

Materials for energy storage: Review of electrode materials and methods of increasing capacitance for supercapacitors

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ABSTRACT

Supercapacitors (SCs) have shown great promise as a possible solution to the increasing world demand for efficient energy storage. Two types of mechanisms for SCs exist (double-layer and pseudocapacitive), and each type utilizes a wide variety of materials. In this review, a detailed overview of the mechanisms employed by SCs

Abbreviations: 25BN-PVA, 0.025 mg·ml⁻¹ hexagonal boron nitride doped polyvinyl alcohol; 25BN-PVA-H₂SO₄ GPEs, hexagonal boron nitride nanosheets-doped poly(vinyl alcohol)-sulfuric acid gel polymer electrolyte; 3D, three-dimensional; 3D, N-doped GCNT three-dimensional nitrogen-doped graphene-carbon nanotubes; A, Ampere; AC, activated carbon; ACB-1(700), activated carbon from tree bark activated at 700°C; BN-Gas, boron and nitrogen co-doped graphene aerogels; Carbon Onions/rGO, carbon onions/reduced graphene oxide; Carbon/PANI, carbon/polyaniline; CB, carbon black; CB/rGO, carbon black/reduced graphene oxide; CC-AA-600, corncob after activation at 600°C; CDC-Aero-700, carbide-derived carbon aerogel activated at 700°C; CDs, carbon dots; cm, centimetre; CMC-2, ZnCl₂ activated carbon material; CMG, chemically modified graphene; CMK-3, ordered mesoporous carbon; CMK-3-MS, ordered mesoporous carbon activated via magnetic stirring; CMK-3-Pure, non-activated ordered mesoporous carbon; CMK-3-US, ordered mesoporous carbon activated via ultrasonication; C-NGNS, highly crumpled nitrogen-doped graphene nanosheets; CNT, carbon nanotubes; CNT/PANI, carbon nanotubes/polyaniline; Coca-ColaCMC-2, ZnCl₂ activated carbon material from coca-cola; CP, conducting polymers; CV, cyclic voltammogram; CVD, chemical vapour deposition; CVD-CNT/CMG, chemical vapor deposition-carbon nanotubes/chemically modified graphene; EDLC, electrochemical double layer capacitor; EMIBF₄, 1-ethyl-3-methylimidazoliumtetrafluoroborate; EPW, electrode potential window; F, Farad; FGH, fluorinated graphene hydrogel; g, gram; G, graphene; GA, graphene aerogel; GA@NF, graphene aerogel on nickel foam; GCNT, graphene-carbon nanotubes network; Gfilms, graphene films; G-GH, hydrogel synthesized from graphene oxide; GH, graphene hydrogel; GH/AC, active carbon/graphene hydrogel; GN, nitrogen-doped graphene; GN-GH, nitrogen-doped graphene hydrogels; GnPs, graphene platelets; GnPs/Epoxy, graphene platelets/epoxy; GNS, graphene nanosheets; GNS/CNT/PANI, graphene nanosheets/carbon nanotubes/polyaniline; GNS/PANI, graphene nanosheets/polyaniline; GO, graphene oxide; GO/CDs/Ppy, graphene oxide/carbon dots/polypyrrole; GOA@NF, graphene oxide aerogel on nickel foam; GPE, gel polymer electrolyte; GR, graphene; h, hour; HRTEM, high resolution transmission electron microscopy; IGNC, interconnected graphene nanocapsules; IL, ionic liquid; kg, kilogram; Laser-rGO aqueous, laser-reduced graphene oxide in aqueous electrolyte; Laser-rGO organic, laser-reduced graphene oxide in organic electrolyte; LED, light emitting diode; m, metre; MCG, mesoporous carbon/graphene; MEGO, microwave-exfoliated GO or Holey GO; MGH, macroscopic graphene hydrogels; MnO₂, manganese dioxide; MnO₂/3D-CMG, manganese dioxide/three-dimensional chemically modified graphene; MS, magnetically stirred; mV, millivolt; MWCNTs, multi-walled carbon nanotubes; N/S-UCN600, N, S-co-doped ultramicroporous carbon nanoparticles activated at 600°C; N-BLPC, nitrogen-doped black liquor-derived porous carbons; NCNT, nitrogen-doped carbon nanotubes; NF, nickel foam; NFS/GF, nanofiber sponge filled graphene foam; NG, nitrogen-doped graphene; N-Graphene, nitrogen-doped graphene; NGS, nitrogen-doped graphene nanosheets; NHCNs-750, nitrogen-doped hierarchical porous carbon nanowhiskers activated at 750°C; NHG, nitrogen-doped Holey graphene; NPAC-Co, biomass-derived carbon by activation with nitrogen and cobalt; NPC, nitrogen-doped porous carbons; N-rGO, nitrogen-doped reduced graphene oxide; NSGH, nitrogen and sulfur co-doped graphene hydrogels; NS-GNR, nitrogen and sulfur co-doped graphene nanoribbons; NS-rGO, nitrogen, sulfur co-doped reduced graphene oxide; PANI, polyaniline; PANI/NCNT, polyaniline/nitrogen-doped carbon nanotube; PANI/rGOw/ catechol, polyaniline/reduced graphene oxide with catechol additive in electrolyte; PANI-IL, polyaniline in ionic liquid electrolyte; PANI-NFS/GF, polyaniline nanofiber sponge filled graphene foam; PEDOT, poly(3,4-ethylenedioxythiophene); PEDOT: PSS, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate); PEG-AD, adamantane end-capped poly(ethylene oxide) polymer linker; PMTA, poly(2-methylthioaniline); PMTA@CNT/RGO, poly(2-methyl thioaniline)/carbon nanotubes/reduced graphene oxide; PPy, polypyrrole; PSD, pore size distribution; PSS, poly(styrenesulfonate); rGO, reduced graphene oxide; RGO, reduced graphene oxide; rGO/PANI, reduced graphene oxide/polyaniline; rGO@β-CDP@PEG-AD, β-cyclodextrin polymers with an adamantane end-capped poly(ethylene oxide) polymer linker; RHAC, rice husk activated carbon; RHAC-800-aqueous, rice husk activated carbon activated at 800°C and tested in aqueous electrolyte; RHAC-800-organic, rice husk activated carbon activated at 800°C and tested in organic electrolyte; RuO, ruthenium oxide; RuO₂, ruthenium dioxide; s, second; SAC, sulfanilic acid; SAC-RGO, sulfanilic acid-reduced graphene oxide; SC, super capacitor; SDS, sodium dodecyl sulfate; SEM, scanning electron microscopy; S-g-A, graphene/poly(styrenesulfonic acid-graft-aniline); SGH, self-assembled graphene hydrogel; SHSG-8, self-propagating high-temperature synthesized graphene; SOHIO, standard oil company of Ohio; SSA, specific surface area; Sulfonated Graphene/MnO₂/PANI, sulfonated graphene/manganese dioxide/polyaniline; TEABF₄, tetraethyl ammonium tetra fluoroborate; TEM, transmission electron microscopy; TMDC, transition metal dichalcogenide; UPS, uninterruptable power supply; US, ultrasonicated; W, Watt

