

Trends and research challenges in supercapacitors

Tendencias y retos de investigación en supercondensadores

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Abstract

Supercapacitors are energy storage devices that will replace or boost batteries in multiple applications. For their widespread utilization and commercialization, however, markets demand a reduction in their cost and an enhancement of their energy density. In this overview, the main challenges and research activities towards the development of cheap and high-performance carbon-based electrodes for supercapacitors are identified and analyzed.

Resumen

Los supercondensadores son dispositivos de almacenamiento de energía que sustituirán o reforzarán a las baterías en múltiples aplicaciones. Sin embargo, para generalizar ampliamente su utilización y comercialización, los mercados demandan una reducción de su coste y un aumento de sus prestaciones en términos de densidad de energía. En esta breve revisión se identifican y analizan los principales desafíos y actividades de investigación orientados hacia el desarrollo de electrodos de carbón de bajo coste y elevadas prestaciones para supercondensadores.

1. Supercapacitors: markets, forecasts and research

Supercapacitors, or electrochemical capacitors, are electric devices that store energy electrochemically in conductive materials, in the presence of a suitable electrolyte (see the main types in Fig. 1), by two different mechanisms, namely, the electrostatic adsorption of ions (charges) on a polarized surface and the reversible redox reactions of surface electroactive species [1]. The first mechanism (pure capacitive) is

predominant in the so called electrochemical double layer capacitors (*EDLCs*) and it is characteristic of high surface area carbon materials. The second one (based on pseudocapacitance) prevails in the so called *active* or redox electrodes (also called pseudocapacitors), like metal oxides/hydroxides (RuO_2 , MnO_2 , VO_x , Co_3O_4 , Fe_3O_4 , $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, etc.) and conductive polymers (polyaniline, polypyrrole, etc.). Both mechanisms involve highly reversible and fast charge and discharge processes that make these materials distinct from the battery-like electrodes. Nevertheless, carbon materials usually contain electroactive surface functionalities that can participate in pseudocapacitive processes, and active materials usually display high surface areas to adsorb electrolyte ions, so they contribute to their total specific capacitance. The third type of electrode for supercapacitors is then the combination of previous ones in the form of *composites*, typically, a redox material finely dispersed on the large surface of a carbon. A simplified classification of electrode materials for supercapacitors is shown in Fig. 1.

As previously mentioned, the characteristic features of supercapacitors involve that they can be charged and discharged very quickly (within few seconds to milliseconds) and several times (usually more than 100000 cycles) without significant capacitance loss. Hence, these devices can complement or replace batteries when high power delivery or uptake, intermittent energy with variable power demands, and/or long cycling stability are required. This is mainly the case of electric vehicles, when accelerating and braking, and modern multifunctional portable electronic devices (Laptops, Mobile phones, Tablet PCs, Cameras, etc.), which require different

