

Cite this: *J. Mater. Chem. A*, 2017, 5, 12653

Carbon-based composite materials for supercapacitor electrodes: a review

Arie Borenstein,^a Ortal Hanna,^a Ran Attias,^a Shalom Luski,^a Thierry Brousse^{bc} and Doron Aurbach^{id}*^a

Electrochemical capacitors, so-called supercapacitors, play an important role in energy storage and conversion systems. In the last decade, with the increasing volume of scientific activity and publications in this field, researchers have developed better tools to improve electrode materials. Although carbonaceous materials seem the most suitable for supercapacitor applications, a large diversity of materials has been proposed and studied. Yet, in order to accomplish performance beyond the limitations of each material, mainly in terms of energy density and durability, composite materials have been implemented, most of them being the combinations of carbon-based materials and other components. In this review, we present the recent advances in the field of composite materials that include at least one carbon-based component for supercapacitor electrodes. We focus on cases in which a single material by itself suffers from a drawback that can be overcome by combining it with other components, enabling the fabrication of a composite material with enhanced performance. We present several important compositions as well as the major routes of synthesis, characterization and performance of composite materials in this field.

Received 25th January 2017
Accepted 10th May 2017

DOI: 10.1039/c7ta00863e

rsc.li/materials-a

Introduction

Electrochemical capacitors, so-called supercapacitors (SCs), are electrochemical energy-storage devices which can provide higher power density than batteries and higher energy density than conventional dielectric capacitors. Supercapacitors possess great advantages, especially in terms of rapid charge and discharge and highly prolonged cycle life. However, they may suffer from low energy density compared to batteries.

Standard supercapacitors use two identical activated carbon electrodes which are arranged in a symmetrical manner and the charges are mainly stored in a capacitive manner in the electrochemical double layer located at each electrode/electrolyte interface. However, supercapacitors may be much more complicated devices when different types of electrodes are used, since composite electrodes can display both capacitive and faradaic charge storage. In this review, we will focus on supercapacitor electrode materials that use at least one carbon component and a composite with another active moiety. The carbon by itself shows a capacitive response due to the accumulation of charges in the electrochemical double layer (EDL). There are few types of supercapacitors. The common type is

a symmetric one using two identical carbon electrodes from the same active material. The electro-adsorption of ions on the positive electrodes (anions) and the negative electrodes (cations) is approximately equal, hence the capacitance of the two electrodes is equal as well. These systems can be roughly described by the equivalent electrical circuit analog of two identical capacitors in series. The total capacitance (in *F*) of capacitors in series should be calculated according to $\frac{1}{C_{\text{tot}}} = \frac{1}{C_1} + \frac{1}{C_2}$. Thus, the total capacitance (in *F*) of a system of symmetric capacitors is $C_{\text{tot}} = \frac{C_{\text{electrode}}}{2}$, and the energy should be calculated as $E = \frac{1}{8} C_{\text{electrode}} \times V^2$ (*V* being the maximal charging potential of the entire cell). In order to obtain gravimetric or volumetric capacitance or energy, the former values need to be divided by the mass or by the volume of the device respectively. The gravimetric capacitance of a lab scale device is often obtained by dividing its capacitance (in *F*) by the total masses of negative and positive electrodes since the packaging weight is usually lacking.

However, carbon electrodes can be involved in much more complex designs in order to improve the energy density of supercapacitors and to try to drive it toward the one of batteries. Usually, this increase in energy density is the result of an increase in the capacitance of both the negative and the positive electrodes. Many studies aim at replacing the carbon electrode by pseudocapacitive (oxides or nitrides) or redox active materials that exhibit higher capacitance due to their charge storage

^aDepartment of Chemistry and Institute of Nano-technology and Advanced Materials (BINA), Bar-Ilan University, Ramat Gan 5290002, Israel. E-mail: aurbach@mail.biu.ac.il

^bInstitut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 44322 Nantes Cedex 3, France

^cRéseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France

mechanism. However, this increase in the overall capacitance of the cell usually occurs concomitantly with lower power density and lower cycle life. Thus, an interesting strategy to overcome these drawbacks is to use carbonaceous materials as a matrix for the electrode while compositing it with some new functionalities in the carbon backbone. For example, high performance nanocarbons can be used to boost the power density of standard activated carbon electrodes. Similarly, the synthesis of finely dispersed pseudocapacitive metal oxides within a carbon matrix can give rise to enhanced energy density while still competing with carbon based electrodes in terms of rate capability and durability. Of course, supercapacitors can also be designed with pseudocapacitive oxides or nitrides without the need for a carbon-based backbone. However, devices using composite electrodes with a carbonaceous component offer many more opportunities for preeminent systems as will be presented in this review.

There are many interesting topics related to supercapacitors that cannot be dealt with within a single article. In this review, we concentrate on compositions containing carbonaceous materials. Carbons are the most widely used materials for supercapacitor electrodes. They are attractive for electrochemical applications since carbon is the sixth most abundant element in the Earth's crust and hence its massive use is cost-effective. Most carbonaceous materials are highly conductive, eco-friendly and easily designed. In addition, carbons are the basic atoms in all organic compounds. Hence, organic materials can also be found in electrochemistry as precursors for carbonaceous materials or as a source of heteroatoms to be incorporated into carbons. The unique stability of carbon in various electrolyte solutions under a wide range of potentials and temperatures enables the utilization of conductive carbon materials (*e.g.*, amorphous carbon and graphite) for various electrochemical systems and devices.^{1,2} Thus, carbons may be considered among the most important electrode materials in applied electrochemistry. Carbons are reasonably electronically conductive solids with tolerable corrosion resistance, low thermal expansion coefficient, low density and low cost, and can easily be obtained at high purities.^{3,4} These properties make carbons top materials for basic electrodes and conductive additives for composite electrodes. Moreover, carbon materials can be produced from many types of precursors in a large variety of structures, such as fibers, hollow fibers, thin films, powders and large blocks.³⁻¹² For supercapacitor applications, carbons possess another great advantage: their porosity and morphology can easily be designed by warm processes using oxidizing agents. This procedure, called activation, forms highly porous materials, whose surface area may range from few hundreds to more than 2000 m² g⁻¹. These pore volumes may occupy a large portion (30–80%) of the total volume of the activated carbon material.^{8,10,14} The pores in carbons are categorized by their size into three groups: micropores with diameters less than 2 nm, mesopores with diameters between 2 and 50 nm and macropores with diameters greater than 50 nm.¹³ Controlling the porosity is important not only for producing materials with a large specific surface area, which in supercapacitors results in a high specific capacity of ion adsorption,

but also for determining the rate of diffusion of ions inside and outside the pores of the electrodes during the charge and discharge processes. Carbide-derived carbons (CDCs) whose porosity can be finely tuned in the nanometer range are considered as appropriate materials, especially for investigating ion–pore interactions and high power applications.¹⁵

In addition to the use of amorphous carbon materials for electro-adsorption applications, three additional graphitic allotropes of carbon have been synthesized and investigated more recently: carbon nanotubes (CNTs),¹⁶⁻¹⁸ fullerenes^{1,3,19} and graphenes.²⁰⁻²⁵ These forms of carbon can be utilized as the sole active electrode materials or can be incorporated together with other additives into the active electrode materials. Due to their unique morphology and relatively high surface area, CNTs and graphene have both been widely explored as candidate electrode materials that may overcome the drawbacks of conventional activated carbon materials (*e.g.*, hindered electrical conductivity and mechanical strength). Yet, these nanosized carbons may suffer from low volumetric capacitance (with low density electrodes), agglomeration, difficult fabrication and high costs for commercial production. Producing composite materials that combine carbonaceous nanomaterials with micro-size carbon particles/matrices, also potentially involving other moieties that possess redox activity (*e.g.* transition metal oxides) may solve these problems.

Compared to batteries, supercapacitors suffer from low energy density, driven by the low-energy electrostatic interactions. In order to increase a supercapacitor's energy density, pseudocapacitive materials such as MnO₂ or RuO₂ can be used as electrode materials. Pseudocapacitance arises when peculiar fast and reversible redox reactions, limited at the surface or subsurface of these materials, give rise to “capacitive-like” behavior, which means that the electrodes exhibit an electrochemical signature typical of a capacitive electrode such as activated carbon but, usually, with much more volumetric capacitance than carbon electrodes.²⁶ Capacitance is also dependent upon the surface area of the pseudocapacitive materials and thereby, elaborating that nanostructured active materials may be required.

Another type of electrodes combines redox active materials that exhibit faradaic behavior (typically a battery-type electrode material such as Ni(OH)₂ or redox active molecules such as anthraquinone) with the double-layer capacitance and good electronic conductivity of carbon-based materials. Typically, the electrochemical behavior (*e.g.*, energy density, power density and durability upon prolonged cycling) of these electrodes is a balance between the performance of the faradaic reactions of batteries and that of electrical double layer (EDL) capacitors. Another critical issue for improved cycling ability is the adhesion of the active material to the host electrode (usually a carbon-based material). In this regard, organic moieties have a great advantage due to their covalent bonding or π – π interactions with the graphite-like structures of carbon.²⁷

Of course, every material has its own advantages and disadvantages. In the last few years, we have seen intensive efforts in the field of supercapacitors, enhancing their performance beyond traditional electrode materials by developing

new composite materials. In the composite materials world, the desired results are materials that not only overcome the drawbacks of their individual components, but also benefit from synergic effects that are derived when the components combine together.

Many review articles on supercapacitors have been published in the last few years. However, many of them describe a specific single topic, for instance graphenes or CNTs as self-standing electrode materials.^{28–33} Many other review articles address several aspects of supercapacitors such as mechanism of charge storage, applications, electrolyte solutions, and characterization, and thus serve as introductory papers to the field of supercapacitors.^{34–38} We could not find a review that covers exclusively composite materials for supercapacitor electrodes. This lack of integral information in the literature is very incomprehensible since it is well agreed that active composite, multi-component materials are required in order to meet high specific capacity requirements. The goal of this review is to comprehensively describe major carbon-based composite electrode materials discussed so far in the literature, key methods of their preparation and characterization, highlighting the impact of the composite structures: how each component influences the final desirable properties and good performance. This review article emphasizes the importance of the composite structures of electrode materials for designing improved supercapacitors. It provides several descriptions of our own new results as comprehensive examples.

Obviously, it is not possible in this short review to discuss new classes of materials which are not carbonaceous such as MXenes.^{39–42} Also, fundamental aspects such as adsorption mechanisms, transport phenomena in porous materials⁴³ and the interactions of ions inside confined spaces^{15,44} are beyond the scope of this review.

Fig. 1 presents a Ragone plot of some of the composite materials (activated carbon matrices containing redox active moieties) reviewed in this article compared to the performance of electrodes comprising the redox moieties alone. Briefly, this

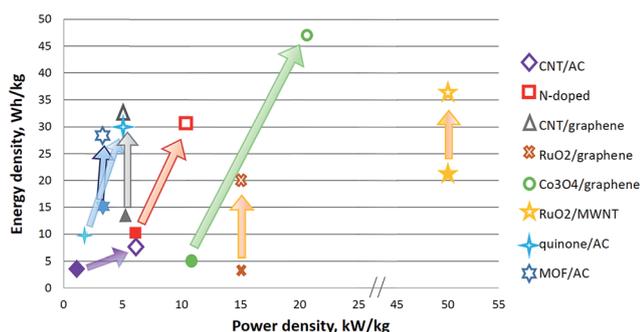


Fig. 1 Ragone plots of some representative sole redox active moieties relevant for pseudocapacitive and/or faradaic charge storage and composite electrodes comprising these moieties in composite structures with carbonaceous materials, reviewed in this article. The filled marks relate to the behavior of electrodes comprising the redox moieties as the main active mass and the unfilled marks relate to the composite materials comprising the redox active moieties with the carbonaceous matrices.

chart reveals the significant improvement that composite materials can demonstrate when properly designed. The values provided in this review are expressed in gravimetric values: gravimetric capacitance ($F g^{-1}$), gravimetric energy density ($W h kg^{-1}$) and gravimetric power density ($W kg^{-1}$). This choice has been made since gravimetric performance is commonly described in the literature. However, readers must be aware that such values are sometimes determined with very low electrode loading (less than $1 mg$ of active mass per cm^2) and it is not correct to extrapolate them to the performance of the corresponding devices as it was carefully explained by Simon and Gogotsi.⁴⁵ It is also important to note that for practical energy storage devices, specific volumetric capacity and volumetric energy density values may be more important than gravimetric values. Dealing with the gravimetric specific capacity of supercapacitors may be misleading, because carbon-based devices use highly porous electrodes which occupy a large volume with only a low amount of active material. Furthermore, the weight of the electrode will be much higher when impregnated with the electrolyte solution inside the pores.

All-carbon composite materials

There are several carbon-based materials such as carbon nanotubes, carbon quantum dots, graphene and nitrogen-doped carbons that can be used as single electrode materials because of their unique structural, electrical and mechanical properties. However, as such they demonstrate low volumetric capacitance and are hard to fabricate. Compositing nanocarbons (*e.g.*, 0-D quantum dots, 1-D nanotubes and 2-D graphenes) into supporting 3-D activated carbon matrices may yield high capacity composite electrodes, as described below. Moreover, the nano-world may be too far from practical realities. Nanomaterials that can exhibit outstanding performance at low electrode loading in lab scale testing may not fit heavily loaded electrodes which are necessary for practical devices. Composite materials may provide the right solution: active nanomaterials embedded in micrometric size carbonaceous matrices can serve as a robust active mass with excellent inter-particle electronic contact and appropriate mechanical stability. Embedding nanocarbons like graphene or nanotubes may form mesoporous structures with high specific surface area and excellent stability. For SC applications, the porosity of the electrode material is a crucial factor, and proves to be highly developed when various nanocarbons are embedded in activated carbon matrices. Hence, we obtain with such materials an interesting synergy in which the carbonaceous matrix stabilizes the active nanoparticles, thus enhancing their charge storage capability and the latter moieties in turn stabilize the mesoporosity of the composite matrices, enabling us to obtain high rate capability.

