacitance, carbon materials

1. Introduction

Rapid growth of human society and subsequent need of energy is driving the manipulation of non-renewable sources in nature leading to depletion of the same. This is simultaneous with the increasing threats such as global warming, energy shortage, air pollution etc. Standardization of our life style and drastic change in dependence on electricity, demanding urgent need for high efficiency energy conversion and storage. Batteries and supercapacitors are excellent means of electrical energy conversion and storage including solar cells [1, 2].

Conventional condensers or capacitors utilize dielectric materials, e.g., ceramics, polymers which are non-conducting in nature, exhibit the capacitance in the range of pico to microfarad. Typically, anodic metal oxides mostly of Ta, Al, Nb are used in electrochemical capacitors which widen the capacity from micro to millifarad level. Recently, supercapacitors are devised involving energy mechanisms; electric double-layer capacitance (EDLC) and pseudocapacitance. Charge separation at electrode/electrolyte interface results in EDLC and fast, reversible reactions occurring on solid electrode surface leads generation of pseudocapacitance. RuO_2 and IrO_2 noble metals exhibit superior specific capacitance value of about 750 F/g but at the same time hazardous and non-economical. For this reason, oxides of transition

metals, e.g., CoO_x , MnO_x , and NiO_x are extensively being studied as supercapacitor electrodes [2, 3].

2. Fundamentals of charge storage in electrochemical supercapacitors

Three categories of supercapacitors are made with respect to the mechanism involved in energy storage in them. The very first category is electrical double-layer capacitor (EDLC), wherein electrostatic charge gathered at the electrode electrolyte interface results in capacitance. Here capacitance is directly proportional to surface area accessed by the ions from electrolyte. Pseudocapacitor is the second category, where in reversible redox reactions by electroactive compounds are considered. In third type, combination of both of these kinds are made use to extract electrical energy. The type of material chosen plays a crucial role in the energy delivery. The challenges posed by supercapacitors are low energy density, low workable potential window, economy and self-discharge. The strategy to overcome these limitations is to design newer energy materials. Popularly, designing hybrid of a carbon material, pseudocapacitive metal compounds and conducting polymers. Synergistic effects, high surface area from carbon materials, high specific capacitance, redox processes from pseudocapacitive materials contribute to achieve high capacitance with good rate capability [1–4].

The first category supercapacitors, which are dependent on the formation of electric double layer, can be fabricated with the help of two carbon related electrode materials, an electrolyte and a separator. There will be no electron exchanges between electrolyte and electrode being non-faradaic. There occurs population of charges on electrodes when voltage is applied which drives the ion diffusion in the electrolytic solution. An electric double layer with oppositely charged ions on the electrode surface is formed to skip ionic recombination. Because of this mechanism, charge take up will be very fast and energy delivery too. Also, electrodes are benefitted with no swelling during charge and discharge cycles similar to the batteries [1, 5–8].

Considering pseudocapacitive materials as electrodes in supercapacitors, redox reactions take place between electrode and electrolyte which stores the charge. Oxidation or reduction reactions occur when a required voltage is applied, on the electrodes involving charge passage across double layer generating faradaic current. Metallic compounds and conducting polymers are best examples for this class of electrodes which suffer with lack of stability during cycling leading to lowering in power density [1]. As these faradaic reactions involve redox reactions, are slower which makes them to exhibit lower power density and poor cycling stability compared to EDLC type [1, 6–9].

There are few criteria to design a high performance supercapacitor electrode materials. To list out, high specific capacitance stands first. To achieve this, electrode material should pose a very high specific surface area which will eventually store high energy per unit mass and volume. So nanomaterials and porous materials can be expected to satisfy this criterion. Large rate capability and high cycle stability are major characteristic to be possessed by an ideal electrode material, which signifies capacitance retention at high scan rate and/or current density. Additionally economically viable and non-toxic materials are preferred.

Majorly the factors that determine the characteristics of high specific capacitance, rate capability and cycle stability are Surface area of the electrode, electronic/ionic conductivity and mechanical/chemical stability. As the charge storage mechanism involves the adsorption and desorption of the ions on the electrode surface, more the surface area higher will be energy storage. Specific capacitance and rate

capability are highly relative to electronic and ionic conductivity. Higher values of these can maintain a rectangular shape of cyclic voltammogram which is typical for an ideal capacitor and symmetric profiles in galvanostatic charge discharge cycles.

3. Aerogels as supercapacitor electrode materials

Carbonaceous aerogels extended to three-dimensional structures are very much potential for high performance electrode materials in supercapacitor because of superior characteristics such as vast surface area and porous nature, facilitating uninterrupted paths for ionic movement by shortening diffusion pathways.

