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Review article

Puzzles and confusions in supercapacitor and battery: Theory and solutions

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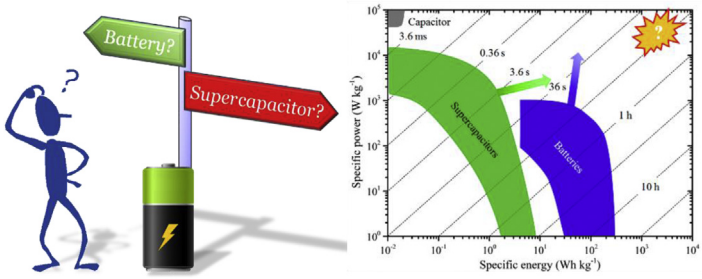
HIGHLIGHTS

- Clarify the puzzles and confusions in supercapacitor and battery.
- Suggest an experimental characterization flowchart to solve the confusions.
- Propose the perspectives for fabricating a supercapacitor with high energy and power.

GRAPHICAL ABSTRACT



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ABSTRACT

Supercapacitors and batteries have been intensively investigated but there is much confusion and misleading between them in publications. In particular, some battery behaviours are incorrectly as supercapacitors and some reported "remarkable" performances like the high specific capacitance of 2188 F g^{-1} for $Ni(OH)_2$ nanospheres are not true. It is likely that the energy storage mechanism and the similar device configuration/characterization techniques cause confusions. It is important to clarify and remove confusion about both theoretical and experimental aspects of these two types of energy devices. This review starts with briefing fundamentals of battery and supercapacitor specifically emphasizing the essential difference on energy storage mechanism between pseudocapacitors and batteries, in which the former undergoes rapid surface-controlled electrochemical reactions without diffusion control and phase transformation, while the latter stores energy in the crystal lattices or porous materials through much slower electrochemical reactions with limits from the phase transformation, chemical binding changes or/and reactant diffusions. Correct characterization and analysis methods such as cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy with a suggested working flowchart to distinguish them are presented while offering thoughtful discussions and explanations about the confusions. Perspectives are also offered for realizing high-energy density ECs without trading off its high power density.

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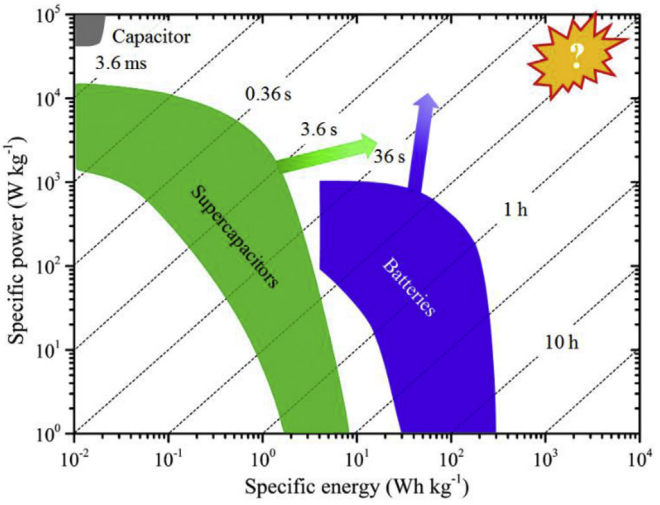

Fig. 1. Ragone plots for batteries, capacitors and ECs. The topical challenge for ECs is to increase energy without compromising power. Times are the characteristic times of devices, obtained by dividing the specific energy by the specific power.

1. Introduction

The rapid development of the global economy has prompted the sober crisis of fast depletion of fossil fuels and increased the environmental pollution. Therefore, the efficient and clean energy sources, as well as their associated advanced technologies, have become highly demanded [1,2]. Since 1975, Conway had conducted extensive fundamental and development works on ruthenium oxide electrochemical capacitors, and then proposed the term "supercapacitor" or electrochemical capacitors (ECs) with a description of the difference between "EC" and "battery" behaviour in electrochemical energy storage [3]. Indeed, EC and battery are two important and commercially available energy storage devices for portable electronics, electric vehicles, and large machines [4–6]. Energies obtained from the intermittent renewable sources such as solar, tide, and wind energy, customer electronics like laptop computers, personal digital assistant (PDA), global positioning system (GPS), portable media players, hand-held devices, and photovoltaic systems as well as the grid power buffers all require batteries or/and ECs for efficient energy storage.