Carbon quantum dots and onion like carbons

Carbon quantum dots (CQDs) are known as zero-dimensional carbon nanomaterials usually less than $10 nm$ in size. As nanomaterials, they have high specific surface area. CQDs have

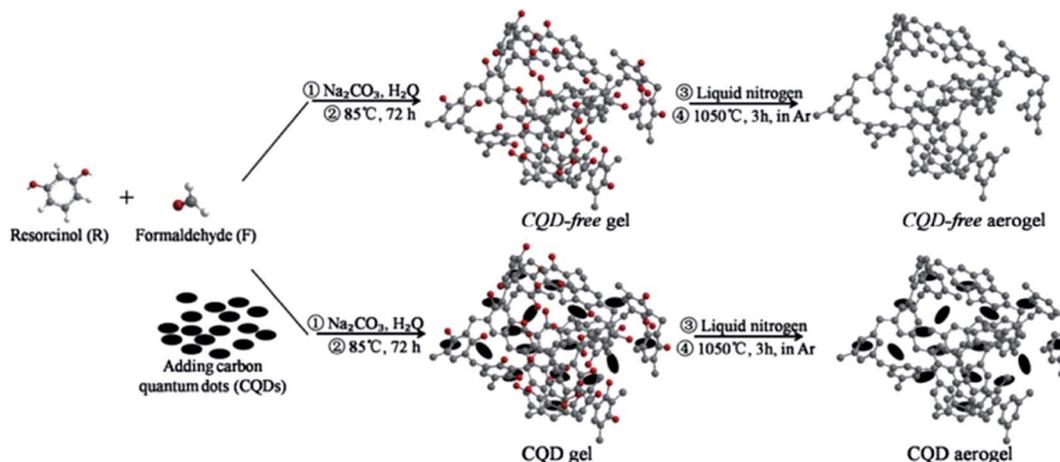


Fig. 2 Schematic presentation for preparing CQDs and CQD-free aerogels by pyrolyzing CQDs and CQD-free polymer gels. The gel structure is for indication only and, for simplicity, the hydrogen atoms in the CQDs and CQD-free gels are not displayed.³⁷

many advantages, such as low toxicity, chemical stability and biocompatibility. Additionally, due to their nanometric scale, their dense electronic structure has some quantum effects such as fluorescence and higher intrinsic capacitance.⁴⁶ Recently, they have attracted much attention in various scientific fields including macroscopic energy devices, one of which is high-performance supercapacitors.

Most of the methods developed for the synthesis of CQDs suffer from some drawbacks: they require expensive equipment, result in low yield or involve complicated processes. Thus, there is a need to develop a facile low-cost high-yield method for the preparation of CQDs. Qu *et al.* prepared a three-dimensional porous CQD aerogel. This 3D material is very attractive since it has extremely low density, large specific surface area and high porosity. By preparing the 3D CQD aerogel, the full potential of CQDs can be applied.⁴⁷ The preparation method includes resorcinol (R) and formaldehyde (F) as the organic precursors to build the polymer gel framework and assemble CQDs in sol-gel polymerization.^{48,49} The wet CQD gels are pyrolyzed under argon to yield a 3D structure, rich in ordered tunnels and mesopores (Fig. 2). The CQD aerogel electrodes show high specific capacitance values of 294 F g^{-1} at a current of 0.5 A g^{-1} . The stability tests show capacitance fading of only 6% after 1000 cycles.

Conducting polymers can be part of composite materials that also contain 2D-materials such as graphene, MoS_2 and BCN (the latter two also being electro-active by themselves).¹⁵³ Kumar *et al.* developed a new method for the deposition of CQDs on AC by applying a simple sonochemical process on PEG as the carbon source. They combined the CQDs into the pores of activated carbon powder (Fig. 3). The AC-CQD electrode composite exhibited a specific capacitance which was three times greater than that of the unmodified AC electrodes.⁵⁰ This work is advantageous over other similar research studies in the field because of the simplicity of the synthesis process (one step by sonication) and the excellent cycling stability with higher capacitance than reference systems.

Recently, supercapacitors based on composites of graphene quantum dots (GQDs) have attracted a lot of attention since they combine the properties of graphene and Q-dots.⁵¹ The micro-supercapacitors based on GQD composites as electrodes display excellent electrochemical properties, including exceptionally high rate capability and excellent cycle stability. Similarly, the recent combination of GQDs with CNTs to create GQD/CNT arrays shows an increase of 200% in performance compared to that of pristine CNTs.⁵² However by comparing this system to the previous work by Kumar *et al.*, one can notice that the

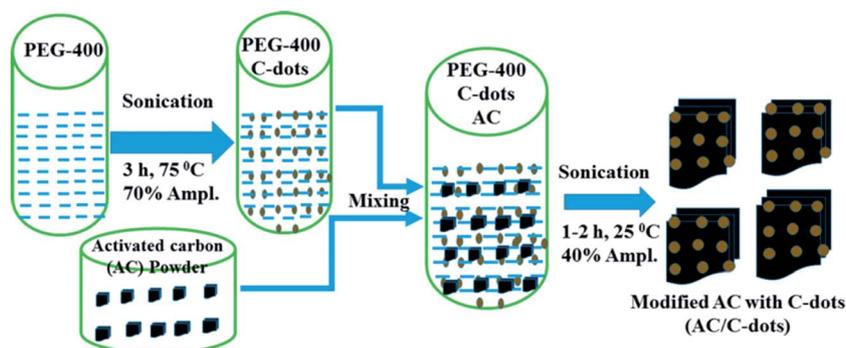


Fig. 3 Scheme of the synthesis process for producing AC modified with carbon dots shown as yellow circles in the modified material.³⁹

performance is less successful than that of the a composite electrode material comprising CQDs embedded in activated carbon matrices. The capacitance obtained here was 0.44 mF cm^{-2} after 1000 cycles compared to 0.185 F cm^{-2} after many thousands of cycles. This may be a consequence of the difficulty in handling graphene due to its tendency of agglomeration, especially in all-carbon matrices. Hence, despite the unique properties of the GQD/CNT composites which make them promising for charge storage devices, there are serious technical barriers to make them relevant for practical energy storage devices.

A recent paper proposes a new method for preparing CQDs by using citric acid (CA) and L-cysteine to produce nitrogen- and sulfur-co-doped CQDs (N,S-CQDs) through a one-step hydrothermal treatment. CA serves as the carbon source, while L-cysteine provides the nitrogen and sulfur. The fluorescent quantum yield (FLQY) resulting from this method is high (73%), compared to other methods.⁵³ According to the transmission-electron microscopy (TEM) image, the size of the N,S-CQDs prepared by this method is between 5 and 9 nm, with an average size of 7 nm. High-resolution TEM (HRTEM) shows very high crystallinity. The atomic-force microscopy (AFM) image shows the topographic height of the obtained CQDs, which is between 0.5 and 3.5 nm, with an average height of 2 nm. To use the CQDs in macroscopic energy devices such as supercapacitors, there is a need to assemble the CQDs on a macroscopic platform. A three-dimensional (3D) porous architecture, when used in supercapacitor electrodes, has high specific surface area and a large electrode-electrolyte interface.⁵⁴ This excellent result emphasizes the great advantage of creating a composite nanomaterial on an appropriate micrometric substrate.

Onion like carbons (OLCs) (also known as carbon onions) are spherical closed carbon shells with a concentric layered structure resembling that of an onion, resulting in high electrical conductivity ($\approx 4 \text{ S cm}^{-1}$). These nanometer size particles are usually synthesized by vacuum annealing of nanodiamond precursors. Their moderate specific surface area ($\approx 500 \text{ m}^2 \text{ g}^{-1}$) is fully accessible to electrolyte ions since it mostly comes from the outer side of the particles which exhibit little or no internal porosity.⁵⁵ Nevertheless, they were reported to allow higher power densities even with more viscous electrolyte solutions, such as neat ionic liquids at room temperature.⁵⁶ Due to the fully accessible surface of OLCs and their excellent electronic conductivity, EDLCs with OLCs show better capacitance retention than EDLCs based on other carbon materials at high charge/discharge rates. OLCs have proven to be an excellent supercapacitor electrode material for high rate and high power applications, and demonstrated capacitance retention as high as 80% at a scan rate of 15 V s^{-1} .^{57,58}

Carbon nanotubes (CNTs)

CNTs are formed by wrapping graphene sheets with carbon atoms that are covalently bonded with each other through sp^2 hybridization. Depending on the number of layers of graphene sheets, they are categorized as single-walled CNTs (SWCNTs) or

multi-walled CNTs (MWCNTs). CNTs can be of great interest to design composite electrodes for supercapacitors, since they have a unique internal structure, excellent physical and chemical stability, low gravimetric density and excellent electronic conductivity.⁵⁹ However, their gravimetric and volumetric capacitances are quite low compared to activated carbons. Thus, combining CNTs with activated carbon by a direct and reproducible synthesis can enhance their electrochemical performance. Noked *et al.* synthesized CNT/AC composites by dissolving the CNTs in a mixture of vinyl dichloride monomer before polymerization (CNTs@PVDC). In this case, after carbonization and activation, the carbon material was supported by a CNT matrix. As the composite materials contained a higher percentage of CNTs, the specific surface area after activation was higher, as was the electric conductivity and stability upon cycling. This is an excellent example of the impact of compositing nanocarbons in amorphous carbon material, while the activated carbon is the main body of the electrode on which the EDLC occurs; the nanotubes dramatically change

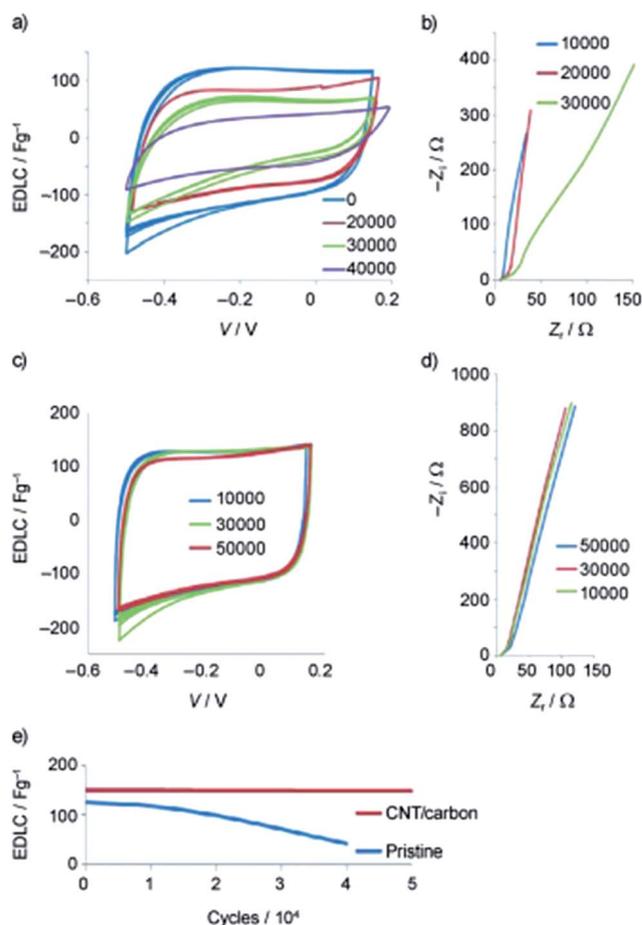


Fig. 4 (a, b) Electrochemical responses of the carbonized activated polymer-based carbon electrodes without CNTs. Two-electrode coin cell with 6 M KOH solution. The cycle number is marked. (c, d) Same measurements for the composite carbon electrodes that contain CNTs (ca. 1.5% by weight). (a, c) Voltammetric response. (b, d) EIS response. (e) Capacity vs. cycle-number plots of typical electrodes (cycle scale of thousands).⁴⁹

their porosity, and provide mechanical strength and conductivity to the composite material. Supercapacitors with the CNT-activated carbon composite as electrodes were able to undergo 50 000 cycles with negligible capacitance fading in aqueous electrolyte solutions, while similar systems under the same conditions without CNTs showed capacitance fading even after 30 000 cycles (Fig. 4).⁶⁰ These composites which combine CNTs with AC gave better results than combining the CNTs with GQDs as discussed previously (200 mF cm^{-2} vs. 0.44 mF cm^{-2}). This proves, again, that despite the interesting properties of graphene it is still far from being implemented in electrodes for practical energy storage devices.

A similar example is the composites of CNTs and polymeric species with activated carbons, which were carbonized and activated to form hierarchical structures containing micro- and mesoporous materials. These composites demonstrated excellent performance in organic electrolyte solutions (a voltage span of 2.5 V), with a capacitance of 170 F g^{-1} at a current density of 118 mA g^{-1} . Over 10 000 cycles a capacitance fading of less than 7% was recorded.⁶¹

There were also recent attempts to combine two different nanocarbons: composite materials comprising CNTs with graphene were tested for SC applications. Their synthesis however was rather complicated: CNTs were attached to the edges and surface of graphene sheets, thereby acting as spacers to increase the electrolyte solution-accessible surface area and to provide 3D electrical conduction pathways.^{62,63} The resulting composite materials demonstrate only moderate performance, so the authors have to explain the benefit of coupling these two nanocarbons together as electrode materials. A new technique for the fabrication of a CNT-carbon composite with uniform pore size distribution was published recently by Mazurenko *et al.* This was achieved by using a stepwise combination of (1) electrophoretic co-deposition of CNTs and polystyrene

beads as the template, (2) polypyrrole electropolymerization within the empty spaces defined by the CNT assembly, (3) template extraction and (4) pyrolysis. The surface area of the CNT-C composite was five times larger than a non-macroporous CNT layer. Moreover, the specific capacitance improved from 6 mF cm^{-2} to 200 mF cm^{-2} with the use of CNT-carbon composites possessing uniform pore size distribution (Fig. 5).⁶⁴ The superior results achieved in this study are a good demonstration of the necessity of robust carbonaceous matrices in order to support the nano-carbonaceous active components, compared to the performance of electrodes comprising the nanoparticles without the robust supporting platform.

