Directional Perspective of Energy Storage Devices

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Abstract

The history of human development has always been accompanied with the revolution of the energy in use. The history of human energy utilization has roughly gone through three periods: firewood, coal and oil. By using firewood, humans began to use heat energy. By using livestock, watermills and windmills, humans learnt to take advantage of new energy sources to provide power for their development.

With the discovery of coal and the combination of the development of machinery manufacturing, the first industrial revolution was born in the 18th century. As the main source of the steam engine, coal provides orders of magnitude of energy larger than that provided by previous energy sources, a new era of using fossil fuels for power was opened up. With the development of petroleum, internal combustion engines and electricity, the Second Industrial Revolution was energized and changed the human energy structure again by bringing oil onto the main stage. The high efficiency and light internal combustion engine makes the automobile and aircraft possible while the easy transportation of electricity provides a worldwide power energy for residences, manufacturing industries and electronic devices.

With the continuous development of human civilization, society's demand for energy has increased dramatically. Energy consumption on the planet is increasing at an alarming rate, and the total energy consumption in the 20th century is almost half of that of the whole last 19 centuries. Fossil fuels, as the ideal energy sources for centuries,

provided 81.46% of the total world primary energy supply in 2015[1], and will remain its

dominance in the near future. However, fossil fuels are non-renewable, and the over-exploiting has caused drastic reduction of their reserves. It is predicted that crude oil, natural gas and coal would be depleted in 35 years, 37 years and 107 years, respectively[2]. Moreover, the use of fossil fuels has caused disastrous environmental problems like acid rain and global warming. Therefore, an energy transition of rational utilization and development of sustainable energy has become the most important issue of the earth[3]. Climate change and the depleting fossil fuels require society to move towards sustainable and renewable resources. As a result, we are observing an increase in renewable energy production from sun and wind, as well as the development of electric

vehicles or hybrid electric vehicles with low CO_2 emissions. Renewable energy sources like solar and wind energy cannot be tapped consistently because of their unpredictable variations, making energy storage systems play a larger part in our lives. A backup power supply system is essential to maintain the reliability and stability of the output provided by renewable energy sources. Energy storage systems and devices can store power at the high output level of the renewable energies and supply power at the low output level, and also can provide off-grid energy supply for poor and remote areas. The smart grid systems built for the utilization of renewable energy that consist of power generators, automatic power control management modules and energy storage systems and devices, are rapidly developed as the new generation of renewable power systems[4]. With the fast development of portable electronics and electric cars, energy storage devices with high energy and power density will play a core role in the future integration of renewable energy sources into the existing power system.

In the present chapter, the development of energy storage devices like supercapacitors for the application of renewable energy sources has been discussed.

Energy storage devices

Energy storage devices (ESDs) of both high energy density and power density have always been the core determinant of better using the renewable energy sources and integrating them into the existing energy system for the development of modern society. The development of high-performance hybrid electric vehicles, pure electric vehicles, laptops and smartphones are all dependent on the innovation of low-cost and high capacity ESDs.

Energy, the ability to perform work, and Power, the rate at which the energy is produced, are two metrics used to compare different kinds of ESDs. For characterizing the amount of energy stored per unit mass/volume/area, the

specific gravimetric/volumetric/areal energy can be obtained and is used to describe the energy density. In this dissertation, specific energy and specific power are defined as the energy density and power density per unit mass, respectively. A simplified "Ragone plot" shown in Figure 1[5]illustrates the energy and power densities of a variety of commonly used energy storage devices. Supercapacitors (SCs)lie in the gap between traditional capacitors and batteries, which have higher specific energy compared with traditional capacitors, and higher specific power compared with batteries. Lithium-ion batteries (LIBs) are popular for their high energy densities by converting chemical energy into electricity, but the power is also limited by the kinetics of chemical reaction. SCs possess several advantages over LIBs, including long charging-discharging cycles, high power capability, and a large operating temperature range[6]. However, the energy density of supercapacitors is much lower than that of LIBs. Thus, improving the energy density of supercapacitors without sacrificing the high power density is desired.
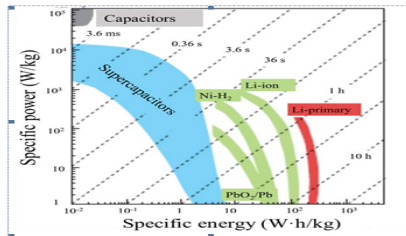

Fig.1 Regone Plot illustrating the specific power versus specific energy for various electrical energy storage devices [5].