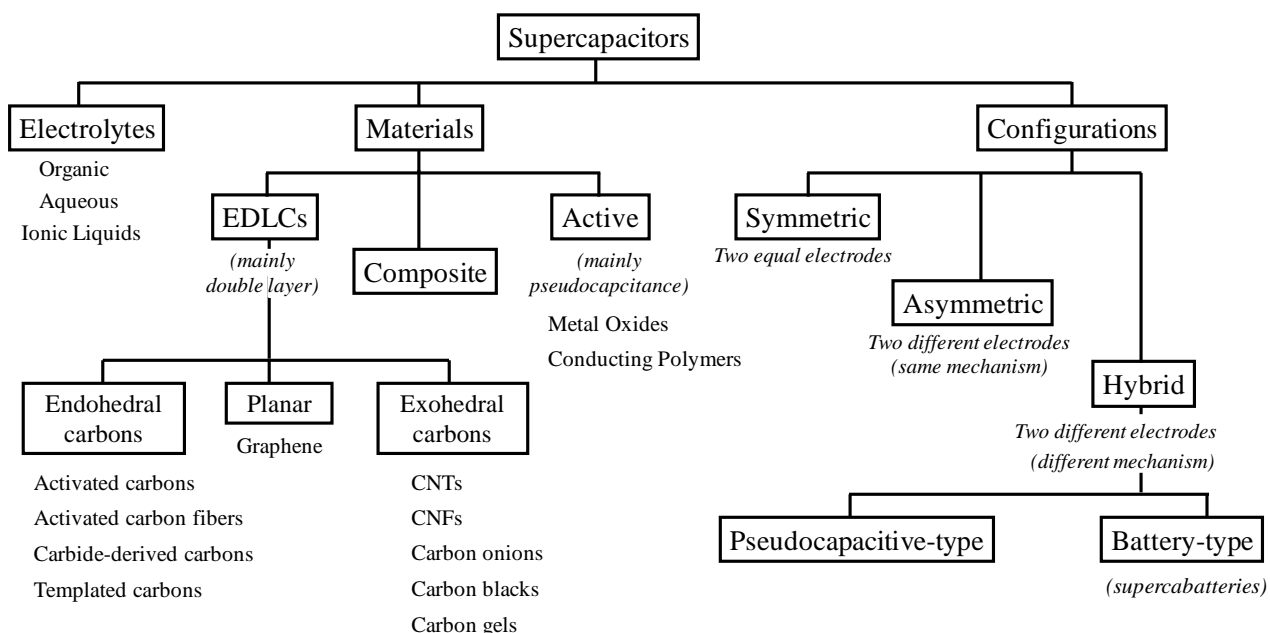


Figure 1. Taxonomy of materials, configurations and electrolytes for supercapacitors (special attention is paid to carbons).

Figura 1. Taxonomía de los materiales, configuraciones y electrolitos para supercondensadores (con especial atención a los materiales carbonosos).

power profiles depending on the function (Fig. 2a). In addition, supercapacitors exhibit excellent low temperature performance and improve efficiencies in supply systems (such as internal combustion engines, renewable energy systems, batteries and fuel cells) by storing energy when in excess or not needed. As a consequence, apart from automotive and portable electronic devices, supercapacitors find potential application in energy harvesting, renewable energy, electrical grids, wireless sensors and Radio Frequency IDentification (RFID) [2].

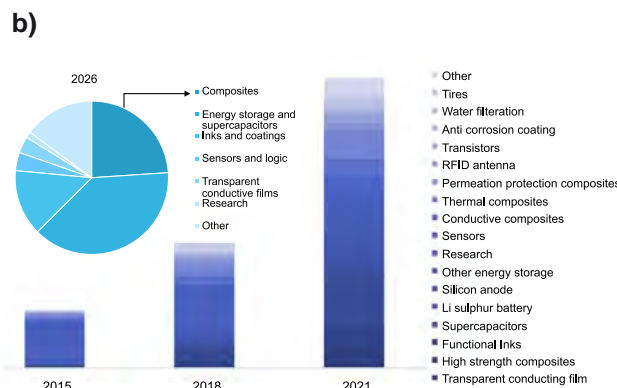
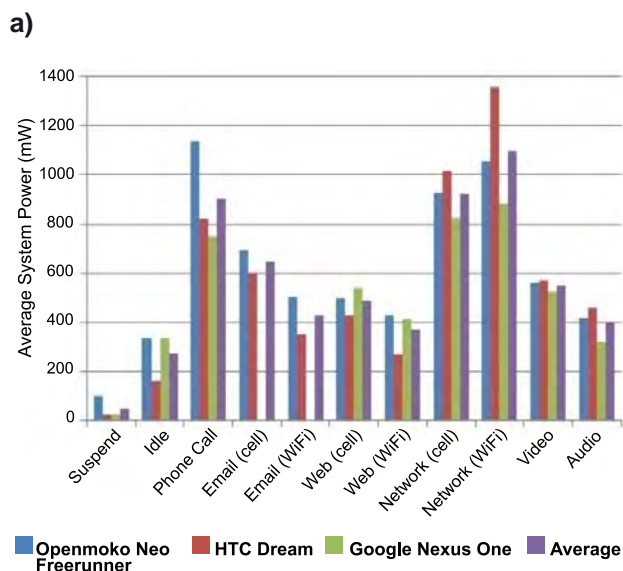


Figure 2. a) Different power profiles for different smartphone uses [3]; b) Graphene market forecast split by application in 2015, 2018, 2021 and 2026 [4]. Source: IDTechEx.

Figura 2. a) Perfiles de potencia para varios usos en diferentes smartphones [3]; b) Predicción del mercado de grafeno según diferentes aplicaciones para los años 2015, 2018, 2021 y 2026 [4]. Fuente: IDTechEx.

Interestingly, new trends on future consumer electronics and portable devices (with \$86 billion market by 2023 [2]) point out they are becoming increasingly thinner and more power-demanding [3]. In this case, the utilization of supercapacitors for a more efficient use of batteries will allow the effective reduction of their capacity and, therefore, size and weight, as well as an enhanced power performance and the extension of their useful time. Because of all these interesting properties and their potential usage for an increasing number of purposes and applications, supercapacitors market is roaring up to over \$11 billion by 2024 with considerable upside potential [5].