Hierarchical structures of CNT composites may lead to better electrochemical performance, thereby enabling elaboration of high-power supercapacitors. A method for synthesizing vertically aligned CNTs grown directly on carbon nanofibers (VCNTs/CNFs) exhibits impressive capacitance performance. The VCNTs/CNFs were assembled into flexible supercapacitors in ionic liquid solution, and the resulting electrode achieved a specific energy density of up to 70 W h kg^{-1} at a current density of 0.5 A g^{-1} at 30°C . Even after 20 000 cycles the capacitance faded by only 3%.⁶⁵ As mentioned above, expressing the specific energy density of SCs on the basis of the weight of the electrodes is misleading, because the weight of the electrolyte solution component in SCs may be much higher than that of the electrodes (depending on engineering aspects that are beyond the scope of this paper).

N-doped carbons

Doping carbonaceous materials with nitrogen induces changes in their physical, chemical and electrochemical properties. Moreover, nitrogen doping can alter the electronic and crystalline structure of the carbons, enhancing their chemical stability, surface polarity, electrical conductivity and electron-

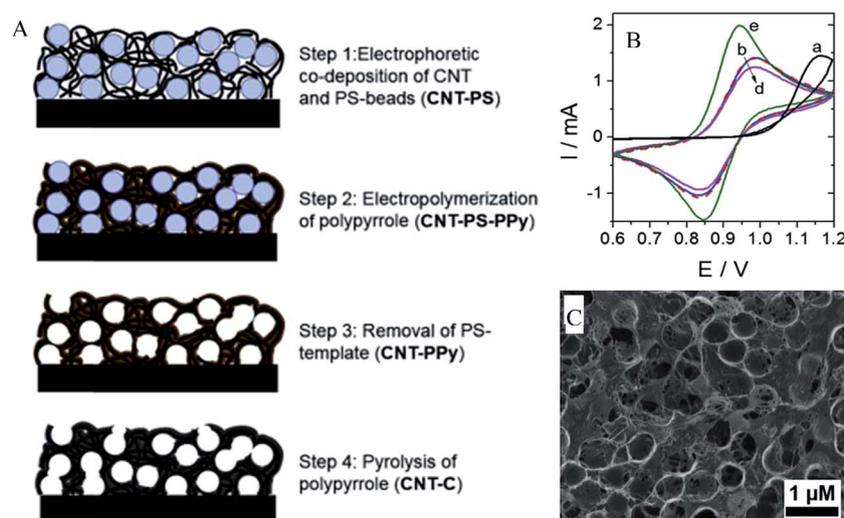


Fig. 5 (A) Schematic representations of the successive steps applied for the fabrication of CNT-C composites. (B) Cyclic voltammograms recorded in $0.15 \text{ M H}_2\text{SO}_4$ solution using (a) bare GCE, (b, c, d) CNT deposits on GCE (1, 2 and 3 layers of CNTs, respectively) and (e) a macroporous CNT layer deposited on GCE. Supporting electrolyte: $3 \text{ M H}_2\text{SO}_4$; scan rate: 10 mV s^{-1} . (C) Scanning-electron micrograph of the macroporous CNT assembly (PS template removed by calcination at 450°C under a nitrogen atmosphere).⁵³

donor properties. Nitrogen-doped carbons are very attractive for many applications, including supercapacitors, catalysis, adsorption and separation.⁶⁶

Most of the synthesis methods for N-doped carbon materials use nitrogen-containing precursors.^{67,68} The challenge in this type of synthesis lies in the limited content of nitrogen in common precursors. An attempt to increase the nitrogen content in the precursors causes degradation in the ordered meso-structure of the carbon materials.^{69,70} A new method of synthesis of N-doped materials that combines carbonization, nitrogen functionalization and activation into a single process was published recently. The obtained N-doped carbon material exhibits a large surface area ($1400 \text{ m}^2 \text{ g}^{-1}$) and high nitrogen content. Using these materials as electrodes for EDLCs enhances the capacitance ($6.8 \mu\text{F cm}^{-2}$ vs. $3.2 \mu\text{F cm}^{-2}$) and reduces the ion diffusion resistance compared to carbon materials without nitrogen.⁷¹

Improving the performance of EDLCs and reducing the charge transfer can be achieved by smaller-sized highly mono-dispersed particles. Synthesizing N-doped carbon material with micro-porous carbon spheres results in higher capacitance, due to the accessibility of the electrolyte solution to the pores inside the particles. Recently, researchers used a sol-gel method to synthesize nitrogen-containing polymer spheres. These N-rich polymer spheres exhibited a high capacitance around 390 F g^{-1} with a current density of 1 A g^{-1} and capacitance retention of 98% after 8000 cycles.⁷²

A different technique for creating microporous carbon with spherical mesopores is atom-transfer radical polymerization (ATRP). In this method, the precursors comprise nanoparticles with organic cores surrounded by a nitrogen-rich carbon source. This procedure eliminates complicated assembly processes and allows a uniform filling of the template with the heteroatom source.⁷³ By using these materials for supercapacitor electrodes, a capacitance of 260 F g^{-1} can be obtained at a current density of 20 mA g^{-1} . Our review clearly concludes that nitrogen doped activated carbon electrodes can be considered as highly important from a practical point of view, since they can contribute to an increase in performance in terms of high specific capacitance and high possible loading per electrode geometrical area vs. relatively easy synthesis from abundant precursors.

Graphene composites

Graphene sheets are advanced 2D carbon nanomaterials composed of carbon atoms arranged in a hexagonal network. Graphene sheets have many advantages, such as high thermal conductivity, high electron mobility and a large surface area.⁷⁴ However, adsorption of the oxidation products reduces the surface area by restacking of oxidized graphene sheets. These graphene sheets must be further activated in order to separate them from one another and thereby maximize the specific area of the active mass. Annealing at high temperature can produce reduced graphene-oxide, in which the sheets become separated. In a recent work, synthesis of reduced-graphene-oxide/activated carbon composites was carried out in one step. After annealing the composite material could exhibit a specific surface area

almost eight times higher than that of the original graphene oxide. Moreover, its electrochemical performance improves, as opposed to the electrochemical performance of graphene without activated carbon.⁷⁵ Another approach that benefits from the surface area of graphene is the assembly of the graphene platelets in a hierarchical porous architecture and thus achieve mesopores between the interconnected macroporous scaffolds. Hence, the electrolyte ions can diffuse more efficiently and the electrochemical performance is improved. Kim *et al.*⁷⁶ fabricated hierarchically porous graphene-derived carbons with mesopores and macropores through the chemical activation of graphene-based hollow carbon spheres. The energy density of the supercapacitors with this composite as electrodes was three times higher than that of supercapacitors made of pristine activated carbons.

Since graphene has a one-atom-thick layer of carbons arranged in a honeycomb lattice, it can serve as an excellent template for preparing 2D porous nanohybrid materials with high efficiency. Schiff-base chemistry is one of the most popular choices for assembling porous organic materials.^{77,78} A Schiff base is a compound with the general structure of $\text{R}_2\text{C} = \text{NR}'$ ($\text{R}' \neq \text{H}$). Using graphene substrates could assist a large-scale production of Schiff-base type 2D porous polymer (TPP) nanosheets, based on melamine and aromatic dialdehydes, resulting in TPP with high nitrogen content and a large specific surface area. By using TPP as a precursor for the production of nitrogen-enriched 2D porous carbon (TPC) nanosheets, the capacitance of the supercapacitors was enhanced to $420\text{--}430 \text{ F g}^{-1}$, with a current density of 0.1 A g^{-1} .⁷⁹

It is important to note that despite the fact that graphene is the most popular example of a 2D carbon nanostructure, graphene nanosheets tend to aggregate during the preparation of composite electrodes, which badly affects the electrochemical performance and reduces the practical surface area.²²

Another advancement related to nano-carbonaceous materials that should be noticed and highlighted is that a new structure of hollow carbon particles (capsules) has the advantage of assimilating into curved porous carbon nanosheets. Since these particles have a curved morphology, the stacking of the particles can be prevented. These carbon capsules can be synthesized by means of nanocasting, based on silica particles with a solid core and a mesoporous shell as a template with a nitrogen-rich substance (Fig. 6). In an aqueous medium, the mesopore carbon capsules exhibit high performance of 240 F g^{-1} with a current density of 0.1 A g^{-1} and capacitance retention of 72% after 10 000 cycles. In an organic medium, these supercapacitors exhibit higher performance of 140 F g^{-1} at a current density of 100 A g^{-1} and capacitance retention of 93% after 10 000 cycles.⁸⁰

The combination of graphene platelets with CDC-tuned porosity has also been achieved by the chlorination of SiC nanosheets obtained by magnesio-thermal reduction of silica/graphene oxide nanocomposites at a moderate temperature.⁸¹

To summarize, all-carbon materials have been studied for electrodes in supercapacitors for many years. Nanocarbons such as graphene, CNTs and carbon nanodots have very high surface area, thus potentially exhibiting the highest specific

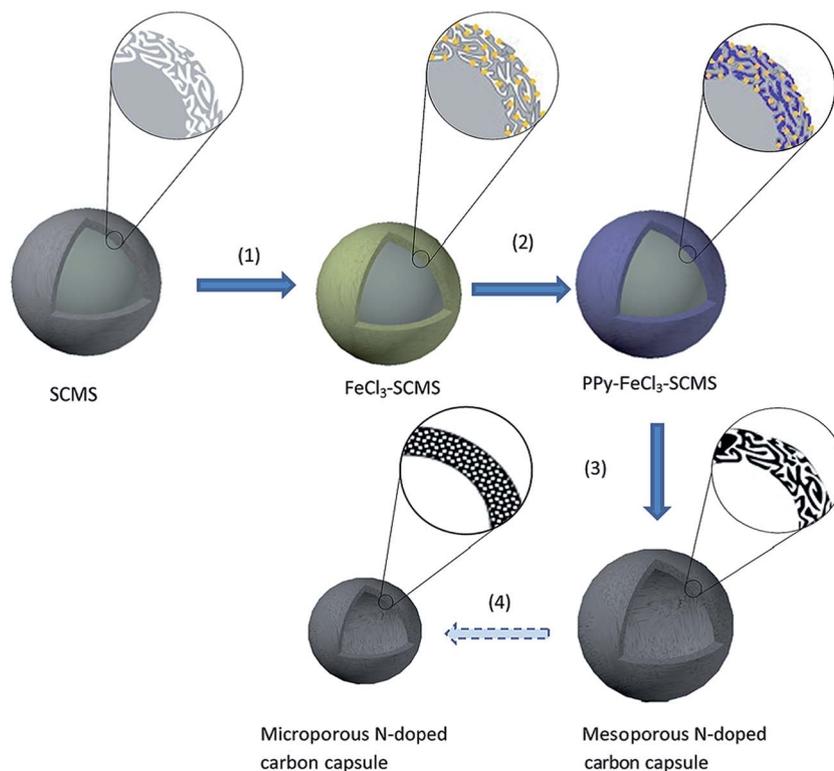


Fig. 6 Schematic illustration of the synthesis procedure: (1) FeCl₃ infiltration, (2) vapor deposition of pyrrole and polymerization, (3) carbonization and etching of the silica framework and (4) chemical activation.⁶⁹

EDL capacitance (per unit volume or weight). Yet, using these materials by themselves in practical cells poses engineering challenges and results in moderate volumetric capacitance. A great progress in this field was marked by coupling different types of carbons in composite structures together. Using such composite materials may facilitate production of practical electrodes, and open the door for fabrication of very robust porous structures of improved properties. Some composite electrodes comprising several types of carbons were able to exhibit capacitance two or three times higher than that of unmodified carbon electrodes. An excellent example for such an improvement and advantage is CNT – activated carbon composites. For many years, CNTs were mixed with electrode materials to improve the conductivity and mechanical strength. However, such mixing had no effect on the active material. With the right compositing process, introducing CNTs embedded and uniformly distributed in activated carbons dramatically changes the morphology of the composite materials and leads to robust and stable mesoporosity. Such materials could demonstrate superior capacity, rate capability and stability over >50 000 cycles. Even more interesting benefits (compared to the use of activated carbons or carbon nanoparticles alone) were observed in composite electrode materials that included carbon-dots embedded in activated carbon matrices.

These approaches are being promoted and pushed further by the impressive development of nanofabrication methods enabling control of materials at the atomic level and by increasing the capability of mass production of nanomaterials.

Metal-oxide composites

Many metal oxides, including RuO₂, MnO₂, V₂O₅, Fe₃O₄, Co₃O₄, NiO and TiO₂, have been extensively investigated in the fields of electrochemical supercapacitors and hybrid devices (combining a battery-type electrode and a capacitive electrode). Some metal oxides, such as RuO₂,^{82,83} MnO₂,^{84,85} V₂O₅ (ref. 2 and 86) and Fe₃O₄,^{87,88} demonstrate pseudocapacitance,²⁶ in which peculiar fast and reversible redox reactions occur on the electrode surface, as opposed to the capacitive charge storage mechanism (EDL) in carbon materials.^{2,89,90} Other oxides (Co₃O₄, NiO, TiO₂) are used as components for battery-type electrodes that can be implemented in hybrid devices together with an activated carbon electrode.^{91–93} The redox behavior of all these oxides relates to the multivalent nature of the transition metals in the oxides. Most of these oxides interact well reversibly with protons and/or hydroxide anions upon changing their oxidation states and the corresponding redox reactions not only occur at the surface of the electrodes but also affect the bulk of the oxides.

