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REVIEW

The role of nanomaterials in redox-based supercapacitors for next generation energy storage devices

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The development of more efficient electrical storage is a pressing requirement to meet future societal and environmental needs. This demand for more sustainable, efficient energy storage has provoked a renewed scientific and commercial interest in advanced capacitor designs in which the suite of experimental techniques and ideas that comprise nanotechnology are playing a critical role. Capacitors can be charged and discharged quickly and are one of the primary building blocks of many types of electrical circuit, from microprocessors to large-sale power supplies, but usually have relatively low energy storage capability when compared with batteries. The application of nanostructured materials with bespoke morphologies and properties to electrochemical supercapacitors is being intensively studied in order to provide enhanced energy density without comprising their inherent high power density and excellent cyclability. In particular, electrode materials that exploit physical adsorption or redox reactions of electrolyte ions are foreseen to bridge the performance disparity between batteries with high energy density and capacitors with high power density. In this review, we present some of the novel nanomaterial systems applied for electrochemical supercapacitors and show how material morphology, chemistry and physical properties are being tailored to provide enhanced electrochemical supercapacitor performance.

1 Introduction

Energy production relying on the combustion of fossil fuels and its environmental impact is forecast to have an adverse effect on world economic activity and ecology. Consequently there is

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intense worldwide activity to develop more sustainable energy conversion and use technologies that will reduce dependence on fossil fuels. Critical to these efforts is the efficient storage of electrical energy generated from intermittent energy sources such as wind and solar, including batteries and capacitors.[1–7] In parallel, consumer and industrial demand for compact, low mass and efficient electrical power devices is also driving the development of higher power and energy density capacitor and batteries. For example, capacitor-based high energy pulsed power conditioning has been achieved for pulse duration of hundreds microseconds at megavolt levels in high frequency power converters for electrical transport applications.[8–10] However, increasing energy density, ripple and load current demands together with the need for reduced physical size and low weight are driving further improvements in capacitor technology.[11]

Electrical storage technologies including batteries and capacitors have been profoundly impacted by nano-science and technology,[10,12–18] particularly in the engineering of bespoke electrode materials for batteries and electrochemical capacitors, designated supercapacitors, which involve the electrochemical processes of either physical adsorption or redox reactions of ions. Redox-based supercapacitors with nanostructured electrode materials have shown the potential to combine the high energy density of conventional batteries and the high power capabilities of electrostatic capacitors at the laboratory scale, but face important challenges related to durability, processability, cost and environmental effects for technological impact.

In this review we focus on recent important developments in redox-based supercapacitors with nanostructured electrodes. We consider the direction of future research and the prospects for future commercialization and application. The research literature relating to nanostructured pseudo-capacitive metal oxides, conducting polymers and their composites is considered. Current commercial supercapacitors make use of activated carbon cathodes and anodes with high specific surface areas up to 2000 m^2 g^{-1} or more. These supercapacitors involve ion absorption over the high specific surface area (termed electric double-layer capacitance) to give power densities approaching 5 Wh kg^{-1} and the reader is directed elsewhere for excellent reviews of carbon-based electrodes for ion adsorption.[16,19–22] In this review carbon materials, particularly carbon nanotubes and graphene, are discussed only in terms of (1) the commercial state-of-the-art performance, and (2) their role when used as a minority phase addition to pseudo-capacitive materials in composite electrodes.

2 Background

2.1 Historical background of capacitors

Fig. 1 shows the evolution of capacitor technology.[10] Electrostatic capacitors are the most direct and literal way of storing electrical energy and have been one of the primary building blocks of electronic circuits since the earliest days of electrotechnology.[10,23] Consisting of two conductive electrodes separated by an insulator or dielectric material, electrostatic capacitors accumulate and store electric charge inside the concentrated electric field between two electrodes (Fig. 2a). This arrangement has low equivalent series resistance (ESR) and low equivalent series inductance (ESL), allowing fast discharge times within tens of microseconds and a high power delivery of over 10 kW kg^{-1}.