Based on the source, the carbonaceous gels are typically classified as (1) Aerogels derived from polymers (2) aerogels derived from carbon nanotubes, (3) Aerogels derived from graphene, and (4) aerogels sourced from biomass.

4. Polymer-derived aerogels for supercapacitors

Carbon aerogels (CAs) derived from polymers belong to wide category of carbonaceous aerogels. Pekala and Kong in 1989 firstly recorded the synthesis of CAs by inert atmosphere pyrolysis of resorcinol–formaldehyde (RF) organic aerogel [10, 11]. The organic aerogel from RF can be synthesized by aqueous mediated sol-gel-based resorcinol and formaldehyde monomeric poly-condensation followed by supercritical drying [12]. Alternatively, polymers of sol-gel source too utilized as starting materials for synthesizing carbon aerogels, such as phenol–melamine–formaldehyde gel [13], poly-benzoxazine gel [14], cresol, resorcinol and formaldehyde gel [15], resorcinol and pyrocatechol gel [16], cresol and formaldehyde gel [17], gel of resorcinol–methanol [18] and poly(vinyl chloride) gel [19]. Additionally, microwave drying [20] air drying [21, 22] and freeze-drying [23] too are preferred as the synthetic procedures for dried organic gels. The process of pyrolysis can also be employed to convert dried organic gel into CAs. Precursor configuration and conditions of pyrolysis process are very crucial parameters to design the desired structure of CAs.

CAs derived from polymers have been studied exclusively as supercapacitor electrode. First, Pekala in 1994 demonstrated capacity of CAs electrodes in supercapacitors [24]. The 3D CAs consist of nanoparticle assembly associated with variable sized pores. CAs possess the merits like of good electrical conductivity, high porosity, high surface area and tunable pore sizes [24, 25]. These unique structure and superior properties, make CAs potential candidates for the application as electrode materials in electrochemical supercapacitors.

An aerogel derived from pyrolysis of polybenoxazine by Katanyoota and coworkers with surface area $368 \text{ m}^2/\text{g}$ with 2–5 nm pore size exhibits 56 F/g of specific capacitance in 3 M sulfuric acid [14]. CAs modified with pseudocapacitive materials such as metal oxides or conducting polymers can be expected to offer higher performances compared to their pristine counterparts. Resorcinol-methanol-derived CA modified with Mn_3O_4 doping shows 503 F/g in 0.5 M Na_2SO_4 [18]. Interestingly it possesses $577 \text{ m}^2/\text{g}$ of surface area associated with 18 nm pore size. CA from RF precursor developed by Chien et al., [26] shows an excellent electrochemical behavior with 1700 F/g in 1 M potassium hydroxide. Though surface area was not so high, i.e., $206 \text{ m}^2/\text{g}$, the doping of pseudocapacitive material NiCo_2O_4 contributes towards high capacity. In an alternate report MnO_2 doped RF-derived CA offers 515 F/g in neutral 1 M Na_2SO_4 and corresponding surface area was $120 \text{ m}^2/\text{g}$ [27]. Conducting polymer, polyaniline being a doping material in a CA for

which RF were the precursors, shows of 710 F/g in acidic electrolyte 1 M H_2SO_4 [28]. There are some research efforts wherein secondary materials were used to modify the carbon aerogel derived from resorcinol-formaldehyde gel. Wang and co-workers doped nickel oxide particles to enhance the activity which resulted in exhibiting 356 F/g at 1 A/g in 6 M KOH medium [29]. In an alternate piece of work, carbon nanotubes were used as dopants to activate the CAs and delivered 141 F/g at 5 mV/s in 30% potassium hydroxide solution [30]. Also there are some reports wherein CAs are activated by CO_2 and KOH to enhance the electrochemical behavior [31]. These activated CAs possess hierarchical porous network structures with microporous, mesoporous and large pores with <2 nm, 2–4 nm and >30 nm correspondingly. These CAs deliver 250 F/g after KOH activation and 8.4 Wh/kg at 0.5 A/g of current density in 6 M potassium hydroxide as electrolyte solution. Doping with metal also found to influence the performance of CAs. Lee et al., [22] doped a series of CAs with different metals. They found metal doped CAs with higher capacitance comparing to pristine ones. Mn doping showed higher capacitance compared to those of Cu, Fe. The metal compounds doped CAs are also studied including Mn_3O_4 [18], NiCo_2O_4 [26], ZnO [32], FeO_x [33], MnO_2 [27], SnO_2 [34], NiO [29] and RuO_2 [35].

5. Carbon nanotube (CNT)-based aerogels for supercapacitors

Porous interconnects in 3 dimensions with carbon nanotubes as skeleton constitute this category. Different processes are employed to synthesize carbon nanotube-based aerogels, such as chemical vapor deposition (CVD), [36] freeze-drying, [37, 38] and critical-point-drying [39–41].