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Polyaniline

is provided in the introduction, and many studies are compared in order to determine which materials produce electrodes with high capacitance and cyclability in SCs, and to summarize and gauge the state of such research. The types of materials looked at include graphene and graphene nanocomposites, activated carbons from renewable materials, conducting polymers, and transition metal dichalcogenides. Additionally, different methods of activation that are meant to increase specific capacitance are examined.

Among the dozens of materials found in the literature during this study, the ones that exhibited the highest specific capacitances are rGO/PANI (Reduced Graphene Oxide/Polyaniline), and PANI-NFS/GF (Polyaniline Nanofiber Sponge Filled Graphene Foam) demonstrated impressive performances. These materials all exceeded the current expectations of SCs by remarkable amounts, and more research into similar materials is highly encouraged.

As more fundamental studies carried out for understanding the mechanisms of SCs, energy density and specific capacitance values continue to improve. Production of SCs from renewable materials encourage optimism for environmentally friendly options soon becoming feasible for use on larger scales.

1. Introduction

In recent years, the scientific community has begun to more seriously consider what needs to be done in order to manage energy consumption and preserve natural resources. A great deal of research is being done on renewable energy, but as the population continues to grow, attention must also be turned to the task of improving or replacing the methods currently used for energy storage. Many renewable sources of energy (most notably, solar and wind energy) have peak seasons and hours that energy storage devices must accommodate. This means that the storage devices must be able to store large amounts of energy during peak hours, until it is to be used during the periods with no energy generation. Boasting incredibly high cyclability (upwards of 100,000 cycles), and fast charge/discharge rates, supercapacitors (SCs) show great promise in the field of energy storage.