Current electrostatic capacitor technologies include electrolytics, ceramics, polymer films and mica, which are typically available in planar and spiral wound constructions and are employed widely in microelectronic circuits and ripple filters. The continuing demand for small, integral passive components with flexible geometry and space-efficient packaging has spurred the development of nanodielectric embedded capacitor technologies to replace discrete decoupling capacitors, and their direct incorporation into passive components such as printed circuit boards (PCBs).[24–29] Although electrostatic capacitor technology

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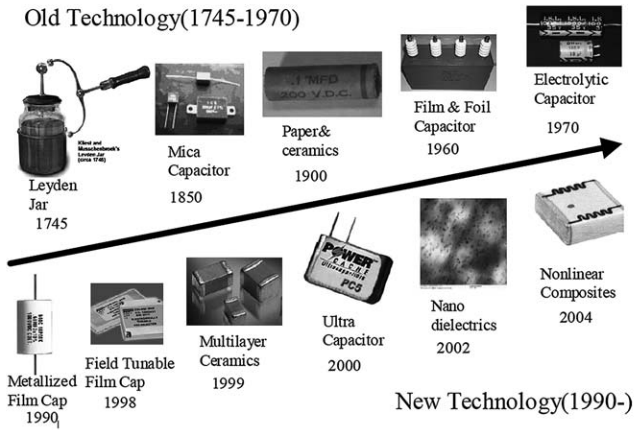

Fig. 1 Development history of advanced capacitors. Reproduced with permission from ref. 10. Copyright 2006 IEEJ.

appears to be the ideal choice for high-speed circuits, they generally provide a capacitance of less than 10 μF g^{-1} and an energy density of less than 0.1 Wh kg^{-1}.

Electrochemical supercapacitors store electrical energy using reversible adsorption of ions from an electrolyte onto two porous electrodes to form an electric double layer at an electrode/electrolyte interface (Fig. 2b).[30] Electrochemical supercapacitors that only involve physical adsorption of ions in this manner, without any chemical reactions, are called electric double-layer capacitors (EDLCs). Fig. 2b shows that unlike a battery, both anode and cathode can be the same high specific surface area material because different reversible chemical reactions at the electrode are not required. Because there is no physical change in the electrodes on charge/discharge, EDLCs can sustain millions of cycles with an energy density of typically 5 Wh kg^{-1}.

The other type of electrochemical supercapacitor is termed a pseudo-capacitor and is fundamentally different from an EDLC in the way in which charge is stored. Early research focused on Faradaic pseudo-capacitance arising from electrosorption of proton monolayers on noble metals such as platinum or gold and electrochemical protonation of metal hydrous oxides such as ruthenium oxide and iridium oxide hydrates.[31–33] More recently, research activity has grown substantially, in particular with regard to the pseudo-capacitance behavior of transition metal oxides that store charge using redox-based Faradaic reactions. This pseudo-capacitance can be superimposed on any electric double-layer capacitance. In principle, pseudo-capacitors can provide a higher energy density than EDLCs, especially in systems where multiple oxidation states can be accessed, but because the electrodes undergo physical changes during charge/discharge they have relatively poor durability compared with EDLCs.

Fig. 3 shows a Ragone plot comparing the performance of a range of energy storage devices.[34] The most promising near-term future markets for supercapacitors are in the same application sector as batteries with which they share similarities.[1] Supercapacitors have been used to complement or replace batteries in energy storage and/or load-levelling applications including portable electronic devices, plug-in hybrid electric vehicles, wind farms and long time constant circuits.[1,30,34] Although supercapacitors offer high power density, market penetration has been limited because of high cost and a low energy density compared with batteries.[35–37] The speciality carbon material generally used in supercapacitor electrodes is presently expensive in terms of the resulting energy-power characteristics, and a reduction in the cost for supercapacitors (US\$10–20 Wh^{-1} and US\$25–50 kW^{-1} compared with US\$1–2 Wh^{-1} and US\$75–150 kW^{-1} for batteries) is the main barrier to wider commercialization. A more detailed comparison of the important parameters of electrostatic capacitors, supercapacitors and batteries is presented in Table 1.[38]

Additional electrode material and supercapacitor aspects that must also be considered in the commercial context include environmental compatibility of the manufacturing, use and disposal cycle, the weight/volume topology (laminated, curved,