The CNT-based aerogels possess benefits of the carbon nanotubes, like excellent electrical conductivities, good mechanical resilience and superior thermal conductivity, and show the special characteristics of aerogels, too; 3D network with pores, less density, porous nature and high specific surface areas. These attractive characters direct carbon nanotube aerogels for applications as supercapacitor electrodes. Also, as these 3D networks possess number of pores facilitate substrate for holding other active materials like metal oxides, carbon, and polymers with conducting nature, improving storage capacities.

Most extensively used method to fabricate CNT-based aerogels is CVD. Bordjiba and coworkers synthesized CNT aerogels by CVD method with surface area $1059 \text{ m}^2/\text{g}$ and modified with microfibrinous carbon offered 524 F/g in 5 M KOH [36]. Polyaniline were made use to modify CNT aerogel by Zhong et al., to improvise the specific capacitance with the contribution from pseudocapacitive conducting polymer. It offered 189 F/g in 1 M H_2SO_4 medium [42]. In an attempt Fang et al., Ni microfiber supported CNT aerogels were designed which showed 348 F/g in 5 M KOH electrolyte [43]. Preparing carbon nanotube layers on other three-dimensional networks using CVD process also results in the synthesis of CNT-based composite aerogels which can be expected to perform better. Bordjiba et al., targeted this kind of composite of CNT aerogel with carbon aerogel by CVD method [44]. This material with around $700 \text{ m}^2/\text{g}$ of surface area delivered 524 F/g of specific capacitance in 5 M KOH electrolyte. Freeze-drying method was employed to design CNT-based aerogel using wet-gel precursors [45]. The aerogels prepared so, exhibit superior properties which include mechanical, thermal, etc. Authors of these report the suitability of cellulose-CNT hybrid aerogels for sensor applications for gases and other volatile organic compounds. Sun et al., demonstrated [46] direct freeze-drying synthesis of CNT-graphene composite aerogels which exhibit superior thermal property, electrical conductivity, and good adsorption characteristic, etc., which advocate suitability for electrodes in supercapacitors. Li and co-workers prepared

CNT aerogel using CVD process which successfully demonstrated capacitive behavior [47]. Under 50% of compressive strain, capacity retention was about 90% and it was 70% under 80% of strain. This demonstrates the quality of electrode as compressible and deformation sustainable electrodes which is of unique quality. A concept of decorating CNT aerogel with a conducting polymer was successful for superior quality supercapacitor electrodes. Lee et al., [48] were successful in doing so as CNT aerogel coating by poly(3, 4-ethylenedioxythiophene) which successful by delivering a volumetric capacitance of about 40 F/cm^3 at 100 V/s and high volumetric energy 70 Wh/cm^3 along with added superior properties including high mechanical flexibility and strength. It will be high interest if a carbon material is composed with CNT aerogels which can eventually improve the storage capacity. There are reports which advocate this fact by fabricating composite materials of CNT aerogels with cellulose nanofibers [49] and mesoporous carbon [50] which successfully showed enhanced properties. Though CNT-based aerogels pose superior electrochemical properties, the high production cost hinders their application.

6. Graphene-based hydrogels and aerogels for supercapacitors

2D carbon material with one atom thick graphene has been very popular among scientific community because of its unique properties like superior thermal and electrical conductivity, appreciable flexibility and high mobility of charge carriers, very high specific surface area, mechanical and chemical stability make it potential for charge storage applications.

Graphene layers are basic skeleton for aerogels of graphene. The aerogels of graphene not only possess the merits of graphene but carry the inherited characters of aerogels. If water is replaced by air from graphene hydrogels, can result in three-dimensional cross-link, graphene aerogels. Mostly used method to prepare graphene aerogel is supercritical freeze-drying of the wet gels of graphene. There are few recent reports on the fabrication of graphene aerogels and their proven ability to behave as superior supercapacitor electrode materials. Liu and coworkers utilized freeze-drying method to prepare graphene aerogel which studied for electrochemical properties. It exhibited 172 F/g of capacitance when utilized as supercapacitor electrode in $1 \text{ M H}_2\text{SO}_4$ [51]. Supercritical-drying also adapted as synthetic route for graphene aerogels by Wu and Si, in a two different studies. The performance of these electrodes were fair enough which exhibited 153 F/g and 279 F/g respectively, where in corresponding electrolytes were ionic liquid and $1 \text{ M H}_2\text{SO}_4$ [52, 53]. Wu et al., [54] fabricated metal oxide composite with graphene aerogel which delivers a specific capacitance of 226 F/g by synergistic contribution from pseudocapacitive material, in $1 \text{ M H}_2\text{SO}_4$. Graphene synthesized via freeze-drying modified with L-ascorbic acid by Zhang et al., measure to be $512 \text{ m}^2/\text{g}$ of surface area. Upon using it as supercapacitor electrodes, it exhibits 128 F/g as a full cell in 6 M KOH electrolyte [55]. Aerogels with modification of nitrogen and some atoms also attempted by scientific community with a hope that to have improved capacitance. Wu et al., were successful in doping nitrogen and Boron which eventually delivers 62 F/g at 5 mV/s in sulfuric acid-PVA medium. The material had a surface area of $249 \text{ m}^2/\text{g}$ [56]. Carbohydrate modified graphene aerogel in neutral medium, i.e., Na_2SO_4 shows 162 F/g at 0.5 A/g [57]. However, this doped graphene had a surface area of about $365 \text{ m}^2/\text{g}$. Pyrolyzation was employed to fabricate graphene aerogel aiming to be used as electrode material for supercapacitor. Carbon modified such a graphene aerogel exhibited 122 F/g at 0.05 A/g in 6 M potassium hydroxide which was having a surface area in the range of $361\text{--}763 \text{ m}^2/\text{g}$ [58]. He et al., designed aerogel of polypyrrole graphene with 3D hierarchical applied as supercapacitor