However, despite this significance and promising perspectives, the widespread utilization of

supercapacitors has not been attained yet. According to manufacturers, developers and suppliers of supercapacitors, this is assigned to their current high cost to performance ratio and low energy density [6]. As a result, great efforts and multiple research activities are currently driven towards the development of advanced materials and configurations for enhanced energy densities, as well as cheaper preparation and processing methods. Some of these currently most important research lines are analyzed in the following sections.

2. Design of morphology and porosity of carbon materials

The study of the relationship between supercapacitor performance and the texture/morphology/dimensions of carbons constitutes a research topic determinant for the optimization of these systems. Fig. 1 includes a possible general classification of carbon materials used as electrodes in EDLCs. It is mainly based on the type of carbon surface curvature that governs the double layer formation, which in turn, depends on the morphology (particle shape and size) and pore texture (micropore and mesopore volume and pore size distribution) of carbons. Apart from the double layer formation, both features determine the extent and accessibility of the specific surface area of carbons and, therefore, the significance of the double-layer charge storage mechanism.

Graphene and 2D derivatives are the only carbon materials showing (theoretically) no curvature. Their morphology optimizes the double-layer formation, so that the theoretical normalized capacitance of graphene is among the highest of carbon materials (0.21 F/m²) [7]. Carbons with spherical, cylindrical and tubular shape (exohedral carbons), like carbon blacks, onions, gels, nanotubes (CNTs), nanofibers (CNFs), etc. display positive surface curvature and mainly external surface area from inter-particle pores [8]. On the other hand, the inner sidewalls of CNTs and the intra-particle pores of carbons (independently of their particle shape) show negative surface curvature [8]. The last is mainly the case of porous carbons (endohedral carbons), like activated, templated, carbide-derived carbons or activated carbon fibers (Fig. 1). Nevertheless, most of carbons show both types of curvatures because of their morphology and porosity. In general, exohedral carbons display lower surface areas, but they have the ability to enable higher power density and normalized capacitance (F/m²) than endohedral ones. On the contrary, the presence of micropores and mesopores remarkably increase the specific surface area of endohedral carbons and, thus, they lead to higher specific capacitances (F/g) and energy densities. Particularly, micropores showing diameters in the range of desolvated ions provide higher normalized capacitances (F/m²) than mesopores, whereas this last type of pores facilitates faster ion diffusion for enhanced power densities.

Apart from all these effects on surface area, the morphology and porosity of carbons determine another important characteristic of carbon electrodes, that is, their conductivity. Thus, the smaller the dimensions or the higher the porosity of carbons (for enhanced extent and accessibility of their surface area) usually results in higher inter- and intra-particle resistances, respectively, causing an overall decrease in their

conductivity when used as electrodes. Hence, this compromise relationship must be taken into account on the design and engineering of carbons for their use in supercapacitors. Considering all these properties and effects, it is quite difficult to choose which carbon material is generally the best electrode candidate for supercapacitors. In addition, the manufacture cost of carbons and that of their processing into electrodes are also crucial factors for the choice.

Up to now, the highest performance devices already on the market have been high surface-area activated carbon supercapacitors with organic electrolytes (mainly based in acetonitrile). At present, while research is concentrated on finding less-toxic and high-performance organic and ionic liquid electrolytes, the supercapacitor industry moves towards safer aqueous electrolytes. Independently of the electrolyte, graphene is considered the carbon material that will gather the best combination of high energy and power densities, as well as suitable flexibility to be used in stretchable supercapacitors [5-7]. Therefore, for the next future, market forecasts in supercapacitor are strongly focused in graphene [5,6]. Similar perspectives are predicted for the application of graphene in batteries, so that analysts expect that a great part of graphene production will be managed by the energy storage sector (Fig. 2b) [4]. Although the prices of graphene are still very high, it is expected that they will fall as applications and supply volumes emerge. In this sense, the high versatility of graphene and the continuous multi-billion-dollar R&D investment suggest that the so-called 'killer application' (in which graphene exhibits a crucial advantage) will be found [4].