1.2   Supercapacitors

Supercapacitors can be classified into three types according to the energy storage mechanisms: electrochemical double layer capacitors (EDLCs), pseudo-capacitors, and hybrid capacitors (a combination of EDLCs and pseudo-capacitors). Although the mechanisms among these three are different, they share similar structure. SCs consists of two electrodes soaked in electrolyte, electric double layers

are formed at the interfaces between the electrolyte and the electrodes to store energy, which is different from conventional capacitors that use dielectric layers to fill; current collectors, which usually are highly conductive materials, are directly connected to the external circuit; a separator, which is a thin, porous, non-conductive and ion-permeable film, is placed between the two electrodes to prevent short circuit.

The concept of the EDL was first introduced by von Helmholtz[7]in the 19th century, unlike conventional capacitors in which the capacity of energy storage is limited by the charge-storage area and the distance. EDL-based capacitors possess large surface area and the separation distance of charges at the nanoscale, they can store much more energy. There are no chemical redox reactions involved in the charge storage. The

capacitance can be approximately calculated as:

$$C_a \propto \frac{\square}{d_H} \tag{1}$$

where is the permittivity of the electrolyte, and d_H is the thickness of the Helmholtz layer.

Stern[8] modified the EDL model, as shown in Fig. 2, which consists of two regions for the distribution of ions — an inner region as the compact layer, where ions (always hydrated) are adsorbed to the electrode, and a diffuse layer, in which electrolyte ions continuously distribute due to thermal motion in electrolyte. The diffusion capacitance can be expressed as:

$$C_{diff} = \frac{\square^-}{|\,|} \tag{2}$$

where D is a temperature, ionic concentration-dependent constant, also is called the thickness of the diffuse electrical double layer.

The capacitance of EDL (C_{dl}) can be calculated as the capacitances of the two

 regions in series, which can be expressed as:

$$\frac{1}{C_{dl}} = \frac{1}{C_s} + \frac{1}{C_{diff}} \qquad (3)$$

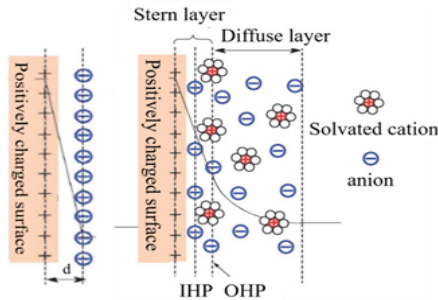where C_s is the Stern layer capacitance.

Fig.2 Schematic of EDL models at a positively charged surface: (a) Helmholtz model and (b) Stern model [9].

EDLCs

EDLCs, whose energy storage is determined by the accumulation of electric charge at the electrode/electrolyte interface, have relatively long cycle lives, and their performance is dependent on several factors including electrical field intensity, electrolyte ions and solvent, and chemical affinity between adsorbed ions and electrode surface. For EDLCs, the two electrodes are always made with the same materials, which are also called symmetrical supercapacitors. Note that there are no terms of "anode" and "cathode" used for EDLCs since there are no redox reactions.