Despite their excellent specific capacitance or capacity, depending on whether they comprise a pseudocapacitive or battery-type material, most of the metal oxides suffer from low conductivity, poor stability and poor rate capability and durability during charge/discharge processes. In contrast, carbon materials exhibit excellent performance in all these aspects but may suffer from relatively restricted specific capacitance. Therefore, the integration of nanoscale metal oxides into carbon materials (such as graphene, carbon nanotubes and

porous carbon materials) may generate composite electrodes in which a conductive backbone supports high capacitance/capacity nanocomponents. Many recent studies have demonstrated the high potential of carbon–metal-oxide composites as electrode materials for supercapacitors and hybrid devices (intermediate devices between supercapacitors and batteries) due to their improved electrochemical performance through the synergistic effect of electrical double layer capacitance and pseudocapacitive or faradaic charge-storage mechanisms.^{94–96}

MnO₂-based composites

There has been increasing interest in MnO₂-based electrodes for energy storage applications because of their cost effectiveness and low toxicity in comparison to other transition-metal oxides. In general, MnO₂ is operated in aqueous solution electrolytes and undergoes a pseudocapacitive charge-storage mechanism in neutral aqueous media in which only a thin layer of MnO₂ is electrochemically active and participates in the redox process.⁹⁷ However, MnO₂ electrodes may suffer from limited capacity and power density due to their low conductivity. Hence, the integration of MnO₂ nanoparticles with conductive and high-surface carbonaceous materials may lead to a larger interfacial area between the MnO₂ particles and the electrolyte solution, resulting in enhanced electrochemical performance in terms of specific capacity, power and energy densities.⁹⁸

Many carbon substrates have been investigated: standard carbon black,^{99,100} activated carbon,¹⁰¹ carbon nanofibers,¹⁰¹ carbon nanotubes,^{100–107} graphene,^{10,20–22,100,108–110} microfibrillar carbon paper,^{23,111} carbon aerogels¹¹² and microporous carbons.^{113,114} Carbon-coated MnO₂ and carbon/MnO₂ core-shell nanoparticles have also been synthesized. Here are some major strategies for combining MnO₂ with carbon materials:

MnO₂-CNT composites have recently gained interest due to the high mechanical stability and high electronic conductivity of the CNTs, and the high specific capacitance of MnO₂. These composite materials exhibit high specific capacitance between 115 and 950 F g⁻¹.^{115,116} Among the highest specific capacitances ever reported is the multi-wall CNT-MnO₂ composite designed by Yan *et al.*, which was synthesized by the reduction of potassium permanganate under microwave irradiation. The electrochemical characterization of the CNT-MnO₂ (15% wt MnO₂) composite electrodes in 1 M Na₂SO₄ aqueous solutions shows maximum specific capacitance based on MnO₂ approaching 950 F g⁻¹ and a capacitance retention of around 95% after 500 cycles. In this study, the CNTs were introduced together with the MnO₂ precursor. MnO₂ can also be directly coated with CNTs, showing good specific capacitance around 200 F g⁻¹ and outstanding cycling stability without capacitance decay after 10 000 cycles.¹¹⁷

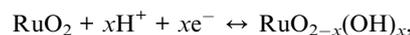
Graphene was also used to support MnO₂ for composite electrodes to demonstrate high conductivity, large surface area and high stability of the graphene. *Via* different methods of synthesis, composite materials possess high specific capacitance between 300 and 520 F g⁻¹ and exhibit reasonable cycling stability.^{118–122} For example, MnO₂-graphene composites have

been synthesized through the quick and facile self-limiting deposition of nanoscale MnO₂ on the surface of graphene sheets under microwave irradiation. This composition displays the maximum specific capacitance of 310 F g⁻¹, which is much higher than that of either graphene or birnessite-type MnO₂ (up to 110 F g⁻¹). In addition to their high capacitance, these composites showed excellent cycling stability and a decrease of less than 5% in the initial capacity after 15 000 cycles. The increased conductivity and surface area due to the presence of the graphene network was suggested as the main cause of their excellent electrochemical performance.¹¹⁹ This research demonstrates that both graphene and CNTs may serve as appropriate backbones for MnO₂ based composite electrodes which exhibit much better electrochemical behavior especially in terms of capacity and cycling stability compared to their single components. We provide herein just a few highlighted examples. The topic is popular in the field and indeed, many hundreds of papers dealing with MnO₂ as a pseudocapacitive electrode material appear in the literature.

It can be noted that a high volumetric capacitance of 90 F cm⁻³ was also obtained using nanoscopic deposits of birnessite ribbons and amorphous MnO₂ throughout the ultraporous carbon structure.¹¹²

RuO₂-based composites

Among the transition metal oxides, ruthenium oxide, RuO₂, is the most studied supercapacitor electrode material, especially in acidic solutions. RuO₂ is considered to have the best pseudocapacity due to its highly reversible redox reactions, three distinct oxidation states accessible within 1.2 V, remarkably high specific capacitance and relatively high conductivity. The pseudocapacitive process can be described as a fast reversible redox reaction with the electrostatic adsorption of protons on the surface of RuO₂ particles. The pseudocapacitive process of RuO₂ generally obeys the equation^{123,124}



where $0 \leq x \leq 2$. Yet, the high cost requires design of electrodes that extract the highest capacitance from the least amount of this metal oxide. The solution lies in composite materials. The integration of an electron-conductive electrochemically stable carbonaceous substrate with a pseudocapacitive material such as RuO₂ has great potential. The development in this field focuses on the best substrate and synthesis method to coat RuO₂ on the surface of the porous electrode.

Warren *et al.* demonstrated the preparation of a RuO₂-CNT composite by uniformly coating ruthenium oxide on a porous structure of vertically aligned carbon nanotubes *via* atomic layer deposition (ALD) and activation of the ALD-RuO₂ by oxidation through cyclic voltammetry potential coulometry. This deposition technique has numerous advantages, which are of great importance for electrode design for energy storage devices, including excellent uniformity, accurate thickness control and deposition on large surface areas (Fig. 7).¹²⁵ This RuO_x-CNT composite displays outstanding electrochemical performance

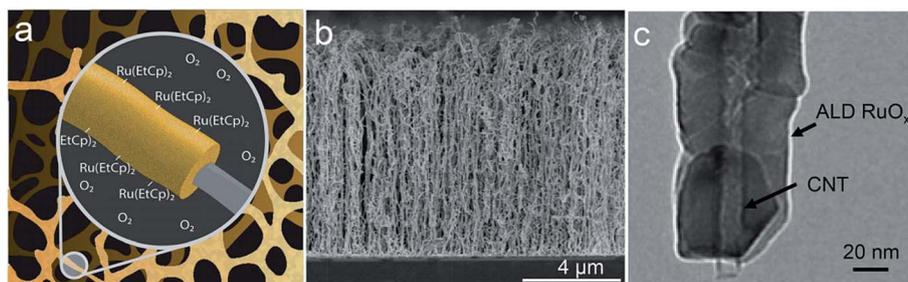


Fig. 7 (a) Schematic drawing of RuO_x deposited uniformly on a large-surface-area porous electrode by ALD. Monolayer by monolayer deposition is achieved by sequential pulsing of $\text{Ru}(\text{EtCp})_2$ and oxygen. (b) SEM image of vertically aligned CNTs coated with ALD RuO_x . (c) TEM image of a single CNT conformably coated with ALD RuO_x .¹¹²

as a supercapacitor electrode material in terms of capacitance, stability, and power density.

The specific capacitance reported in several publications for RuO_x -CNTs was around 650 F g^{-1} (considering only the RuO_2 mass) and high power density of 17 kW kg^{-1} .^{126–128} As a further example, Fig. 8 displays representative data related to RuO_2 -graphene composite electrodes.¹¹³ Other interesting composites of RuO_2 can be made by the deposition of RuO_2 particles onto graphene sheets. Such a composition may lead to higher energy densities compared to the graphene sheets, but slightly less energy densities than that of RuO_2 as a single active electrode material. However, at high power densities ($>1000 \text{ W kg}^{-1}$) such composites show higher energy densities (7.2 W h kg^{-1} at 5000 W kg^{-1}) than electrodes based on RuO_2 or graphene only (1.3 W h kg^{-1} at 5000 W kg^{-1}). Moreover, RuO_2 -graphene composite electrodes exhibit excellent cycling stability. Fig. 8 displays some representative data related to RuO_2 -graphene composite electrodes.¹²⁷

Fe_3O_4 - and V_2O_5 -based composites

Aside from RuO_2 and MnO_2 , other metal oxides have been investigated in connection with supercapacitors, having advantages in terms of cost-effectiveness and electrical conductivity that make them interesting. Magnetite-carbon composites have been investigated as an electrode material in energy-storage devices due to their low cost and relatively high

reversible redox activity.⁹⁴ These electrode composites exhibit a specific capacitance between 115 and 220 F g^{-1} , with a good cyclability.^{129–131} A Fe_3O_4 -CNT composite supercapacitor electrode was reported by Guan *et al.* They used simple hydrothermal treatment that can easily produce the CNT- Fe_3O_4 composite material. The electrode showed a specific capacitance of 117 F g^{-1} and a maximum energy density of 16 W h kg^{-1} .¹²⁹ In a similar method, RGO instead of CNTs demonstrated superior electrochemical performance of the Fe_3O_4 -RGO. In this study, the Fe_3O_4 -RGO composite exhibits a high specific capacitance of 220 F g^{-1} , which remains stable after 3000 charge/discharge cycles.¹³¹ This good performance could be achieved due to a better active mass integration by 3D graphene or a 2D CNT backbone.

Fe_3O_4 -RGO nanocomposites have also been prepared using benzyl alcohol.¹³² The amount of iron precursor was proved to have a great impact, when higher concentration of iron leads to full surface coverage of the RGO nanosheets by FeO_x nanoparticles, forming a close-packed layer that limits the restacking of the RGO nanosheets in the dry state. The resulting FeO_x -RGO composite gains the same power capability as the RGO and a higher energy density than raw FeO_x , owing to this well-designed morphology. The homogeneity of the surface coverage was improved by using 4-carboxyphenyl groups covalently grafted onto graphene oxide *via* diazonium chemistry to study their role in the adsorption of iron-oxide nanoparticles,¹³³ with

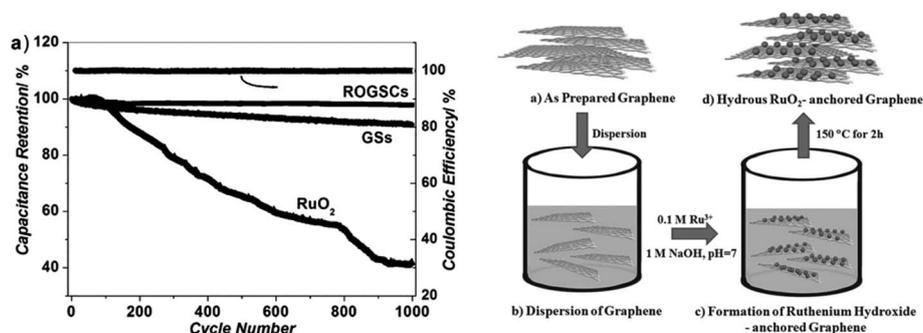


Fig. 8 Left: cycling stability of the as-prepared graphene sheets, RuO_2 and RuO_2 -graphene (Ru , 38.3 wt%) measured with a two-electrode cell at a current density of 1 A/gr (right axis: coulombic efficiency of ROGSCs). Right: conceptual illustration of the preparation process of (RuO_2)-graphene sheet composites by combining the sol-gel method and low-temperature annealing.¹²⁷

some success in improving the rate capability in the case of the nanocomposite grafted electrode.

Carbon nanofoam was also used as a substrate for the electrodeless deposition of conformal nanoscale iron oxide with capacitance up to 84 F g^{-1} and moderate fading over 1000 cycles.¹³⁴

V_2O_5 is known for its high faradaic activity and stable crystal structure. However, its poor conductivity limits its electrochemical performance. Studies on V_2O_5 -RGO composite electrodes demonstrated their good electrochemical performance in neutral aqueous electrolytes. These composite electrodes exhibit high specific capacitance approaching 550 F g^{-1} , as well as a power density of 500 W kg^{-1} .¹³⁵ Summarizing this section, the composite materials mentioned exhibit improved specific capacitance, beyond the limitations of the carbonaceous materials, and enhanced cycling stability of the electrochemically active metal oxide moieties thanks to the electronically interconnected backbone formed by the carbonaceous components.

NiO-based composites

Composites containing nickel oxide are also considered to be promising candidates for hybrid supercapacitor electrode materials, mainly due to their high specific capacity and structural stability, as well as their high rate capability, which can promote elaboration of devices with relatively high energy density without sacrificing too much power density. As previously mentioned, NiO-carbon composites can be envisioned as a positive battery-type electrode in hybrid activated carbon-Ni(OH)₂ cells. The redox reaction of nickel oxide in alkaline solution involves the equation^{136,137}



It must be noted that most of the studies provide capacitance values in F g^{-1} units, which is wrong and misleading, since capacitance cannot be calculated from the typical redox-type CVs of these electrodes. Thus, all the reported capacity values must be converted into mA h g^{-1} from F g^{-1} units, using the width of the electrochemical window in which the capacitance was calculated. Only few studies point out the faradaic nature of Ni-based electrodes for hybrid supercapacitors.¹³⁸

NiO composites have a big advantage over pure NiO, especially in terms of electrical conductivity and electrochemical stability, due to the positive synergistic effects upon incorporating the NiO inside the carbonaceous network.¹³⁷ The integration of battery type materials into the carbonaceous networks may help to overcome diffusion and electron transfer limitations from which intercalation materials usually suffer. Alleviating these limitations results in high rate capabilities, which is a major requirement for supercapacitors. We provide below typical examples (out of many). Trung *et al.* studied the electrochemical behavior of the 3D porous reduced graphene oxide-NiO nanoparticle (3D-RGNi) composite and its performance as a battery-type electrode material. The 3D-RGNi composite was synthesized in three steps, which involved the

adsorption and decoration of the graphene surface by NiO nanoparticles *via* thermal treatment. The 3D-RGNi composite exhibits specific capacity that is higher than those of the RGNi composite and 3D-RG. In addition, this composite electrode material possesses good cycling stability with 87% retention of the capacity after 2000 cycles. Such electrochemical performance was attributed to the unique porous structure of the graphene network, which provides a large electro-active surface area and shorter diffusion length, in addition to the excellent synergistic effect of the incorporation of the NiO nanoparticles in the 3D-RGO network.¹³⁹

Other suitable carbonaceous backbones for battery type active materials that are implemented in supercapacitors are CNTs and carbon nanofoam. Rajendran *et al.* presented a ternary nanocomposite containing NiO nanoparticles distributed on the surface of reduced graphene sheets and CNTs, synthesized *via* a one-step solvothermal process. This ternary composite delivers the maximum specific capacity in a 6 M KOH electrolyte, which is more than twice that of pure NiO, and exhibits a cycling performance of 94% capacity retention after 1000 cycles.¹⁴⁰