From the scientific point of view, however, the theoretical specific capacitance of graphene (550 F/g) is still far to be achieved. This is mainly caused by the strong tendency of graphene layers to stack [7]. Hence, most research activities on graphene-based electrodes are focused on new preparation, modification and assembling routes to avoid graphene stacking [7]. In parallel to graphene, carbon nanotubes (CNTs) are considered attractive potential candidates for future supercapacitors. However, they show lower theoretically-achievable surface area, less expectation for cost reduction and considerable stacking problems too, so their popularity among manufactures seems to have progressively decreased in the last years. On the other hand, because of their high conductivity and electrochemical stability, exohedral carbons (like carbon blacks, carbon onions, etc.) are nowadays used as conductive additives in electrode pastes, but they could be also potential candidates as electrode materials for high power supercapacitors [8]. Besides the high price, their wider usage is highly limited by their low surface area and, therefore, low energy density. Considering all the mentioned drawbacks of graphene, CNTs and exohedral carbons, much research work is being carried out on porosity development by suitable activation treatments [9]. By using this strategy the capacitance and energy density provided by these materials has been successfully increased. However, the overall utility of this strategy should be reconsidered if degradation of their exceptional structure and conductivity (power density) occurs.

On the other part of the wide spectrum of carbon materials, activated carbons are comparatively much cheaper and can exhibit much larger surface areas (above 3000 m²/g) because of their well-developed porosity (endohedral curvature). Nevertheless, their amorphous and highly defective structure and their large porosity make them to display low conductivity and electrochemical stability, while their intricate (randomly connected) pore system causes poor ionic transport [1]. As a result, these materials rarely show high power density and their energy density is commonly much lower than that expected from their high surface area [1]. In order to solve these problems, the optimization of the pore size distribution with an adequate proportion of micropores (for optimum charge storage) and mesopores (to favor micropore's accessibility), by carefully controlling the activation process, is the preferred strategy. Although more expensive, another approach is the utilization of activated carbon fibers, which show a lower interparticle resistance and a better exposed microporosity [1].

For the best design of pore texture, two new families of endohedral carbons have emerged and greatly developed as electrodes for electrochemical capacitors in last decade. These families are carbide-derived and templated carbons. Manufactured by the chlorination of metallic carbides (such as TiC, SiC, etc.) at temperatures of 800–1200 °C, carbide-derived carbons exhibit average pore widths below 2 nm and very narrow pore size distributions (S_{BET} over 1600 m²/g) [1]. On the other hand, templated carbons are produced by filling the pores of an inorganic sacrificial template (zeolites, silica or scaffolds) with a carbon precursor, followed by carbonization and subsequent removal of the template. The use of the template results in a well-defined pore diameter, high surface areas and three-dimensionally interconnected pore networks. Thus, templating is considered the best technology for pore design and engineering hierarchical architectures, giving rise to the highest specific capacitances (among carbons) and fast ion diffusion [1,10]. Due to the high control on the pore texture, both types of carbons show unequalled relevance from a research point of view. Nevertheless, because of their high cost, low carbon yields, as well as safety and environmental concerns associated with production, these materials have limited commercial potential.

Finally, carbon gels (including xero-, aero- and cryo-gels; sometimes called polymer-derived carbons) are a unique family of exohedral materials with a well-developed porous system [1,11]. These carbons are prepared from organic gels (such as resorcinol formaldehyde) with much more control of the pore size distribution than in the case of activated carbons. In addition, they gather advantages of both exohedral and endohedral materials and can be prepared at relatively low cost (mainly in the case of xerogels). As a result, their specific capacitance outperforms that of the activated carbons so they are considered the most promising alternatives to these conventional materials.

3. Functionalization of carbon materials

The role of surface chemistry of carbon materials, i.e. carbon-bonded functionalities containing

heteroatoms like O, N, P, S, B, in their electrochemical behavior has been extensively studied. In the context of supercapacitors, these groups essentially affect the conductivity, wettability, ion diffusion blockage in pores, pseudocapacitance, stability and dispersion of active materials (in the case of composite electrodes) of carbons. Specially, the increase in total capacitance by faradic reactions and effects on electrochemical stability are very important for the energy density of supercapacitors [1]. In spite of such a huge influence and the abundance of related studies, however, little is unambiguously known respect each of these functionalities. This must be mainly due to two factors, namely, (i) the lack of selectivity of current preparation methods and post-functionalization techniques to introduce exclusively the desired surface groups; and (ii) the strong difficulty to assess the sole effects of these groups, while simultaneously affecting the nature and physical properties of carbon materials. In this sense, fundamental research on selective functionalization methods [12,13] and careful systematic studies controlling all the involved parameters are highly demanded.