electrodes [59]. It showed a considerably high 418 F/g at 0.5 A/g with an appreciable cyclability with 74% capacity retention in 1 M KOH. It can be noticed some literatures on rGO-based aerogel and their hybrids. In an attempt related to this, Boota's research group, utilized 2,5-dimethoxy-1,4-benzoquinone and rGO to synthesize an electrode material which showed up to 650 F/g of specific capacitance at 5 mV/s in an acidic environment and interestingly 99% of initial capacity retained even after 25,000 cycles [60].

7. Biomass-derived aerogels for supercapacitors

Several merits of carbonaceous materials including low cost, easy accessibility and eco friendliness attracted appreciable interest for different applications. Especially, hydrogels and aerogels of biomass source consisting of 3D solid networks and porous structures carry excellent properties which make them being utilized as supercapacitor electrodes. Key factor to consider biomass-derived aerogels for supercapacitor application is its low production cost. Along with this, considerably high surface area unique structure in addition to greater mechanical behavior add to list.

- Carbonaceous gels were aimed by X L Wu from watermelon as a crude biomass source [61]. This showed interconnected network with an average 46 nm pore diameter. The Fe_2O_3 composite of this material showed a great electrochemical behavior with 333 F/g of capacity. In another effort, Lee and group used bacterial cellulose as carbon source to fabricate carbon fibers [62]. This nanocarbon electrode delivers 42 F/g specific capacitance and area normalized capacitance was 1617 F/cm^2 . Graphene also made use to design composites with biomass-derived aerogels. Hybrid aerogels consisting of cellulose nanofibers and rGO designed by Gao et al., showed 207 F/g when used as supercapacitor electrode material [63]. CNTs also found place in the composite with aerogel derived from biomass. Cellulose nanofiber-multi walled CNT aerogels synthesized by Kang et al., which showed 178 F/g of specific capacitance [49]. Bacterial cellulose with lignin-resorcinol-formaldehyde carbon aerogel synthesized aiming towards efficient supercapacitor electrodes [64]. It performed well and showed 124 F/g at 0.5 A/g with $62.2 \mu\text{F/cm}^2$ of aerial capacitance. Conducting polymer is frequently used to modify the aerogels to enhance the performance. Zhao and co-workers designed a 3D porous pectin/polyaniline aerogel in which functional groups of pectin such as carboxylic acid and hydroxyl groups ascribed to have hydrogen bonding with polymer leading to cross linking network [65]. This aerogel exhibits 184 F/g at 0.5 A/g and 71% of initial capacity retention. Cheng et al., prepared a cotton-derived carbon fiber aerogel and tested its electrochemical performance [66]. This carbon fiber aerogels were having $2307 \text{ m}^2/\text{g}$ of surface area and possessed tubular morphology which facilitate conductive pathways for electron transport. This advocates shortening the ion transport lengths which eventually result in higher electrochemical performance with 283 F/g at 1 A/g and 224 F/g at 100 A/g.

8. Conclusion

In this chapter, fundamentals of supercapacitors and the utilization of carbonaceous aerogels in the fabrication of electrode materials of supercapacitors are acquainted along with their evaluations are successfully presented. The carbon

aerogels sourced from polymers have rich resources, have highly tunable pores which make them to deliver high specific capacitance. But, poor mechanical stability restrict them from finding deployed in flexible supercapacitors. CNT and graphene-derived aerogels can overcome the shortcoming from having found application based on flexibility. Additionally, these aerogels exhibit properties such as excellent conductivity, superior mechanical properties, good flexibility and high surface area and stand potential candidates for electrodes for high performance electrochemical supercapacitors.

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