Noce *et al.* studied the electrochemical performance of a NiO_x-carbon nanofoam composite which was produced using one-step anodic electrodeposition. The capacity retention was 88.5% after 2500 cycles. This capacity, in addition to a very broad operating potential window of 2.2 V, demonstrates the potential of this composite as an electrode material for high-energy density nanocomposites, which are also good candidates for battery-type positive electrodes in hybrid supercapacitors.¹⁴¹ Not only NiO has been used to form composite electrodes with carbon materials. An outstanding example of the crucial role of composite electrode materials compared to electrodes comprising active materials alone can be found in a work on MoO₃/CNTs as the active material for supercapacitor electrodes coupling EDL and redox reactions. Okashy *et al.* demonstrated a superb behavior of a composite electrode material in which MoO₃ was incorporated into CNT/activated carbon composite material obtained by carbonization of the mixture of CNTs and a polymer. The excellent result of 400 F g^{-1} , stable for more than 10 000 cycles was observed only when the metal-oxide particles were loaded into the CNT/activated carbon framework. When loading the MoO₃ on a CNT platform, the results were even worse than the performance of the neat activated carbon electrodes (Fig. 9). The authors explain that the open structure of the CNT/activated carbon together with the stabilization impact of the carbon platform yielded these excellent results.¹⁴²

Here we have a very good example of how the judicious preparation of composite materials comprising active nanoparticles (MoO₃), CNTs and a porous carbonaceous matrix leads to the formation of high performing electrodes for supercapacitors, possessing very high specific capacity and superb stability upon prolonged cycling. The MoO₃ nanoparticles are responsible for the high specific capacity, while the CNT component contributes to the stability and electrical integration of the entire active mass. Highly important was the synthesis route of the CNTs/AC matrix which included optimal

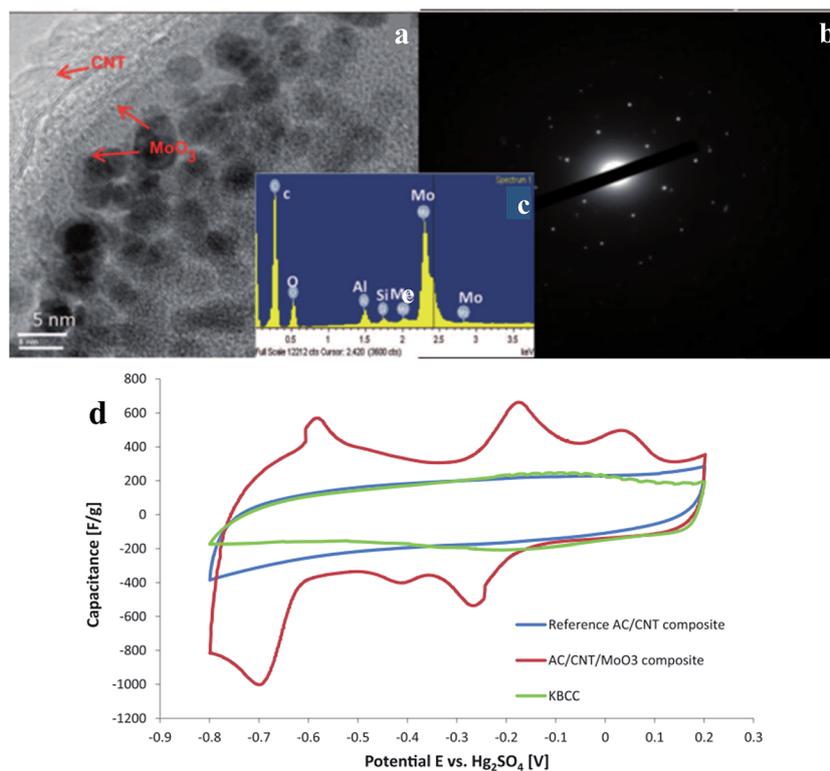


Fig. 9 (a) HRTEM image of MoO_3 nanoparticles next to a CNT, within the carbonaceous matrix $\text{MoO}_3/\text{CNT}/\text{activated carbon}$, as marked therein. (b) Typical selected area electron diffraction (SAED) patterns of the particle presented in (a) that demonstrate the presence of nanocrystalline MoO_3 . (c) The EDS image of the same location demonstrating the presence of the molybdenum oxide moieties attached to the carbon. The aluminum and silicon peaks are artifacts, related to the substrate (sample holder). (d) Typical cyclic voltammogram of AC/CNT/ MoO_3 composite electrodes (red curve), reference AC/CNT electrodes (blue curve), and only carbon (Kynol based carbon cloth, KBCC) electrodes (green curve) in three electrode cells containing 1 M H_2SO_4 solution, using $\text{Hg}/\text{Hg}_2\text{SO}_4$ as a reference electrode. For all the experiments, KBCC electrodes were used as counter electrodes. The scan rate was 0.5 mV s^{-1} .¹²⁸

dispersion of the CNTs in the precursor for the AC preparation. Then, carbonization and activation were carried out while the CNTs are well distributed within the carbonaceous material. In order to optimize the carbonaceous/metal oxide composite materials several factors should be considered such as the synthesis method, cost effectiveness, good adhesion and optimized mass ratio between the components. Among the pseudocapacitive metal oxides, RuO_2 will probably result in the best specific energy and power density, however its high cost and relatively low abundance limit the practical importance of RuO_2 based supercapacitors. On the other hand, the inexpensive MnO_2 and Fe_3O_4 , introduced in the right process with nano-carbon materials such as graphene and CNTs, may be practical options and exhibit very high specific capacitance. Integration of battery materials such as NiO into carbonaceous electrodes can also improve the specific capacity. In that case, the composite materials gain much higher conductivity and electrochemical stability than the pristine metal oxides. Additionally, the developed structure of the carbons and their porous morphology enable optimized exposure of the metal oxides to the electrolyte solution. Yet, the cycling stability and the power density of integrated battery materials can be further improved beyond the state-of-the-art. Ideal composite materials should have a robust porous structure that is fully electronically

conductive and is open enough to allow full accessibility of the redox moieties embedded therein to the electrolyte solution. This situation ensures high specific capacity and rate capability of the active mass. Designing such morphologies must utilize nanofabrication methods. Among the nanofabrication methods, atomic layer deposition (ALD) seems to be a very promising technique for judicious metal oxide loading onto porous carbon substrates. New ways to synthesize highly controlled electrode structures in terms of thickness and morphology are now under development and will probably contribute to this emerging field.

Nitride-based composites

Although this paper is aimed at describing electrode materials for supercapacitors based on carbonaceous components predominantly, there are some similar developments of nitride based composites that deserve discussion for comparison.

Mo_xN was the first to be investigated by Conway *et al.*¹⁴³ as a pseudocapacitive electrode material. Impressive specific-capacitance values were reported for VN.¹⁴⁴ According to Choi *et al.*, the high specific capacitance of VN is due to its high electronic conductivity coupled with fast and reversible redox reactions at the surface of the material. The successive redox

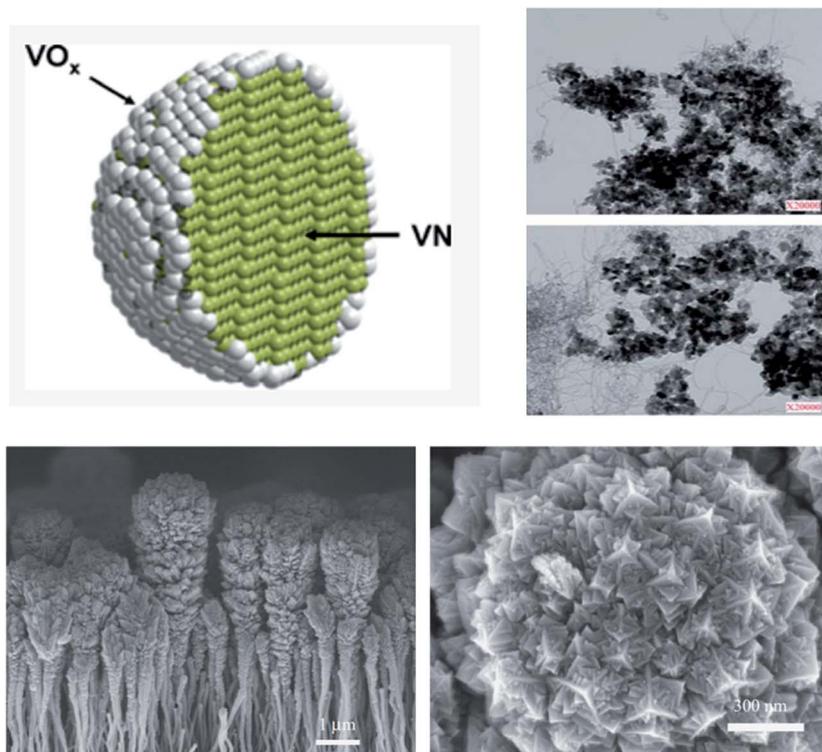


Fig. 10 Vanadium and titanium nitrides used as electrode materials for pseudocapacitors. Top left: schematic core/shell structure of VN@VO_x. Top right: TEM images of the VN-CNT composite obtained by a sonication process. Bottom: cross-section SEM image of CNTs coated with 500 nm-thick TiN film and the top view in high magnification (bottom).^{150–153}

reactions are due to the partially oxidized surface of VN(VN_xO_y) (Fig. 10, top right), in the presence of OH⁻ ions from the electrolyte. VN nanocrystallites were grown on carbon nanotubes to create a composite material with a surface area of about 100 m² g⁻¹ (Fig. 10 top left). The electrochemical measurements exhibit specific capacitance of 250 F g⁻¹ for the VN with improved rate capability.¹⁴⁵ The same performance was recorded for a TiN layer deposited by PVD on carbon nanotube substrates¹⁴⁶ (Fig. 10 bottom).

Composites based on organic active moieties

There are many organic compounds that exhibit reversible redox reactions in electrochemical systems, which may promote their usage in composite electrodes for energy storage devices. The advantages of using organic molecules may include low weight, low cost, large-scale fabrication, environmental friendliness and bio-compatibility. It is possible to attach such electroactive molecules onto the surface of activated carbons either by adsorption or by chemical bonds, thus increasing pronouncedly the reversible capacity of the composite materials thus formed, compared to that of the activated carbons. Such composite electrode materials combine the faradaic capacity of organic-based compounds together with the high electronic conductivity and double-layer capacitance of the carbon substrates. It should be noted that for such composite

electrodes which include redox moieties, it may be more correct to measure and report specific capacity in mA h g⁻¹ units, rather than specific capacitance in F g⁻¹ unit.

A classic example of a family of organic moieties with reversible redox activity that makes them interesting for pseudocapacitive energy storage is electronically conducting polymers (CPs) based on conjugated structures.¹²⁴ In 2000, Heeger, MacDiarmid and Shirakawa were awarded the Nobel Prize in chemistry for their work on CPs in the 1970s. Among the most studied conducting polymers are polyaniline (PANI), polypyrrole (PPy), polythiophene (PT) and polypyridine.^{18,147} Electronically conducting polymers have many advantages that make them suitable materials for supercapacitors, such as possibly high specific storage capacity *via* reversible redox activity that involves also reversible chemical changes and counter-ion desorption, high conductivity in their doped state ($\sim 100\text{--}10\,000\text{ S m}^{-1}$), intrinsic porosity, low cost and low negative environmental impact. Conducting polymers can be part of composite materials that also contain 2D-materials such as graphene, MoS₂ and BCN (the latter two also being electroactive by themselves).¹⁵³

Besides CPs, there is an important class of electroactive polymers in which redox active moieties (such as quinones) are incorporated into the polymeric backbone. In this type of redox materials, protonation (reduction) and deprotonation (oxidation) processes usually take place.^{148,149} Despite the above-mentioned advantages, conducting polymers may suffer from

rapid degradation due to structural complexity and instability.¹⁵⁰ Some CPs may exhibit specific capacity close to that of rechargeable batteries.^{6,149,154–158} In fact, due to possible N and P doping of electronically conducting polymers such as those based on substituted thiophene¹⁵⁹ molecules, it was possible to develop prototypes of plastic batteries, containing no metallic parts. Cycling instability is a major obstacle for practical applications of conductive polymer electrodes in energy storage devices.^{151,152} Since a highly prolonged cycle life and high rate capability are elementary demands from supercapacitors (on account of high energy density), their relatively limited stability in prolonged repeated redox reactions makes them less important electrode materials for energy storage, compared to all the materials discussed in this paper. Here we find again the advantage in fabricating and using composite electrode materials, based on the combination of a porous carbonaceous backbone and active organic moieties (electronically conducting polymers in the present case). The electrochemically stable carbon matrices ensure long term stability and a robust porous structure during prolonged cycling. High surface area is maintained during prolonged operation because the composite structure avoids formation of crystalline clusters of the polymers.

Organic electroactive molecules in conjunction with activated carbons

Since there are so many organic materials with pronounced redox activity, it is possible to exploit some of them as electroactive moieties that can be linked or adsorbed to carbonaceous matrices and obtain composite materials with relatively high and stable specific capacitance. Bonding of such electroactive organic moieties to carbonaceous frameworks may be achieved by forming covalent C–C bonding using diazonium chemistry.¹⁶⁰ Alternatively, the coupling of aromatic electroactive molecules to the carbon matrices can be achieved using

non-covalent π – π interactions between aromatic rings and nanographitic sub-structures on the activated carbon surfaces.^{160,161} Many organic compounds showing reversible redox activity can be good candidates for enhancing the specific capacitance of activated carbon electrodes *via* such a coupling between the porous carbon double-layer capacitance and their faradaic capacity.

One of the most studied and effective compounds is quinone and its derivatives.¹⁶² Due to the small size and low mass of quinone, the redox reaction of quinone/hydro-quinone coupled with 0.4 M of quinone in aqueous solutions results in very high gravimetric and volumetric specific capacitance. Hence, by promoting adsorption of active quinone type molecules on activated carbons a gain of three-fold in capacitance could be achieved. Fig. 11 presents an example showing how the typical EDL behavior of the positive electrode in a supercapacitor changed to a typical redox behavior due to the adsorption of quinone to the activated carbon surface, which dominates its electrochemical response.

