Implementation of Graphene in Supercapacitor Electrodes

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Electrochemical capacitors (ECs), also known as supercapacitors, store charge in a double layer of ions formed at the electrode/electrolyte interface. ECs are attracting a compounding amount of interest due to their high charge storage densities, extended lifetimes, and high efficiencies and charge/discharge rate capabilities. These devices may be integrated as standalone power sources for small electronics or in parallel with batteries and fuel cells to maximize operating efficiencies. Various carbon allotropes have found great success as electrode materials due to their high conductivities, high specific surface areas, and high capacitance resulting from ion confinement in pores. While endohedral particles with hierarchical porous structures, such as activated carbon and carbide-derived carbons, have been conventionally used in the past, their power densities and efficiencies at high rates are limited by ionic transport. This is particularly inhibiting for novel electrolytes, such as ionic liquids, preventing novel supercapacitors from optimizing their capabilities and fully benefitting from increased voltage windows.

Figure 1. Schematic of a supercapacitor electrode composed entirely of stacked graphene layers, showing most ion mobility directions and limitations imposed by multiple layer stacking[6].

Multiple recent efforts have focused on developing supercapacitor electrodes via customization of exohedral carbons, which rely on charge storage on outer surfaces of the particles and suffer no diffusion limitation from long and intricate pore channels[1]. In particular, graphene materials, which consist of single or few stacked ordered sp^2 carbon sheets, have attracted substantial interest. Their graphitic structure results in high electrical conductivity, and the two-dimensional nature of this material allows for specific surface area reaching 2,630 m^2/g .[2] While these properties yield optimal gravimetric capacitance and specific energy and power densities when a single sheet is used in a supercapacitor device, such configurations are impractical in most applications due to low volumetric densities and limited scaling ability. As a result, most emerging graphene-based supercapacitor research focuses on stacks of few graphitic sheets arranged in a three-dimensional structure, commonly as a composite with another material.

Although physical exfoliation of graphite was sufficient for initial characterization of single graphene sheets, this approach cannot be applied to meet existing production demands. The most practical method for developing few-layer graphene for electrochemical capacitor electrodes is annealing and exfoliation of graphite oxide, most commonly prepared using Hummers' Method. Zhu et. al. successfully advanced this approach in 2011, defunctionalizing and separating oxidized graphite flakes using a microwave and producing Microwave Exfoliated Graphite Oxide (MEGO)[3]. This material exhibited specific surface area exceeding 460 m^2/g and gravimetric capacitance of 191 F/g, benefitting from the intercalation of tested electrolyte (5.0 M KOH) between carbon sheets. This method was further improved by adding some graphene to graphene oxide[4]. In addition to microwave irradiation, other methods of exfoliating or chemically reducing graphite oxide, including hydrazine reduction, laser beam heating, and argon and vacuum annealing were all attempted. Subsequent increases of active material area were achieved using chemical activation of the annealed material, driving specific surface areas above the theoretical specific surface of perfect single graphene sheet. These structures may be further annealed to remove surface functional groups, increasing their stability in high-performance organic electrolyte and ionic liquids. Three-dimensional electrodes may be constructed by binding graphene particles with a polymeric binder, inkjet printing of graphite oxide prior to reduction synthesis,[5] or by depositing and subsequently drying them on a current collector substrate[6], achieving high volumetric charge storage densities and resulting in practical structural device concepts (Figure 1). A route currently attracting significant attention involves self-assembly of graphene sheets on carbon surfaces using chemical vapor deposition or similar synthesis pathways[7]. This method produces free-standing, flexible three-dimensional structures with exceptionally high conductivities, rate handling ability, and sufficient mass loading to be scaled for powering small electronic devices.
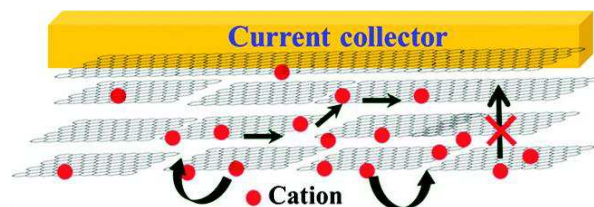
While multiple approaches implementing solely graphene flakes in supercapacitor electrodes have been developed, the integration of graphene sheets into composites with other carbon materials has recently attracted substantial interest. Layered structures of graphite oxide sheets and other carbon materials such as carbon nanotubes[8], fibers, and nanodiamonds, have been assembled using variety of methods such as electrostatic assembly or vacuum filtration. Following appropriate reduction methods, resulting scaffolded configurations yield a conductive carbon network with three-dimensional scalability and acceptable mass loading parameters.

An additional promising graphene supercapacitor electrode route is designed to enhance charge storage as a result of pseudocapacitance due to reversible faradic reactions during charge/discharge cycles. One approach involves the nitrogen doping of the surface by reduction of graphene with ammonia, melamine, and other nitrogen-containing compounds. However, capacitance contributions and their specific causes are still disputed. An alternative approach involves using metal oxides, such as MnO_2 and RuO_2, which serve as both structural support features (when they are implemented using needle-like crystals) and as electrode components adding pseudocapacitance contributions to total charge storage[9].

Due to their high electrical conductivity, mechanical and electrochemical stability, high surface area, and accessible surface, graphene and graphene-based composite materials will continue to receive increased interest as supercapacitor electrodes. Primary research efforts focus on maximizing mass loading while taking optimal advantage of the high surface area of graphene and developing binderless freestanding films that can be integrated into various power envelopes. Coupled with novel high-performance electrolytes [10]and implemented in composite configurations with other carbon structures, graphene is emerging as a promising electrochemical capacitor material for electronics. With decreasing price of graphene and increasing production volumes, grid and transportation electrical energy storage applications may become possible.

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