Electrochemical Energy Storage: Supercapacitors

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Various technologies are operated to supply the energy demands such as fossil fuels, nuclear energy, and renewable energy sources. Fossil fuels are depleting at an alarming rate emphasizing the need of alternative greener energy sources like solar and wind. The discrepancy between peak supply and demand from energy sources like solar and wind intensifies the necessity of high-performance energy storage systems.

Batteries possess high energy density with low power density whereas conventional capacitors exhibit high power with lower energy density. Supercapacitors also known as ultracapacitors possess a balance of energy and power densities which bridge the gap between conventional capacitors and batteries. Supercapacitors are capable of delivering more power than batteries and store higher energy density than conventional capacitors. This nature of electrochemical performance of supercapacitors makes them for many useful application like alternative energy industries, transportation, electronics, and communication.

Increasing the energy density of supercapacitors while maintaining the other fascinating properties has become an emerging field of research on energy storage. Depending on the energy storage mechanism they possess, supercapacitors can be classified in to two major categories, as pseudocapacitors and electrochemical double layer capacitors (EDLCs). Pseudocapacitors store energy by fast oxidation reduction reactions between electrode material and electrolyte ions.[1] Although this mechanism yields higher energy density it suffers from poor cycling stability and low conductivity, which hinder it the usability of pseudocapacitors in real world applications. On the other hand EDLCs store energy through pure electrostatic charges accumulated at the electrode/electrolyte interface. Since the EDLCs have electrostatic mechanism it can rapidly release charges, while maintaining exceptional cycle life. Electrochemical performance of supercapacitors depends upon the specific surface area, pore size distribution, and conductivity of the electrode material.

Capacitance (C) is the charge (Q) per unit voltage (V) which is shown in equation 1.1.

$$Q=CV \qquad 1.1$$

$$C=\varepsilon_o\varepsilon_r\frac{A}{d} \qquad 1.2$$

Capacitance related to the geometry of electrode which can be expressed as equation 1.2, where ε_r, dielectric constant of the electrolyte, ε_0, dielectric constant of vacuum, d is the thickness of the double layer.[1] EDLCs, as the name imply two electrodes make two double layers upon charging, which represents a combination of two capacitors in series and the capacitance can be shown by equation 1.3.

$$\frac{1}{C_T}=\frac{1}{C_1}+\frac{1}{C_2} \qquad 1.3$$

The energy density and power density of a supercapacitor expressed in equation 1.4 and 1.5.

$$E=\frac{1}{2}CV^2 \qquad 1.4$$

$$P=\frac{V^2}{R_S} \qquad 1.5$$

Capacitance is directly proportional to surface area and inversely proportional to the thickness of the double layer. Increasing the capacitance enhances the overall electrochemical performance of supercapacitor. The distance between double layer is several Angstroms apart, which is at a minimum level. Therefore, increasing the surface area of electrode is a vital technique to enhance the capacitance, and hence the overall electrochemical performance.

EDLCs primarily utilize carbon materials as electrodes. Variety of carbons such as carbon nanofibers (CNFs), carbon nanotubes (CNTs), carbon aerogels (CAGs), mesoporous carbon,[2] and graphene have been explored as electrode materials. Surface area of the carbons can be increased upon activation at high temperatures. Activation is a widely used technique to increase the surface area. Activated carbons considered as highly porous, which contain micro (< 2 nm), meso (2-50 nm), and macro (> 50 nm) pores. These pore architectures involved as ion buffering reservoirs, decreasing ion transport resistance, and absorbing electrolyte ions to form the double layer.[3]

On the other hand CNFs possess superior properties such as high surface area, high mechanical strength, flexibility and relatively good conductivity. Due to these properties CNFs are a promising candidate for supercapacitor electrode materials. CNFs can be derived from carbon containing polymers after electrospinning.

Electrospinning is a versatile technique to obtain fibers with a size range of nanometers to several microns. Basic electrospinning station consist of three main components; a high voltage source, a capillary spinneret, and a collector (grounded/oppositely charged). In brief the polymer solution is filled to a syringe and connected to a needle. Upon application of the voltage, the polymer solution makes a hemispherical shape at the needle tip which is known as a Taylor cone. At the point where the repulsive electrostatic force exceeds the threshold surface tension the polymer solution is drawn out as strands. These strands are deposited on the collector and make a non-woven fibrous mat. Electrospinning depends on several parameters such as the nature and characteristics of the polymer, solution properties (e.g. conductivity, viscosity, and surface tension), magnitude of the electric field, tip to collector distance, temperature, relative humidity, and needle gauge. The electrospun fiber mat is subjected to a heat treatment process in order to obtain carbon with better performance. There can be further heat treatments depending on the activation method used to obtain better surface area.

Recently novel 6FDA-based polymers were explored so that the amount of the in-situ porogen, DABA (diaminobenzoic acid) moiety is adjustable. 6FDA-DABA (100% DABA), 6FDD (6FDA-DAM:DABA 3:2) (40% DABA), and 6FDA-DAM (2,4,6-trimethyl-1,3-phenylenediamine) (0% DABA) were synthesized, electrospun and carbonized. Carbon fibers obtained from 6FDA-DABA and 6FDD displayed a specific capacitance of 89 Fg-1 whereas 6FDA-DAM exhibited essentially no capacitance upon carbonization. As expected, subsequent activation with CO_2 at 1000 °C increased the surface areas and electrochemical performance of all three family members with the 6FDA-DABA-derived fibers exhibiting the highest performance. 6FDA- DABA exhibited the best performance with specific capacitance of 147 Fg^{-1}, energy density of 66 $Whkg^{-1}$, power density of 3.4 $kWkg^{-1}$ with 96% capacitance retention after 3000 cycles and is a promising candidate for supercapacitor electrode material for high energy and power applications.[4]

References

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