Following the great success demonstrated by the combination of quinone molecules and activated carbons, several derivatives of this compound were tested and compared as well. Anthraquinone, for example, can be covalently attached to various carbon substrates including Black Pearl 2000.^{163–168} The capacity of carbon-based electrodes can be improved by a factor of 2 when such composite electrodes are used. Depending on the grafting parameters, activated carbon/anthraquinone composite electrodes were operated for long-term cycling up to 10 000 cycles, proving the strategic stability gained by attachment of the organic compounds to the carbon platform. Cyanides such as tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) were also reported as redox active moieties on carbon-based electrodes. The electrolyte solutions in all of these systems were aqueous, and the redox reactions were protonation or formation of hydroxide. Adsorbing the redox moieties onto the electrode has two major advantages: first of all, they can be specifically adsorbed onto the

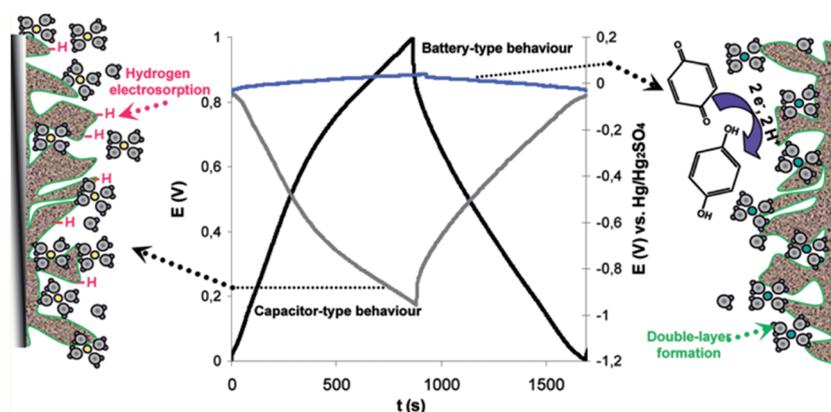


Fig. 11 Black curve: a typical voltage profile of a full, 2 electrode cell comprising a negative activated carbon electrode (left side) and a positive activated carbon electrode (right side) to which quinone/hydroquinone redox moieties are adsorbed in aqueous H_2SO_4 solution containing the redox moieties, upon galvanostatic cycling (left Y axis). The other two plots are the individual voltage profiles of the electrodes (right Y axis). The blue curve is the voltage profile of the positive electrode after adsorption of quinone to the activated carbon, demonstrating a fully redox type behavior. The grey curve is the voltage profile of the counter (negative) electrode in the cell which demonstrates the typical capacitive behavior. Current density 8.8 mA cm^{-2} .¹⁴⁸

electrodes with the desired potential (for oxidation or reduction reactions). Secondly – after adsorption they cannot migrate to the counter-electrodes where undesired parasitic side-reactions may occur.¹⁶⁹ The redox activity of organic molecules may also involve formation of radical moieties. Lebègue *et al.* have produced such a system with the dimethoxybenzene radical and the diradical benzyne. After oxidative ether cleavage of the dimethoxybenzene, the molecules were covalently attached to the surface of the activated-carbon electrodes. The resultant catechol-modified carbon electrodes served as faradaic materials in aqueous electrochemical capacitors.¹⁷⁰ The fabrication of the modified carbon depended on the potential, so capacity improved only at high cell voltages. It is important to emphasize the importance of surface chemistry engineering for such electrodes. The organic molecules have to be attached onto the carbon surface at optimal coverage. Too high coverage may decrease the surface area, conductivity and rate capability of the electrodes.^{171–173} Similar electrodes were also tested in organic electrolyte solutions, leading to impressive capacity with wide cell voltage.¹⁷³ There are also reports on supercapacitor electrodes comprising redox-active organic molecules, loaded onto nanocarbons. Polyoxometalates were coupled with carbon nanotubes to improve the capacity of composite electrodes based on carbonaceous matrices.¹⁸² The chemical bonds to CNTs were harder to achieve, due to the low concentration of heteroatoms and defects to be anchored to, and hence, the electrode shows lower stability than activated carbon compositions. In this regard, it may have been a good idea to graft the organic compound on graphene, which is known to have more oxide on its surface ready to create the desired covalent bond. These carbon–organometallic compositions possess high chemical complexity. Thus, further studies are needed in order to understand how the gain in specific capacitance is achieved as a function of the composite structure and the choice of the individual components.

Metal–organic complexes

A novel group of redox materials suitable for doping the capacity of supercapacitor EDL electrodes is metal–organic

complexes. For these types of materials, the metal can undergo redox reactions that are coordinatively stabilized by organic ligands. In addition, the type of organic ligand controls the adhesion of the complex to the electrode (*e.g.*, ligands with aromatic rings will create π – π bonds with the graphitic sub-structure of the activated carbon). Several methods may be used to attach such complexes on the carbon electrode surface such as wet physical adsorption, chemical or physical vapor deposition, and electrodeposition (in the case of charged complexes). Borenstein *et al.* presented a composite material consisting of iron metal–organic complexes such as ferrocene and ferriin and activated carbon in aqueous and organic electrolyte solutions. The conductivity of the composite electrodes doubled and tripled that of the unmodified carbon electrodes. The specific surface areas of the composite materials were smaller than that of the bare activated carbon and varied from 300 to 1000 m² g^{−1}, depending on the amount of complex grafted on the AC, since excess of complex blocks the pores of the AC (Fig. 12a). Hence, there is a tradeoff between the amount of active redox material adsorbed and the overall specific surface area of the composite electrodes. Optimization studies determined that adding 10% redox moieties by weight to the activated carbon leads to the highest capacitance. The specific capacitance of such electrodes also depends on the number of faradaic reactions of the complexes. 165 F g^{−1} could be obtained with optimal activated-carbon/ferrocene electrodes in neutral aqueous solutions (Fig. 12b) and 330 F g^{−1} could be obtained with activated-carbon/ferriin electrodes in non-aqueous electrolyte solutions, also taking benefit from a wide electrochemical operating window (Fig. 12c).^{174,175}

Metal–organic frameworks

Metal–organic frameworks (MOFs) are materials consisting of metal centers linked by organic ligands forming multi-dimensional structures. Some of these metal–organic frameworks contain developed voids within the coordination network of the organic ligands, and a surface area of several thousand square meters per gram may be achieved. Taking into account the fact

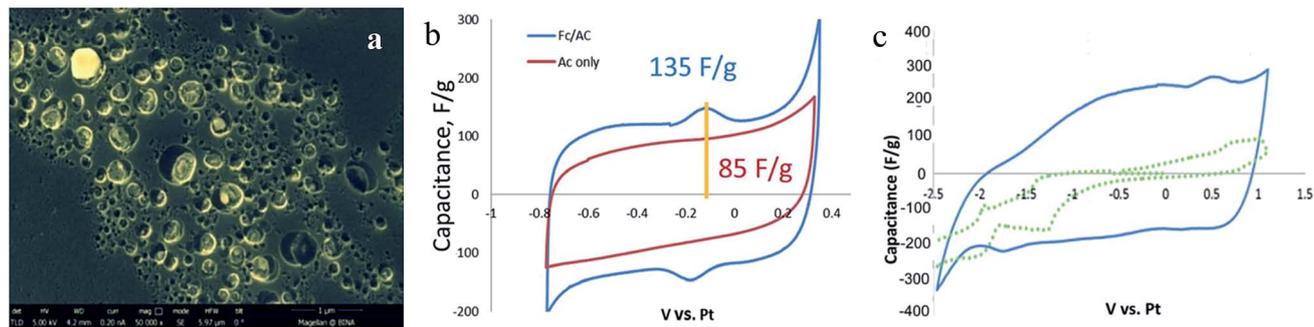


Fig. 12 (a) Vapor-deposited ferrocene (yellow) peering out of activated carbon pores. (b) Typical CV measured at 1 mV s^{−1} in three-electrode cells of the Fc/AC powder 1 : 1 (w/w) composite electrode, with a Pt-wire quasi-reference electrode in 1 M aqueous Li₂SO₄ (blue line). The red curve represents the AC powder electrodes without Fc. The oxidation potential of unbound Fc in the same solution is marked by a yellow line. (c) Typical CV response of three-electrode cells comprising composite ferriin-chloride/ACF electrodes in 1.4 M TEABF₄/AN, with a Pt wire as a quasi-reference electrode. Typical CV curves of a composite electrode (blue line) and unbound ferriin chloride in the same system on glassy carbon electrodes (dashed green line) are presented. The scan rate was 1 mV s^{−1}.¹⁶⁰

Table 1 The challenges and advantages of composite materials and expected future developments for the main groups of materials reviewed and discussed herein

Group of materials	Challenges and drawbacks	Composite electrode advantages	Future developments
Activated carbons	Specific surface area, conductivity, specific capacitance	Developed porous structures, strength, very good electrical integration	Integrated carbonization with nanocarbons
Nanocarbons (CNTs, graphene, C-dots)	Volumetric capacitance, agglomeration, nano–micro transformation	Easy handling, reasonably easy preparation, conducting platforms	3D micro-level assembly of nanomaterials
Metal oxides-pseudocapacitance type behavior (e.g. MnO ₂)	Conductivity, ion accessibility, intrinsic stability	Porosity, adhesion, conductivity	Thin film coating methods on carbonaceous porous materials, development of practical ALD processes
Metal oxides – faradaic redox activity (e.g. RuO ₂)	Conductivity, cost, abundance	Porous structure, conductivity	Chemical bonding to porous activated carbons and to nanocarbons
Redox active organic molecules	Chemical and mechanical stability, capacitance fading	Stability, covalent bond, conductive platform	Integration of 3D MOFs with 3D carbon complexes, stability
Metal–organic frameworks	Conductivity, stability	Conductivity, chemical stability, maximizing capacitance	

that these metal ions may undergo reversible redox interactions, MOFs are desirable candidates for energy storage and supercapacitors in particular.^{176–179} However, their non-conducting nature prevents them from being widely used in electrochemical systems. As explained before, combining redox active but electronically insulating materials with conducting carbons produces composite materials that gain advantages from both components: redox activity which ensures high specific capacity, good electron accessibility and long term mechanical and electrochemical stability. To address the non-conductive nature of MOFs, an outcome of the coordinative bonds of the network, Fleker *et al.* synthesized compositions of MOF-activated carbon in which the AC serves as the conducting host to the nanoparticles of the MOF. The MOF's precursors were introduced into the pores of the AC, and then the MOFs were synthesized inside the nanopores. An interesting electron paramagnetic resonance (EPR) signal suggests that the MOF nanoparticles that are in contact with the activated carbon become electron-conductive.¹⁸⁰ The Cu²⁺/Cu⁺ redox couple of the MOF adds 30% capacity to the double-layer capacitance of the AC. Growing the MOF on graphene sets was tried comprehensively by Yaghi *et al.* They studied the electrochemical performance of an inclusive series of 23 different MOFs with multiple organic functionalities and metal ions, different pore sizes and shapes and a variety of structure types. The graphene sheets serve as a conducting platform for the active MOF. Several MOFs show high performance, with top areal capacitance of 5.09 mF cm⁻² for a zirconium-MOF for over 10 000 charge/discharge cycles.¹⁸¹

In summary, it can be said that organic redox-active materials cannot be implemented in SC electrodes without the support of stable and conductive matrices possessing a developed porous structure. Thereby, combining activated carbons or nanocarbons with high surface areas and high EDLC with electrochemically active organic molecules which possess high specific redox capacity can provide superb composite materials with high specific capacity and long term stability. Bonding

such molecules onto carbon surfaces either chemically or *via* adsorption processes requires careful optimization in order to assure high porosity, electrical conductivity and cycling stability of the electrodes.

Nanofabrication techniques, both wet and dry, may produce better composite materials. Nanoparticle fabrication techniques of organic materials were recently revolutionized for the pharmaceutical and medical fields as they become more and more homogeneous and reproducible. These include photo- and soft-lithography, thin film deposition, etching, molecular self-assembly, electrically induced nanopatterning, colloidal based approaches and more. The new field of rapid prototyping also opens new strategies for generating desirable designs of complex composite materials. Each technique must of course be adjusted for fabricating high surface area materials, which requires additional developments. We expect to see in the next years increasing utilization of novel nanofabrication techniques for the production of stable integrated composite materials possessing extremely high surface area (>1000 m² g⁻¹) and uniformly covered by low molecular weight organic redox-active molecules that achieve together very high specific gravimetric capacity.

Conclusions

The field of supercapacitors has gained much attention in the last few years and it is in the focus of intensive, multidisciplinary studies by materials, surfaces and electrochemical science groups throughout the world. The importance of supercapacitors for energy storage pronouncedly increases as well. The field benefits from extensive work, but also suffers from confusing presentation of results as well. While it is always important to achieve high energy density for energy storage devices, the major advantages of supercapacitors should be very long cycle life and impressive durability, together with high power density and as low as possible voltage/current hysteresis between charge and discharge processes. In this article, we

review typical recent leading and frontier studies of composite materials for supercapacitor electrodes, based on carbonaceous material backbones. The composite electrode materials described herein usually comprise high specific capacity and rate capability active materials which are supported by large-surface-area carbon platforms, which form the necessary mechanically stable and electronic conductive frameworks. The combination of electro-active moieties possessing high specific capacity together with conducting, high surface area and mechanically robust carbonaceous matrices can provide superb composite electrodes for energy storage devices. We present many types of active materials to be coupled with carbons, including nanocarbons, metal oxides and organic compounds. We explained how the composites can pertinently address traditional obstacles that the individual components face when formulated in standard electrode designs. Finally, we discussed the advantages and drawbacks and the best synthesis methods for each kind of material. We believe that this review article covers well the frontier and state-of-the-art of composite electrode materials for advanced supercapacitors. Table 1 provides a short summary of major groups of materials discussed herein. It addresses in brief the drawbacks, challenges, and advantages, and mentions future developments.

Acknowledgements

A partial support for this work was obtained from the Israel National Science Foundation (ISF) in the framework of the INREP project.