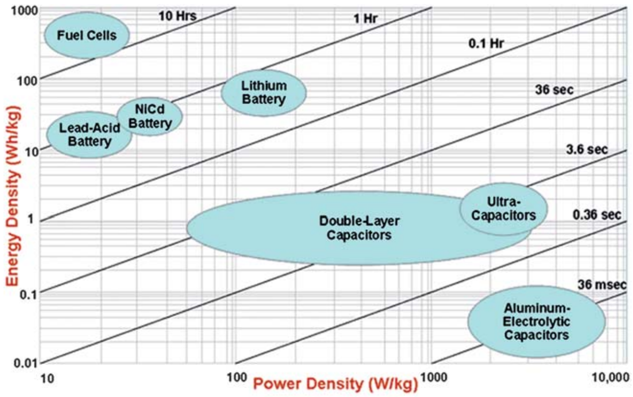

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Fig. 3 A Ragone plot showing the specific energy density *versus* power density for various energy storage devices.[34]

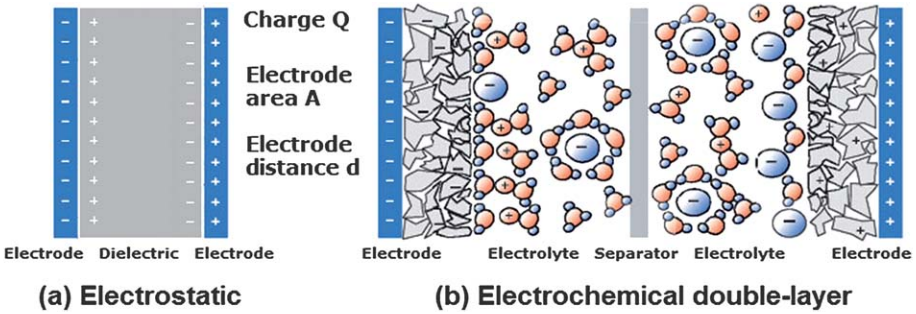

Fig. 2 Schematic of (a) a parallel-plate capacitor and (b) an electrochemical supercapacitor.

Table 1 A comparison of electrostatic capacitors, supercapacitors and batteries.[38]

Parameters	Electrostatic Capacitor	Supercapacitor	Battery
Charge Time	10^{-6}–10^{-3} s	1–30 s	0.3–3 h
Discharge Time	10^{-6}–10^{-3} s	1–30 s	1–5 h
Energy Density (Wh kg^{-1})	<0.1	1–10	20–100
Power Density (W kg^{-1})	>10 000	1000–2000	50–200
Cycle Life	>500 000	>100 000	500–2000
Charge/Discharge Efficiency	~1.0	0.90–0.95	0.7–0.85

spiral, flexible, *etc.*) and lifetime.[37,39] The fastest growing and largest energy storage market is mobile energy storage,[39,40] and where an improved supercapacitor energy capacity can be cost-effectively combined with their intrinsic high power capability and almost unlimited cycle life, significant market penetration can be expected.

2.2 Principle of redox supercapacitors and the influence of the nanoscale

For an electrochemical supercapacitor with charge accumulated in the electric double layer as previously shown in Fig. 2b, the capacitance C is given by:

$$C = \frac{Q}{V} = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{1}$$

where Q is the total charge on the plates, V is the voltage imposed across the capacitor, A is the specific area of the electrode/electrolyte interface accessible to ions, d is the thickness of the electric double layer, $\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1} is the permittivity of free space and ε_r is the dielectric constant of the electrolyte. The charge density in the double layer is made up of the charge density from specifically adsorbed ions in the inner Helmholtz plane (IHP) and the charge density in the outer diffuse layer (Fig. 4[41]). Thus the total double-layer capacitance C_{dl} of the electric double layer includes the Helmholtz type compact double-layer capacitance C_H and the diffuse region of the double-layer capacitance C_{diff}:[30]

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \tag{2}$$

The formation of the double layer associated with the charge rearrangement rather than a chemical reaction takes place in *ca.* 10^{-8} s and the thickness d ($= x_1 + x_2$ in Fig. 4) is generally less than 1 nm, giving rise to a rapid response to voltage changes and a specific capacitance of approximately 0.1 F m^{-2}. The exact specific capacitance, layer thickness and the kinetics of adsorption depend on the potential and the extent of participation of the IHP in the electric double layer.[1]