Ragone chart in Fig. 1 presents specific power vs. specific energy of various capacitors and batteries (all Ragone plots are obtained based on total mass of packaged devices), showing that ECs bridge the gaps of power density and energy density between batteries, and conventional solid-state and electrolytic capacitors, but are usually limited by relatively low energy density. A battery has a higher energy density, such as modern lithium-ion batteries with a range of 100–265 W h kg^{-1}, but the main drawback for the battery is its relatively low power density. ECs normally have the energy densities below 20 W h kg^{-1}, and a high power density above 10 kW kg^{-1}, which is typically 10 to 100 times greater than the batteries [7]. In addition, apart from these three energy storage devices in Fig. 1, conventional gasoline and hydrogen combustion engines could reach very high specific power density and energy density, of which petrol fuel has a specific energy of 12,300 W h kg^{-1} and can still offer 3700 W h kg^{-1} considering a typical 30% internal combustion engine efficiency [8], although these internal combustion engines need fossil fuels with contamination concerns. The energy density and power density of both battery and EC are still far from the fossil fuels. Therefore, the great challenge for ECs and batteries is to achieve high power and high energy densities as the "question" marked goal shown in Fig. 1.

Nowadays, intensive research efforts have been devoted to the improvement of both energy density and power density by innovating new materials, engineering unique nanostructures, developing highly ion-conductive electrolytes and creating both energy and power boosting configurations for ECs in various important applications [9–17]. In particular, the efforts for research and development of ECs have been focused on increasing the energy density. It is an essence of increasing the operation voltage window and the specific capacitance, because that the energy (E) follows the formula $E = 1/2CV^2$, where C is the capacitance and V is the voltage window. For enlarging the voltage window, non-aqueous ionic liquid electrolytes can be selected due to their higher decomposition potential window than the aqueous electrolytes [18]. Significant progress has been achieved. Asymmetric device configuration is another strategy to expand the operation voltage window. Even a 2.6 V voltage window has been accomplished in an aqueous electrolyte with the asymmetric configuration of $Na_{0.5}MnO_2$// Fe_3O_4@C [19], which exhibits a large energy density of up to 81 W h kg^{-1}. Nanostructures are tailored to improve the specific surface area and the rational pore size distribution such as carbide-derived porous carbons for greatly increased specific capacitance [20–22]. The novel intercalation energy storage mechanism can utilize the internal surface area between adjacent layers. Nb_2O_5 and MXene are very attractive materials for intercalation pseudocapacitance [23,24]. The most intuitive approach to fabricate an EC with both high energy and high power density is to combine battery and capacitive materials in a device [25–27]. Activated carbon (AC) is the most popular material for EDLC electrodes, which could typically have a surface area of about 1000 $m^2 g^{-1}$ resulting in a specific capacitance of 100 F g^{-1}. Oxides of transition metals including RuO_2, IrO_2, Fe_3O_4, MnO_2 and sulphides such as TiS_2 as well as their combinations have demonstrated high specific pseudocapacitance by their fast electron transfer reactions and high conductivity [28]. Hydrous RuO_2 in H_2SO_4 electrolyte offers a specific capacitance of 720 F g^{-1} and a high specific energy density of 26.7 W h kg^{-1} [29]. Remarkably, RuO_2-base EC made from its electrodeposition onto porous single wall carbon nanotube (SWNT) electrode even achieves the highest specific capacitance value (1715 F g^{-1}) up to date, which closely approaches its theoretically predicted maximum specific capacitance of 2000 F g^{-1} [30]. Carbon aerogel, multiwall carbon nanotubes (MWNTs) and SWNTs have achieved the specific capacitances of 104 F cm^{-3}, 102 F g^{-1}, and 180 F g^{-1}, respectively [31]. Graphene has a superior electronic conductivity over AC and possesses a theoretical specific surface area of 2630 $m^2 g^{-1}$ leading to a specific capacitance of 550 F g^{-1} [32]. A graphene-based ECs made from the curved graphene sheets with mesopores in ionic electrolytes provides voltages up to 4 V and a specific energy of 85.6 W h kg^{-1}, which is equal to a conventional nickel metal hydride battery but has 100–1000 times greater specific power density [33]. However, almost all the large-scale produced commercial ECs are made from coconut shells-derived activated carbon. Due to the issues of cost and difficulty of production in large scale, none of these reported favourable high-energy density pseudocapacitors such as metal oxides are fabricated on a large scale for commercial uses [34].

It is also noted that some reported "superior" ECs with "remarkable" high energy density and breakthrough specific capacitance have never been realized for practical devices, because they are actually battery like performance or mainly contributed from battery behaviours but incorrectly considered as those for ECs. Additionally, some "high specific capacitances" are often measured at very slow scan rates from cyclic voltammetry or made incorrect evaluations from the "battery'-behavioural charge/discharge curves [35–37]. Meanwhile, some capacitance calculation and expression are also improper or contradictory. The expression of gravimetric capacitance instead of unit area-based or volumetric capacitance for low density materials such as carbon aerogel, carbon nanotubes, and graphene, as well as some thin-film/fibre electrode-based devices, could greatly overestimate the performance of electrode materials [38]. Device performance and material property could have huge differences, and the latter cannot be used as the device performance. To evaluate the realistic device performance of