Though much of the most ground-breaking research has been done relatively recently, the original concept of SCs dates back to the 19th century, with work done by Hermann von Helmholtz on colloidal suspensions [1]. After that, little attention was paid to the technology until 1957, when General Electric demonstrated and patented a double-layer capacitor [2]. With the granting of another patent in 1966 to the Standard Oil Company of Ohio (SOHIO) [3], the technology saw more small advancements, and was eventually licensed to the US National Electrical Code (NEC) in 1971. At that point in history, SCs still experienced rather low voltage and high internal resistance [4]. Today, the performance of SCs has been drastically improved, but there are still aspects that can be significantly enhanced. Much of the research being done on SCs concerns the improvement of their energy density which, for typical SCs, is significantly lower than that of batteries. The energy density of SCs is proportional to the square of the cell's voltage, so it is

of interest to improve the voltage window in which SCs can operate [5].

SCs are often looked at as the bridge between capacitors and batteries. With capacitors being able to charge and discharge incredibly quickly, and batteries having the ability to store a great deal of energy, SCs provide the best of both options. In a typical SC, there are two electrodes with each being comprised of a metal current collector coated with a highly porous material, and being submerged in an electrolyte with an electrolyte-porous separator between them. When the cell is being charged, one electrode becomes positively charged, and the other becomes negatively charged. At this point, the ions in the electrolyte are attracted to the surface of the electrodes (anions to the positive electrode, and cations to the negative electrode). This creates a “double-layer” at the interface of the electrode surface and the electrolyte. It is for this reason that this kind of capacitance is commonly called Electrochemical Double-Layer Capacitance (EDLC). Fig. 1 shows a schematic of this process.

The EDLC mechanism is what allows SCs to be cycled so many times since there are no chemical reactions taking place, and the electrolyte is not being depleted at all. There is also no volume change in EDLC, which is significant, as volume change would put stress on the materials involved, drastically reducing the cycling ability of the SC. However, while this performance is much better than that of a regular capacitor, the energy density achieved is still far inferior to that of a battery. In order to attain a higher energy density, some of an SC's cyclability is often compromised through the employment of pseudocapacitance. In pseudocapacitance, energy is stored through fast surface redox reactions that take place at the electrode-electrolyte interface. This mechanism is illustrated below in Fig. 2. These reactions are in addition to the EDLC, and can significantly increase the capacitance and energy density of the SC. The downside to using pseudocapacitance lies in the

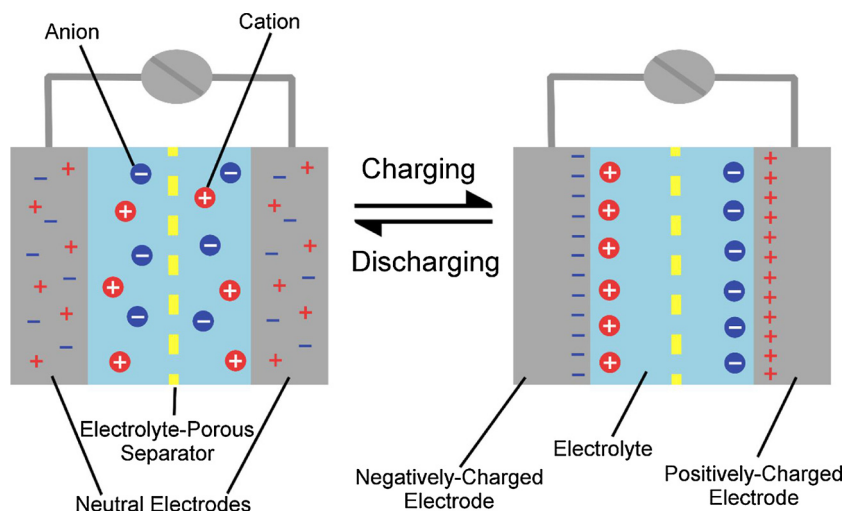


Fig. 1. Schematic illustration of the charging/discharging process in a basic EDLC supercapacitor.

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