For supercapacitors additionally or alternatively utilizing pseudo-capacitance, reversible redox processes take place in which the valence electrons of electroactive materials are transferred across the electrode/electrolyte interface, resulting in a potential-dependent capacitance. Studied by Conway in 1975 for the first time,[30,31] the term pseudo-capacitance was coined to distinguish this mechanism of charge storage from double-layer capacitance where only electrostatic interaction occurs. The pseudo-capacitance is characterized by an approximate linear variation of capacitance with the extent of charge stored ΔQ and related to the change of the potential ΔV as follows:

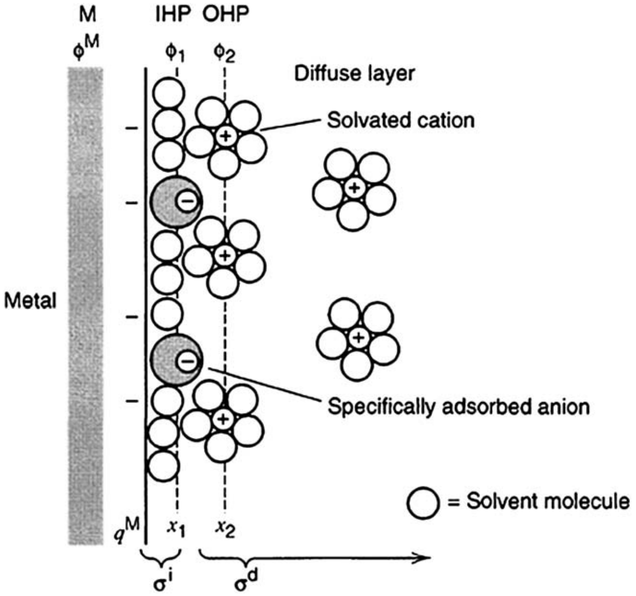

Fig. 4 Proposed model of the double-layer region under conditions where anions are specifically adsorbed. IHP is the inner Helmholtz plane, OHP is the outer Helmholtz plane, M refers to metal, σ^i is the total density in the IHP and σ^d is the excess charge density in the diffuse layer.[41]

$$C = \frac{\Delta Q}{\Delta V} \tag{3}$$

Unlike redox processes in a battery, Faradaic processes in a pseudo-capacitor are subject to a thermodynamic change of potential during charge accumulation and have better reversibility. Consequently redox supercapacitors can be thought of as possessing both battery-like behaviour with Faradaic reactions occurring across the double layer, and electrostatic capacitor-like behaviour with high reversibility and high power.

Several types of Faradaic processes occur in the pseudo-capacitive electrodes:[35,42] (1) reversible surface adsorption of proton or metal ions from the electrolyte; (2) redox reactions involving ions from the electrolyte; and (3) reversible doping-dedoping processes in conducting polymers. The first two processes are primarily surface reactions and hence are highly dependent on the surface area of the electrodes. The third process is more of a bulk process and the specific capacitance of the electrode materials is much less dependent on surface area, although a relatively high surface area with micropores is desirable to distribute efficiently the ions to and from the electrodes.[35] Redox reactions are usually accompanied by an electrostatic double-layer capacitance component proportional to their electrochemically accessible interfacial area, and typically contributes 5–10% of the total capacitance. A specific capacitance of over 1 F m^{-2} can be reached in pseudo-capacitance based materials.

The energy density W and power density P of an electrochemical supercapacitor is defined as:

$$W = \frac{1}{2}CV^2 \tag{4}$$

$$P = \frac{V^2}{4R_s} \tag{5}$$

where C is the specific capacitance, V is the voltage applied on the cell and R_s in ohms is the equivalent series resistance (ESR). The operating voltage is determined by the stability window of the electrolyte. Capacitors in organic electrolytes, for example Li ion containing carbonate and acetonitrile based electrolytes, can operate in the range of 2–3 V, and the use of ionic liquids can extend this range to 3.5–4 V, whereas in aqueous electrolytes the electrochemical stability window is generally below 1 V.[35,43]

The typical advantages that can be conferred by nanostructured electrode materials include:

1. Reduced dimensions of the electrode materials can enlarge the electrode/electrolyte contact area per unit mass significantly, providing more ion adsorption sites for double-layer formation and charge-transfer reactions. In some cases, micropore (<2 nm) dimensions and their distribution may be tailored to optimize the areal or volumetric density of pseudo-capacitive (and EDLC) electrolyte/electrode interactions.