Carbon-based materials

Electrode is the most important component of SCs. The electrode of EDLCs is usually made from porous materials with high specific surface area (SSA), which makes it more complex than solid surface due to the irregular paths for mass transport, the pore-space constraint, the Ohmic resistance associated with electrolyte, and the wetting behavior of electrolyte on the pore surface. Carbon-based materials are the widely-used electrode materials for EDLCs, including activated carbons (ACs), carbon aerogels, carbon fibers, carbon nanotubes (CNTs), templated porous carbons (TPCs) and graphene. The pore population usually includes micropores (< 2 nm), mesopores (2-50 nm) and macropores (> 50 nm).Both pore sizes and the distribution of pore sizes play important roles in determining electrochemical behavior of the EDL-based capacitors made from porous materials. There are several modified models for the EDLCs from porous materials. The traditional porous carbon-based EDLC model is based on that sub micropores are inaccessible to large solvated ions, and do not contribute to capacitance[10]. However, a significant contribution of micropores to the overall capacitance has also been reported[11],suggesting the presence of partial de-solvation of hydrated ions (Fig. 3). It has been observed [5]that a maximum capacitance is contributed by pore sizes less than 1 nm, which is close to the ion size. The observation of the capacitance contribution from pores with sizes smaller than the solvated ion size leads to the development of several models taking pore curvature into consideration. One is the electric double-cylinder capacitor (EDCC) model for mesoporous carbon electrodes, and the other is electric wire-in-cylinder capacitor (EWCC) model for microporous carbon electrodes[12]. The roles of micropores/mesopores/macropores in charge storage still remain elusive, however, the wide distribution of the pore sizes is always detrimental for the energy density of SCs.
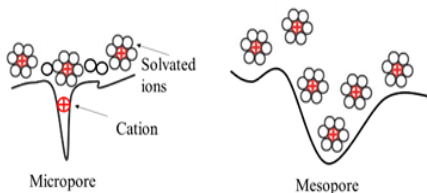
Fig.3 Schematic of Adsorption of Solvated ions to different pore size [11].

Table 1 Characteristics of Carbon structures used in EDLCs [5].

Material	Carbon onions	Carbon nanotubes	Graphene	Activated carbon(ACs)	Carbide derived carbon	Templated carbon
Dimensionality	0 D	1 D	2 D	3 D	3 D	3 D
Conductivity	High	High	High	Structure dependent	Moderate	Low
Volumetric capacitance	Low	Low	Moderate	High	High	Low
Cost	High	High	Moderate	Low	Moderate	High
Structure						

The advantages of using carbon materials of various micro textures in EDLCs include high SSA, good electrical conductivity, interconnected pore structure and facile adjustable pore size. Among carbon materials of various micro textures, 3D carbon-based nanostructures such as AC-based architectures, CNT-based structures, graphene-based nanostructures, and hierarchical porous carbon-based networks likely possess high capacitive capacities due to interconnects of 3D networks. The skeleton of the porous structures provide the path for electric conduction and better integrity. The characteristics of several carbon structures are listed in Table 1[5].

Activated carbons (ACs)

ACs with large SSA (~3000 m^2/g) and highly porous structure have potential applications of EDLCs. There are two activation categories of preparing ACs. One is chemical activation, using chemical agents such as potassium hydroxide (KOH) [13]and sodium hydroxide, acid and zinc chloride. The other is physical activation[14], using gaseous (oxidizing gasifying) agents such as carbon dioxide (CO_2) and steam activation (H_2O). Chemical activation as one of the methods to activate carbon has been used and studied in the past decades. Among various chemical reagents, KOH is widely used due to its efficiency in generating micropores and small mesopores into the skeleton of various structured carbons. Various activation mechanisms have been proposed, while the fundamental mechanisms controlling chemical activation remain elusive due to a large number of factors contributing to the activation processes. Generally, the reaction between carbon and KOH starts with dehydration of KOH into K_2O at 673 K, then the oxidation of carbon with H_2O to carbon oxide and carbonate. At higher temperature (~1073 K), the potassium carbonate largely decomposes into potassium oxide (K_2O) and CO_2 and finally be reduced by carbon to metallic potassium at 1073 K[15].All the redox reactions etch the carbon matrix to form the pore network, and then the generated H_2O and CO_2 through the gasification of carbon further contribute the development of the porosity (i.e. physical activation). Finally, metallic potassium inflow into the carbon structure and expands the carbon skeleton. The expansion is irreversible, and a high microporous structure is created after the removal of the metallic potassium and other potassium compounds through washing.KOH, $ZnCl_2$and CO2 have been used as chemical agents, respectively, in the activation of Bituminous coal[16]to study the effects of the processing parameters on the chemical activation and to determine the optimal conditions for the chemical activation of bituminous coal. The results show that the impregnation ratio

plays the most important role in the chemical activation, and the effects of the carbonization temperature and time are dependent on the chemical agents used. The gas evolution of hydrogen on the activation of carbon in KOH[17]was also analyzed. It has been suggested that higher KOH/C mass ratio, faster sweep gas flow and higher temperature can increase the hydrogen content, and large amounts of hydrogen is favorable for the increase of porosity during the chemical activation.