References

- 1 E. Frackowiak and F. Béguin, *Carbon*, 2001, **39**, 937–950.
- 2 T. Cottineau, M. Toupin, T. Delahaye, T. Brousse and D. Bélanger, *Appl. Phys. A: Mater. Sci. Process.*, 2006, **82**, 599–606.
- 3 A. G. Pandolfo and A. F. Hollenkamp, *J. Power Sources*, 2006, **157**, 11–27.
- 4 M. Noked, A. Soffer and D. Aurbach, *J. Solid State Electrochem.*, 2011, **15**, 1563–1578.
- 5 E. Frackowiak, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1774–1785.
- 6 E. Pollak, N. Levy, L. Eliad, G. Salitra, A. Soffer and D. Aurbach, *Isr. J. Chem.*, 2008, **48**, 287–303.
- 7 E. Frackowiak and F. Béguin, *Carbon*, 2001, **39**, 937–950.
- 8 T. Kyotani, *Carbon*, 2000, **38**, 269–286.
- 9 S. Jagannathan, T. Liu and S. Kumar, *Compos. Sci. Technol.*, 2010, **70**, 593–598.
- 10 M. Noked, E. Avraham, Y. Bohadana, A. Soffer and D. Aurbach, *J. Phys. Chem. C*, 2009, **113**, 7316–7321.
- 11 L. L. Zhang and X. S. Zhao, *Chem. Soc. Rev.*, 2009, **38**, 2520–2531.
- 12 E. Pollak, N. Levy, L. Eliad, G. Salitra, A. Soffer and D. Aurbach, *Isr. J. Chem.*, 2008, **48**, 287–303.
- 13 C. B. Roop and G. Meenakshi, *Activated carbon adsorption*, CRC Press, Boca Raton, 2005.
- 14 J. Lee, J. Kim and T. Hyeon, *Adv. Mater.*, 2006, **18**, 2073–2094.
- 15 J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet and P. L. Taberna, *Science*, 2006, **313**, 1760–1763.
- 16 B. Kim, H. Chung and W. Kim, *J. Phys. Chem. C*, 2010, **114**, 15223–15227.
- 17 Y. C. Choi, S. M. Lee and D. C. Chung, *J. Phys. Chem. B*, 2001, **105**, 497–500.
- 18 P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845–854.
- 19 M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nano-Tubes*, Academic Press, San Diego, 1996.
- 20 C. Liu, Z. Yu, D. Neff, A. Zhamu and B. Z. Jang, *Nano Lett.*, 2010, 4863–4868.
- 21 S. R. C. Vivekchand, C. S. Rout, K. S. Subrahmanyam, A. Govindaraj and C. N. R. Rao, *J. Chem. Sci.*, 2008, **120**, 9–13.
- 22 M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, *Nano Lett.*, 2008, **8**, 3498–3502.
- 23 Y. Huang, J. Liang and Y. Chen, *Small*, 2012, **8**, 1805–1834.
- 24 K. Sheng, Y. Sun, C. Li, W. Yuan and G. Shi, *Sci. Rep.*, 2012, **2**, 247.
- 25 Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychoz, M. Thommes, D. Su, E. A. Stach and R. S. Ruoff, *Science*, 2011, **332**, 1537–1541.
- 26 T. Brousse, D. Bélanger and J. W. Long, *J. Electrochem. Soc.*, 2015, **162**, A5185–A5189.
- 27 B. D. Assreshegn, T. Brousse and D. Bélanger, *Carbon*, 2015, **92**, 362–381.
- 28 A. M. Abioye and F. Nasir, *Renewable Sustainable Energy Rev.*, 2015, **52**, 1282–1293.
- 29 A. M. Saleem, V. Desmaris and P. Enoksson, *J. Nanomater.*, 2016, 1–7.
- 30 E. T. Mombeshora and V. O. Nyamori, *Int. J. Energy Res.*, 2015, **39**, 1955–1980.
- 31 V. C. Lokhande, A. C. Lokhande, C. D. Lokhande, J. Hyeok and T. Ji, *J. Alloys Compd.*, 2016, **682**, 381–403.
- 32 Y. Deng and X. Ji, *J. Mater. Chem. A*, 2016, **4**, 1144–1173.
- 33 W. K. Chee, H. N. Lim, Z. Zainal, N. M. Huang, I. Harrison and Y. Andou, *J. Phys. Chem. C*, 2016, **120**, 4153–4172.
- 34 A. González, E. Goikolea, J. Andoni and R. Mysyk, *Renewable Sustainable Energy Rev.*, 2016, **58**, 1189–1206.
- 35 Z. S. Iro, C. Subramani and S. S. Dash, *Int. J. Electrochem. Sci.*, 2016, **11**, 10628–10643.
- 36 F. Yao, T. Pham and Y. Hee, *ChemSusChem*, 2015, **8**, 2284–2311.
- 37 Q. Wang, *Energy Environ. Sci.*, 2016, **9**, 729–762.
- 38 E. Lim, C. Jo and J. Lee, *Nanoscale*, 2016, **8**, 7827–7833.
- 39 V. B. Kumar, A. Borenstein, B. Markovsky, D. Aurbach, A. Gedanken, M. Talianker and Z. Porat, *J. Phys. Chem. C*, 2016, **120**, 13406–13413.
- 40 N. Kurra, B. Ahmed, Y. Gogotsi and H. N. Alshareef, *Adv. Energy Mater.*, 2016, **8**, 1–8.
- 41 M. Zhao, C. E. Ren, Z. Ling, M. R. Lukatskaya, C. Zhang, K. L. Van Aken, M. W. Barsoum and Y. Gogotsi, *Adv. Mater.*, 2014, **27**, 1–7.
- 42 Y. Dall, P. Rozier, P. Taberna, Y. Gogotsi and P. Simon, *J. Power Sources*, 2016, **306**, 510–515.

- 43 S. Sigalov, N. Shpigel, M. D. Levi, M. Feldberg, L. Daikhin and D. Aurbach, *Anal. Chem.*, 2016, **88**, 10151–10157.
- 44 J. Chmiola, R. Dash, G. Yushin and Y. Gogotsi, *J. Power Sources*, 2006, **158**, 765–772.
- 45 Y. Gogotsi and P. Simon, *Science*, 2011, **334**, 917–918.
- 46 S. N. Baker and G. A. Baker, *Angew. Chem., Int. Ed.*, 2010, **49**, 6726–6744.
- 47 L. Lv, Y. Fan, Q. Chen, Y. Zhao, Y. Hu, Z. Zhang, N. Chen and L. Qu, *Nanotechnology*, 2014, **25**, 235401.
- 48 S. A. Al-Muhtaseb and J. A. Ritter, *Adv. Mater.*, 2003, **15**, 101–114.
- 49 M. A. Worsley, P. J. Pauzauskie, T. Y. Olson, J. Biener, J. H. Satcher and T. F. Baumann, *J. Am. Chem. Soc.*, 2010, **132**, 14067–14069.
- 50 V. B. Kumar, A. Borenstein, B. Markovsky, D. Aurbach, A. Gedanken, M. Talianker and Z. Porat, *J. Phys. Chem. C*, 2016, **120**, 13406–13413.
- 51 W.-W. Liu, Y.-Q. Feng, X.-B. Yan, J.-T. Chen and Q.-J. Xue, *Adv. Funct. Mater.*, 2013, **23**, 4111–4122.
- 52 Y. Hu, Y. Zhao, G. Lu, N. Chen, Z. Zhang, H. Li, H. Shao and L. Qu, *Nanotechnology*, 2013, **24**, 195401.
- 53 Y. Dong, H. Pang, H. Bin Yang, C. Guo, J. Shao, Y. Chi, C. M. Li and T. Yu, *Angew. Chem., Int. Ed.*, 2013, **52**, 7800–7804.
- 54 M. Zhi, C. Xiang, J. Li, M. Li and N. Wu, *Nanoscale*, 2013, **5**, 72–88.
- 55 Y. Gogotsi, *Electrochem. Soc. Interface*, 2016, **18**, 1–6.
- 56 K. L. Van Aken, J. K. McDonough, S. Li and G. Feng, *Angew. Chem., Int. Ed.*, 2015, **54**, 4806–4809.
- 57 J. K. McDonough, A. I. Frolov, V. Presser, J. Niu, C. H. Miller, T. Ubieto, M. V. Fedorov and Y. Gogotsi, *Carbon*, 2011, **50**, 3298–3309.
- 58 M. M. Hantel, V. Presser, J. K. McDonough, G. Feng, P. T. Cummings, Y. Gogotsi and R. Kötz, *J. Electrochem. Soc.*, 2012, **159**, A1897–A1903.
- 59 X. Sun, H. Sun, H. Li and H. Peng, *Adv. Mater.*, 2013, **25**, 5153–5176.
- 60 M. Noked, S. Okashy, T. Zimrin and D. Aurbach, *Angew. Chem., Int. Ed.*, 2012, **51**, 1568–1571.
- 61 A. Borenstien, M. Noked, S. Okashy and D. Aurbach, *J. Electrochem. Soc.*, 2013, **160**, A1282–A1285.
- 62 N. Jung, S. Kwon, D. Lee, D. M. Yoon, Y. M. Park, A. Benayad, J. Y. Choi and J. S. Park, *Adv. Mater.*, 2013, **25**, 6854–6858.
- 63 Z. D. Huang, B. Zhang, R. Liang, Q. Bin Zheng, S. W. Oh, X. Y. Lin, N. Yousefi and J. K. Kim, *Carbon*, 2012, **50**, 4239–4251.
- 64 I. Mazurenko, M. Etienne, G. Francius, I. Vakulko and A. Walcarius, *Carbon*, 2016, **109**, 106–116.
- 65 Y. Qiu, G. Li, Y. Hou, Z. Pan, H. Li, W. Li, M. Liu, F. Ye, X. Yang and Y. Zhang, *Chem. Mater.*, 2015, **27**, 1194–1200.
- 66 H. Chen, F. Sun, J. Wang, W. Li, W. Qiao, L. Ling and D. Long, *J. Phys. Chem. C*, 2013, **117**, 8318–8328.
- 67 J. Yang, Y. Zhai, Y. Deng, D. Gu, Q. Li, Q. Wu, Y. Huang, B. Tu and D. Zhao, *J. Colloid Interface Sci.*, 2010, **342**, 579–585.
- 68 C. Feng, H. Li and Y. Wan, *J. Nanosci. Nanotechnol.*, 2009, **9**, 1558–1563.
- 69 G. Hao, W. Li, D. Qian, G. Wang, W. Zhang, T. Zhang, A. Wang, F. Sch, H. Bongard and A. Lu, *J. Am. Chem. Soc.*, 2011, **133**, 11378–11388.
- 70 Z. Wu, P. A. Webley and D. Zhao, *J. Mater. Chem.*, 2012, **22**, 11379–11389.
- 71 X. Wang, C.-G. Liu, D. Neff, P. F. Fulvio, R. T. Mayes, A. Zhamu, Q. Fang, G. Chen, H. M. Meyer, B. Z. Jang and S. Dai, *J. Mater. Chem. A*, 2013, **1**, 7920.
- 72 N. P. Wickramaratne, J. Xu, M. Wang, L. Zhu, L. Dai and M. Jaroniec, *Chem. Mater.*, 2014, **26**, 2820–2828.
- 73 D. Wu, Z. Li, M. Zhong, T. Kowalewski and K. Matyjaszewski, *Angew. Chem.*, 2014, **126**, 4038–4041.
- 74 V. Chabot, D. Higgins, A. Yu, X. Xiao, Z. Chen and J. Zhang, *Energy Environ. Sci.*, 2014, **7**, 1564.
- 75 Y. Chen, X. Zhang, H. Zhang, X. Sun, D. Zhang and Y. Ma, *RSC Adv.*, 2012, **2**, 7747.
- 76 T. Kim, G. Jung, S. Yoo, K. S. Suh and R. S. Ruoff, *ACS Nano*, 2013, **7**, 6899–6905.
- 77 M. Mastalerz, M. W. Schneider, I. M. Oppel and O. Presly, *Angew. Chem., Int. Ed.*, 2011, **50**, 1046–1051.
- 78 F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki and O. M. Yaghi, *J. Am. Chem. Soc.*, 2011, **133**, 11478–11481.
- 79 X. Zhuang, F. Zhang, D. Wu and X. Feng, *Adv. Mater.*, 2014, **26**, 3081–3086.
- 80 G. A. Ferrero, A. B. Fuertes and M. Sevilla, *J. Mater. Chem. A*, 2015, **3**, 2914–2923.
- 81 P.-C. Gao, W.-Y. Tsai, B. Daffos, P.-L. Taberna, C. R. Pérez, Y. Gogotsi, P. Simon and F. Favier, *Nano Energy*, 2015, **12**, 197–206.
- 82 S. Trasatti and G. Buzzanca, *J. Electroanal. Chem. Interfacial Electrochem.*, 1971, **29**, A1–A5.
- 83 J. P. Zheng, *J. Electrochem. Soc.*, 1995, **142**, 2699.
- 84 H. Y. Lee and J. B. Goodenough, *J. Solid State Chem.*, 1999, **144**, 220–223.
- 85 M. Toupin, T. Brousse and D. Bélanger, *Chem. Mater.*, 2002, **14**, 3946–3952.
- 86 H. Y. Lee and J. B. Goodenough, *Solid State Ionics*, 2002, **153**, 833–841.
- 87 N. L. Wu, *Mater. Chem. Phys.*, 2002, **75**, 6–11.
- 88 T. Brousse and D. Bélanger, *Electrochem. Solid-State Lett.*, 2003, **6**, A244.
- 89 W. Deng, X. Ji, Q. Chen and C. E. Banks, *RSC Adv.*, 2011, **1**, 1171.
- 90 A. L. M. Reddy and S. Ramaprabhu, *J. Phys. Chem. C*, 2007, **111**, 7727–7734.
- 91 W. G. Pell and B. E. Conway, *J. Power Sources*, 2004, **136**, 334–345.
- 92 J. P. Zheng, J. Huang and T. R. Jow, *J. Electrochem. Soc.*, 1997, **144**, 2026–2031.
- 93 G. G. Amatucci, F. Badway, A. Du Pasquier and T. Zheng, *J. Electrochem. Soc.*, 2001, **148**, A930.
- 94 M. Y. Ho, P. S. Khiew, D. Isa and T. K. Tan, *World*, 2014, **9**, 1–25.
- 95 Y. Chen, Z. Hu, Y. Chang, H. Wang, Z. Zhang and Y. Yang, *J. Phys. Chem. C*, 2011, **115**, 2563–2571.