2. The tortuous ionic and electronic diffusion distance through porous electrodes may be reduced, resulting in shorter diffusion times, improved high rate charge/discharge capability, and energy densities that approach those of conventional lead-acid and Ni–MH batteries. Contiguous ion channels of mesoporosity ensure that the accessible electrode area is maximized and that the kinetics of electrolyte/electrode reactions are sufficiently fast at all points over the electrode surface. In particular, three-dimensional (3-D) nano/meso-architectures can be exploited without increasing the overall areal footprint of the electrochemical device.

3. The confinement of material dimensions to the nanoscale in the electrodes may cause deviations from their equilibrium structure, modifying phase transformations upon ion insertion/extraction and other reactions and engineering an improved tolerance to the otherwise pulverizing volumetric changes. Nanostructured electrodes in supercapacitors that show enhanced tolerance to strain and structural distortion can then be cycled many times at high rates.

4. Nanoscale electrode materials can offer exciting combinations of properties that will allow supercapacitors to address new markets. For example, supercapacitors that combine low weight, transparency, flexibility and biodegradability.

3 Nanomaterials for redox supercapacitors

3.1 Metal oxides

Transition metal oxides are generally considered the best candidates as electrode material for redox supercapacitors, because they have a variety of oxidation states available for redox charge transfer. The most studied metal oxide in supercapacitors is hydrous ruthenium oxide (RuO_xH_y or $RuO_2{\cdot}xH_2O$) because of its ultrahigh theoretical capacitance of *ca.* 2000 F g^{-1} in a wide potential window of 1.4 V, a nearly metallic electrical conductivity of the order of 10^5 S cm^{-1} at room temperature and excellent chemical stability.[33,44,45] However, the practically attainable capacitance of bulk RuO_2 is usually at least one order of magnitude smaller than theory because of highly crystalline RuO_2 and power constraints.[42,46] Recent studies recognize that a rutile-like nanocrystalline network interpenetrated by a disordered hydrous domain is required to achieve both high ionic conductivity and metallic electrical conductivity, which exemplifies the necessity of nanoscopic architectures to balance the electronic and ionic transportation inside these materials.[17,47] To achieve such nanostructures, attempts have been made in the fabrication of nanostructured RuO_2 with controlled water content and crystallinity to enable rapid proton and ionic transportation while maintaining the metallic electrical conductivity.

RuO_2 in the form of porous films,[48,49] nanorods,[50] aligned plates, exfoliated nanosheets[51] and nanoparticles decorating conducting matrices[45,52] have offered improved specific capacitance and rate capability. Amongst these, a mesoporous hydrous RuO_2 nanotube array prepared by anodic aluminium oxide (AAO) membrane-templated electrodeposition displayed the highest specific capacitance of 1300 F g^{-1} at 1000 mV s^{-1}. This approach combined favourable electron hopping along the rigid, crystalline thin walls with efficient electrolyte penetration inside the open tubular structures, as shown in Fig. 5.[46] The tiny rutile-structured nanocrystallites on the walls of the annealed tubes facilitated ion transportation and there was a 40% loss only of capacitance as the scan rate increased from 10 to 1000 mV s^{-1}.