Physical activation always needs a longer time, higher temperature (973 K~1473 K) than chemical activation [18]. However, it is easier and safer than chemical activation to operate, including the use of no corrosive agents and no need for a washing process. The mechanisms of physical activation are relatively simpler than chemical activation so the activation process is more controllable. No matter which activation methods are used, the key point is to achieve well-tuned pore sizes[19]and optimal distribution of pore sizes[20].

Graphene

Graphene, a two-dimension carbon monolayer, has recently drawn great interest in the applications of supercapacitors. Graphene is a single atomic layer of graphite, so it is known as the thinnest material, and has excellent properties including good conductivity(thermal conductivity: 5000 W/(m•K) and electrical conductivity: 6000 S/cm[21]),large SSA and large mechanical strength (Young's modulus: 1 TPa[22])[23].

The effective surface area of a graphene-based electrode highly depends on the number of layers. Electrodes made from single or few-layer graphene can have large capacitance due to the large SSA. Xia et al.[23] reported that the capacitance of an ideal single layer graphene-based EDLC can reach up to 500 F/g. However, it needs to break the strong van der Waals interaction of the π-stacked layers in

graphite in order to produce graphene sheets (GNSs)[24]. There are several methods available to prepare GNSs. The first approach is to grow GNSs on substrate, including chemical vapor deposition (CVD) on metal foil substrate like Cu and Ge [25], epitaxial growth on single-crystal silicon carbide substrate[26], and thermo-splitting on polycrystalline silicon carbide[27]. The second one is the oxidation–exfoliation–reduction[28] of graphite powder (also called as reduced graphene oxide, r-GO). GNSs can also be directly exfoliated from graphite[29]by sonication, intercalation or quenching. Organic coupling reactions[30]are an important bottom-up fabrication method for nano-GNSs. When using graphene as the electrodes in EDLCs, the r-GO is treated with chemical or thermal reduction in aqueous dispersion/organic dispersion/dry system [31]to maintain a high SSA or high-porosity structure. In general, capacitance can be larger than 200 F/g. Introducing three-dimensional, macroporous structure or "spacer materials" such as nano-diamond particles and carbon black particles[32] can help maintain the high SSA of individual sheets, however, regional aggregation of single-GNSs and GNSs is inevitable, which makes it difficult to realize GNSs in large scale.

Carbon nanotubes(CNTs)

CNTs are tubular structured graphene layers, including single-walled carbon nanotubes (tube diameter: 1-2 nm) and multi-walled carbon nanotubes. They have the potential as electrode materials of high power density due to the tubular structure, good electrical conductivity and strong mechanical resilience, which is 100 times higher than steel. Although CNTs have smaller SSA than ACs, the storage of electric charges is strongly dependent on the surface area of CNTs[33]. Also, the tubular structure allows fast diffusion of electrolyte ions, resulting in a small equivalent series resistance and high energy density. Vertically aligned CNTs grown on conductive substrates have been widely used since

entangled CNTs hinder fast ionic transport[34]. However, the high cost of CNTs hampers the use of CNTs for large scale fabrication.

Carbon aerogels and carbon mixtures

Another approach to increase the power densities of carbon-based supercapacitors is to use mixtures of different carbon-based materials. For example, Aerogels are always used in carbon-based composites with CNTs.

Carbon aerogels are mesoporous carbon materials with interconnected networks of carbon nanoparticles, which can be used as electrode materials without binder. It has been prepared via the sol-gel method and controlled by catalysts and the mass ratio of reactants [35].

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