- 96 C. P. Rhodes, T. M. Mcevoy, E. Bourg and A. M. Lubers, *Chem. Soc. Rev.*, 2009, **38**, 226–252.
- 97 M. Toupin, T. Brousse and D. Bélanger, *Chem. Mater.*, 2004, **16**, 3184–3190.
- 98 W. Wei, X. Cui, W. Chen and D. G. Ivey, *Chem. Soc. Rev.*, 2011, **40**, 1697–1721.
- 99 A. Zolfaghari, H. R. Naderi and H. R. Mortaheb, *J. Electroanal. Chem.*, 2013, **697**, 60–67.
- 100 J. Zhang and X. S. Zhao, *Carbon*, 2013, **52**, 1–9.
- 101 Y. Zhang, Q. Yao, H. Gao, L. Wang, X. Jia, A. Zhang, Y. Song, T. Xia and H. Dong, *Powder Technol.*, 2014, **262**, 150–155.
- 102 T. Bordjiba and D. Bélanger, *Electrochim. Acta*, 2010, **55**, 3428–3433.
- 103 J. Cai, M. He, Y. Gu, L. Kang, Z. Lei, Z. Yang and Z. H. Liu, *Colloids Surf., A*, 2013, **429**, 91–97.
- 104 Q. Li, J. M. Anderson, Y. Chen and L. Zhai, *Electrochim. Acta*, 2012, **59**, 548–557.
- 105 K. W. Nam, C. W. Lee, X. Q. Yang, B. W. Cho, W. S. Yoon and K. B. Kim, *J. Power Sources*, 2009, **188**, 323–331.
- 106 Y. Wang, H. Liu, X. Sun and I. Zhitomirsky, *Scr. Mater.*, 2009, **61**, 1079–1082.
- 107 X. Xie and L. Gao, *Carbon*, 2007, **45**, 2365–2373.
- 108 G. Yu, L. Hu, M. Vosgueritchian, H. Wang, X. Xie, J. R. McDonough, X. Cui, Y. Cui and Z. Bao, *Nano Lett.*, 2011, **11**, 2905–2911.
- 109 Q. Tang, M. Sun, S. Yu and G. Wang, *Electrochim. Acta*, 2014, **125**, 488–496.
- 110 S.-W. Lee, S.-M. Bak, C.-W. Lee, C. Jaye, D. A. Fischer, B.-K. Kim, X.-Q. Yang, K.-W. Nam and K.-B. Kim, *J. Phys. Chem. C*, 2014, **118**, 2834–2843.
- 111 T. Bordjiba and D. Bélanger, *J. Electrochem. Soc.*, 2009, **156**, A378.
- 112 A. E. Fischer, K. A. Pettigrew, D. R. Rolison, R. M. Stroud and J. W. Long, *Nano Lett.*, 2007, **7**, 281–286.
- 113 Y. Lei, C. Fournier, J. L. Pascal and F. Favier, *Microporous Mesoporous Mater.*, 2008, **110**, 167–176.
- 114 W. Wei, X. Huang, Y. Tao, K. Chen and X. Tang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 5966.
- 115 J. Yan, Z. Fan, T. Wei, J. Cheng, B. Shao, K. Wang, L. Song and M. Zhang, *J. Power Sources*, 2009, **194**, 1202–1207.
- 116 D. Z. W. Tan, H. Cheng, S. T. Nguyen and H. M. Duong, *Materials Technology*, 2014, **29**, A107.
- 117 L. Li, Z. A. Hu, N. An, Y. Y. Yang, Z. M. Li and H. Y. Wu, *J. Phys. Chem. C*, 2014, **118**, 22865–22872.
- 118 Y. Qian, S. Lu and F. Gao, *J. Mater. Sci.*, 2011, **46**, 3517–3522.
- 119 J. Yan, Z. Fan, T. Wei, W. Qian, M. Zhang and F. Wei, *Carbon*, 2010, **48**, 3825–3833.
- 120 Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya and L. C. Qin, *Carbon*, 2011, **49**, 2917–2925.
- 121 X. Feng, Z. Yan, N. Chen, Y. Zhang, Y. Ma, X. Liu, Q. Fan, L. Wang and W. Huang, *J. Mater. Chem. A*, 2013, **1**, 12818–12825.
- 122 C. Ramirez-Castro, O. Crosnier, L. Athouel, R. Retoux, D. Belanger and T. Brousse, *J. Electrochem. Soc.*, 2015, **162**, A5179–A5184.
- 123 P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845–854.
- 124 G. Wang, L. Zhang and J. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 797–828.
- 125 M. Ritala and M. Leskela, *Handb. Thin Film Mater.*, 2002, 103–159.
- 126 R. Warren, F. Sammoura, F. Tounsi, M. Sanghadasa and L. Lin, *J. Mater. Chem. A*, 2015, **3**, 15568–15575.
- 127 Z. S. Wu, D. W. Wang, W. Ren, J. Zhao, G. Zhou, F. Li and H. M. Cheng, *Adv. Funct. Mater.*, 2010, **20**, 3595–3602.
- 128 Y. Feng Su, F. Wu, L. Ying Bao and Z. Hui Yang, *New Carbon Mater.*, 2007, **22**, 53–57.
- 129 D. Guan, Z. Gao, W. Yang, J. Wang, Y. Yuan, B. Wang, M. Zhang and L. Liu, *Mater. Sci. Eng., B*, 2013, **178**, 736–743.
- 130 N. Sinan and E. Unur, *Mater. Chem. Phys.*, 2016, 1–9.
- 131 Q. Wang, L. Jiao, H. Du, Y. Wang and H. Yuan, *J. Power Sources*, 2014, **245**, 101–106.
- 132 P. C. Gao, P. A. Russo, D. E. Conte, S. Baek, F. Moser, N. Pinna, T. Brousse and F. Favier, *ChemElectroChem*, 2014, **1**, 747–754.
- 133 V. Rebutini, E. Fazio, S. Santangelo, F. Neri, G. Caputo, C. Martin, T. Brousse, F. Favier and N. Pinna, *Chem.–Eur. J.*, 2015, **21**, 12465–12474.
- 134 N. Electrochemical, M. B. Sassin, A. N. Mansour, K. A. Pettigrew, D. R. Rolison and J. W. Long, 2010, **4**, 4505–4514.
- 135 M. Li, G. Sun, P. Yin, C. Ruan and K. Ai, *ACS Appl. Mater. Interfaces*, 2013, **5**, 11462–11470.
- 136 T. Nathan, A. Aziz, A. F. Noor and S. R. S. Prabakaran, *J. Solid State Electrochem.*, 2008, **12**, 1003–1009.
- 137 M. M. Sk, C. Y. Yue, K. Ghosh and R. K. Jena, *J. Power Sources*, 2016, **308**, 121–140.
- 138 Q. Zhou, X. Wang, Y. Liu, Y. He, Y. Gao and J. Liu, *J. Electrochem. Soc.*, 2014, **161**, A1922–A1926.
- 139 N. B. Trung, T. Van Tam, D. K. Dang, K. F. Babu, E. J. Kim, J. Kim and W. M. Choi, *Chem. Eng. J.*, 2015, **264**, 603–609.
- 140 R. Rajendran, L. K. Shrestha, R. M. Kumar, R. Jayavel, J. P. Hill and K. Ariga, *J. Inorg. Organomet. Polym. Mater.*, 2015, **25**, 267–274.
- 141 L. Yang, S. Cheng, Y. Ding, X. Zhu, Z. L. Wang and M. Liu, *Nano Lett.*, 2012, **12**, 321–325.
- 142 S. Okashy, M. Noked, T. Zimrin and D. Aurbach, *J. Electrochem. Soc.*, 2013, **160**, A1489–A1496.
- 143 Y.-J. B. Ting, H. Wu, N. P. Kherani and K. Lian, *Mater. Chem. Phys.*, 2015, **154**, 118–124.
- 144 D. Choi, G. E. Blomgren and P. N. Kumta, *Adv. Mater.*, 2006, **18**, 1178–1182.
- 145 C. M. Ghimbeu, E. Raymundo-Piñero, P. Fioux, F. Béguin and C. Vix-Guterl, *J. Mater. Chem.*, 2011, **21**, 13268.
- 146 a. Achour, J. B. Ducros, R. L. Porto, M. Boujtita, E. Gautron, L. Le Brizoual, M. A. Djouadi and T. Brousse, *Nano Energy*, 2014, **7**, 104–113.
- 147 P. Article, 2002, 19–24.
- 148 S. Patra and N. Munichandraiah, *J. Appl. Polym. Sci.*, 2007, **106**, 1160–1171.
- 149 G. P. Pandey, A. C. Rastogi and C. R. Westgate, *J. Power Sources*, 2014, **245**, 857–865.
- 150 D. M. Anjos, J. K. McDonough, E. Perre, G. M. Brown, S. H. Overbury, Y. Gogotsi and V. Presser, *Nano Energy*, 2013, **2**, 702–712.

- 151 F. Guo, Q. Liu and H. Mi, *Mater. Lett.*, 2016, **163**, 115–117.
- 152 Y. Yin, K. Feng, C. Liu and S. Fan, *J. Phys. Chem. C*, 2015, **119**, 8488–8491.
- 153 K. Gopalakrishnan, S. Sultan, A. Govindaraj and C. N. R. Rao, *Nano Energy*, 2015, **12**, 52–58.
- 154 G. A. Snook, P. Kao and A. S. Best, *J. Power Sources*, 2011, **196**, 1–12.
- 155 G. A. Snook, P. Kao and A. S. Best, *J. Power Sources*, 2011, **196**, 1–12.
- 156 A. Rudge, I. Raistrick, S. Gottesfeld and J. P. Ferraris, *J. Power Sources*, 1994, **47**, 89–107.
- 157 M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621–629.
- 158 R. Liu, S. Il Cho and S. B. Lee, *Nanotechnology*, 2008, **19**, 215710.
- 159 H. U. Sarker, Y. Gofer, J. G. Killian, T. O. Poehler and P. C. Searson, *Synth. Met.*, 1997, **88**, 179–185.
- 160 D. Bélanger and J. Pinson, *Chem. Soc. Rev.*, 2011, **40**, 3995–4048.
- 161 C. Ehli, G. M. A. Rahman, N. Jux, D. Balbinot, D. M. Guldi, F. Paolucci, M. Marcaccio, D. Paolucci, M. Melle-franco, F. Zerbetto, M. Prato, O. Chemistry, C. G. Ciamician, V. Uni and V. F. Selmi, *J. Am. Chem. Soc.*, 2006, **137**, 11222–11231.
- 162 S. Rold, M. Granda, R. Men, R. Santamaría and C. Blanco, *J. Phys. Chem. C*, 2011, **115**, 17606–17611.
- 163 K. Kalinathan, D. P. DesRoches, X. Liu and P. G. Pickup, *J. Power Sources*, 2008, **181**, 182–185.
- 164 Z. Algharaibeh, X. Liu and P. G. Pickup, *J. Power Sources*, 2009, **187**, 640–643.
- 165 T. E. Society, C. P. Electrode and E. Capacitor, 2013, 863–866.
- 166 M. Weissmann, O. Crosnier, T. Brousse and D. Bélanger, *Electrochim. Acta*, 2012, **82**, 250–256.
- 167 G. Pognon, T. Brousse, L. Demarconnay and D. Bélanger, *J. Power Sources*, 2011, **196**, 4117–4122.
- 168 G. Pognon, T. Brousse and D. Bélanger, *Carbon*, 2011, **49**, 1340–1348.
- 169 L. Madec, A. Bouvrée, P. Blanchard, C. Cougnon, T. Brousse, B. Lestriez, D. Guyomard and J. Gaubicher, *Energy Environ. Sci.*, 2012, **5**, 5379.
- 170 E. Lebègue, T. Brousse, J. Gaubicher and C. Cougnon, *Electrochem. Commun.*, 2013, **34**, 14–17.
- 171 Z. Algharaibeh and P. G. Pickup, *Electrochem. Commun.*, 2011, **13**, 147–149.
- 172 C. Cougnon, E. Lebègue and G. Pognon, *J. Power Sources*, 2015, **274**, 551–559.
- 173 E. Lebègue, T. Brousse, J. Gaubicher, R. Retoux and C. Cougnon, *J. Mater. Chem. A*, 2014, **2**, 8599.
- 174 A. Borenstein, O. Fleker, S. Luski, L. Benisvy and D. Aurbach, *J. Mater. Chem. A*, 2014, **2**, 18132–18138.
- 175 A. Borenstein, S. Hershkovitz, A. Oz, S. Luski, Y. Tsur and D. Aurbach, *J. Phys. Chem. C*, 2015, **119**, 12165–12173.
- 176 D. Y. Lee, S. J. Yoon, N. K. Shrestha, S.-H. Lee, H. Ahn and S.-H. Han, *Microporous Mesoporous Mater.*, 2012, **153**, 163–165.
- 177 A. Sachse, R. Ameloot, B. Coq, F. Fajula, B. Coasne, D. De Vos and A. Galarneau, *Chem. Commun.*, 2012, **48**, 4749–4751.
- 178 R. Díaz, M. G. Orcajo, J. A. Botas, G. Calleja and J. Palma, *Mater. Lett.*, 2012, **68**, 126–128.
- 179 Y. Shim and H. J. Kim, *ACS Nano*, 2010, **4**, 2345–2355.
- 180 O. Fleker, A. Borenstein, R. Lavi, L. Benisvy, S. Ruthstein and D. Aurbach, *Langmuir*, 2016, **32**, 4935–4944.
- 181 K. M. Choi, H. M. Jeong, J. H. Park, Y. Zhang, J. K. Kang and O. Yaghi, *ACS Nano*, 2014, **8**, 7451–7457.
- 182 A. K. Cuentas-Gallegos, S. López-Cortina, T. Brousse, D. Pacheco-Catalán, E. Fuentes-Quezada, H. Mosqueda and G. Orozco-Gamboa, *J. Solid State Electrochem.*, 2015, **20**, 67–79.