Particularly, in recent years the benefits from carbon functionalization with N- and P-containing surface groups have been claimed in several papers [14,15]. Nevertheless, the mechanisms of pseudocapacitance and induced stability are still uncertain. On the other hand, the influence of the various functionalities of carbons on their pseudocapacitance and electrochemical stability in non-aqueous electrolytes constitutes less explored topics, despite these aspects could be significant for battery-competing present and future high-energy supercapacitors. Finally, a present challenge under intense study is to optimize the profit of different redox reactions in both the positive and negative potential ranges (in two electrode cells) for the usage of maximum potential pseudocapacitance of carbons. This can be done by balancing the mass of the electrodes and/or the utilization of different optimized carbons for the positive and negative electrodes in an asymmetric configuration [1].

4. Combining carbons with other carbons or redox materials. Composites and configurations

Another important approach to increase the energy density of carbons is their combination with other carbons or redox active materials (see Fig. 1). The first type of combination is obtained by mixing carbons with active metal oxides or conducting polymers to form carbon composites with an extra pseudocapacitance contribution [16,17]. Despite the increase in the overall specific capacitance, however, the active additives usually reduce the surface area, rate performance and cycling stability of the carbon electrodes. Moreover, a marked increase in the price of the electrode is expected. Among different possibilities, the combination of CNTs with different active materials like MnO_2 seems to be one of the most studied and successful composites.

In the second approach, a carbon electrode is externally connected to a different carbon electrode (asymmetric configuration) or a pseudocapacitive- or battery-like electrode in the so called hybrid or asymmetric-hybrid configuration. In this case, however, the objective is not only to introduce

pseudocapacitance or faradic capacity (like in batteries), but also to greatly expand the operating voltage [17,18]. Among the proposed hybrid devices, the lithium ion capacitor (LIC) has attracted most attention because of its wide operating voltage (3.8 – 4.0 V), high energy (> 20 Wh/kg) and cycling life in between those of LIBs and EDLCs [18,19]. These devices use a graphite anode for Li^+ insertion/extraction and AC as positive electrode and their related research is mainly focused on the control of the optimal potential window of both electrodes and the careful selection of the electrolyte.

5. Reducing the manufacturing costs

The utilization of a given carbon material and, therefore, the cost of supercapacitors will rely on the demanded performance for specific applications. Thus, it is expected that different carbon materials will occupy different applications and market niches. Graphene, carbon aerogels and activated carbons are currently considered the main materials to govern these niches. Nevertheless, as the performance of these materials is being progressively optimized by fundamental research, the widespread commercialization of supercapacitors demands greater efforts on a reduction of their manufacturing costs [6]. For a given electrolyte and type of current collectors, the decrease in supercapacitor price can be addressed by using low-cost carbon precursors and simpler and cheaper preparation procedures and electrode processing methods.

Because of their abundance, biomass and natural polymers have been identified as the currently most viable precursors for carbon-based supercapacitors, from both economic and sustainability points of view [20]. In the case of activated carbons and carbon gels, this is already a fact. Remarkably, the valorization of lignin (the second most abundant polymer in nature and substantial by-product of paper and pulp industry and bio-refineries) into different carbons materials for supercapacitors is recently receiving a growing interest [21]. In the case of graphene, however, this approach becomes conceptually more complex. Nevertheless, the preparation of graphene-like materials from natural resources recently constitutes a research subject of increasing attention [22,23].

As for the preparation of carbons showing excellent performance, simpler procedures and approaches without the need of expensive catalysts, templates, reagents and/or excessive temperatures are highly demanded. Furthermore, the simplification of existing methods by reducing the number and length of necessary steps would be desirable. Among different alternatives, the high versatility, simplicity and low-cost of sol-gel [11], electrospinning [24] or hydrothermal carbonization [25] techniques make them very attractive for the production carbons for supercapacitors.

Most of carbons display a small particle size so that, for their usage as electrodes, they necessarily have to be processed in the form of carbon pastes or slurries by the aid of an appropriate binder (usually from 5 to 15 wt%). This binder normally blocks (decreases) the surface, reduces the electrochemical stability and strongly increases the electrical resistance of the electrode. As a result, the utilization of a conductivity promoter (usually carbon black) becomes necessary.

Because of both additives, the total weight and price of the carbon electrodes increase. Moreover, they have to be finely dispersed throughout the fine carbon particles, increasing the time, complexity and cost of the whole process. Hence, the main consequence of pasting is that a carbon electrode is more expensive and shows much lower performance than that expected from the corresponding carbon material. Taking into account all these drawbacks, the preparation of binderless carbon electrodes is the subject of intense research. Among different strategies, the preparation of 3D seamless and/or self-standing architectures (like monoliths, fabrics, webs, nets, etc.) or the deposition of carbon particles directly on current collectors have been found promising approaches [26].

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