Despite these very appealing electrochemical characteristics, commercial applicability of RuO_2 is so far hindered by the material cost. Ruthenium containing ternary oxides and composites might help to reduce cost and increase the utilization of RuO_2, although these approaches undermine the specific capacitance to some extent.[52–58]

More cost-effective transition metal oxide systems in which the metal cations occupy alternate layers or can support multiple valences have been investigated to replace RuO_2 for pseudo-capacitive electrodes. Manganese oxides have shown attractive versatility in energy storage applications, such as cathodes in alkaline-MnO_2, Li-MnO_2 primary batteries and Li ion rechargeable batteries, as well as an electrocatalyst in metal-air batteries and alkaline fuel cells.[59–67] The versatility of manganese oxide is mostly attributed to the tunnel and layered crystalline structures of MnO_2 that constitute a large family of porous materials, from ultra-micropores to mesopores. Depending on the linkage of the MnO_6 octahedral structural units, MnO_2 can exist in diverse crystalline phases which exhibit different cation exchange, adsorptive and electrochemical responses.[65,68–70] Unlike RuO_2, most metal oxides do not possess high acidic resistance and fast protonic diffusion in bulk form, and thus the pseudo-capacitance is primarily contributed by surface reactions in a neutral or basic electrolyte system.

MnO_2 exhibits pseudo-capacitive behaviour owing to the surface adsorption and insertion/extraction of metal alkali cations inside the open crystalline framework. Due to the low diffusion coefficient of protons and alkali cations to the interior of MnO_2 particles, the specific capacitance of conventionally

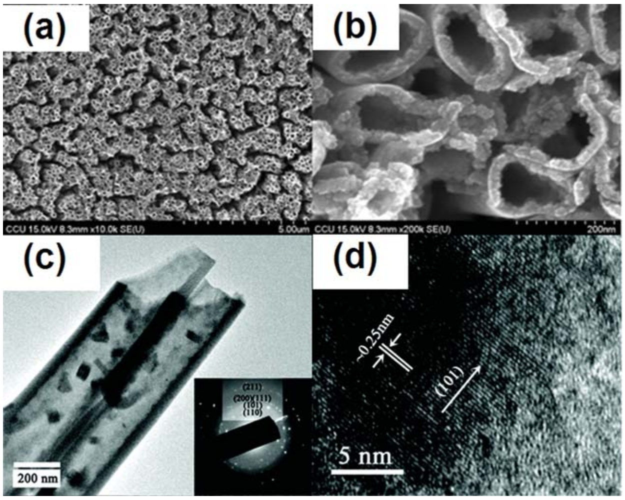

Fig. 5 (a, b) SEM images of a hydrous RuO_2 nanotube arrayed electrode, (c) TEM image and (d) HRTEM image of hydrous RuO_2 nanotubes annealed in air at 200 °C for 2 h. The inset of electron diffraction pattern shows diffraction rings of polycrystalline RuO_2 in the rutile form. Reproduced with permission from ref. 46. Copyright 2006 American Chemical Society.

prepared MnO_2 electrodes in the presence of binder and conductive additives is often inhibited to below 200 F g^{-1}, while binder-free nanostructured MnO_2 with reduced electronic and charge diffusion distances is expected to promote charge-transfer reactions.[71–77] Toupin *et al.* demonstrated that an ultrahigh specific capacitance of 1380 F g^{-1} was achievable in Pt supported amorphous MnO_2 nanometric thin film electrodes at low charge/discharge rates.[78] Electrodeposited α-MnO_2 nanoplates with a wall thickness of 20 nm displayed a high specific capacitance of over 500 F g^{-1}, although the rate capability of these monolithic nanostructures is usually unsatisfactory for practical purposes.[79] Co-deposition of nickel or cobalt with MnO_2 has been suggested to improve the long-term cyclability of MnO_2.[80] Another limitation of MnO_2 based materials is the restricted electrochemical stability window (0–0.9 V *vs.* Ag/AgCl) to avoid the irreversible reduction of Mn^{4+} and subsequent electrode dissolution at low voltage. Therefore, MnO_2 electrodes are preferentially coupled with an electrode whose electrochemical window is complementary to build a hybrid device, so that the safe operating voltage can be maximized.[16,81,82]

Fe_3O_4 is another pseudo-capacitive material with attractive natural abundance and reasonable metallic electrical conductivity of 10^2–10^3 S cm^{-1} at room temperature. The specific capacitance achievable using Fe_3O_4 as a supercapacitor electrode has a strong dependency on the electrolyte anion species and the dispersion of the oxide crystallites.[83–89] Although the electrochemical performance of Fe_3O_4 appears to be inferior in common neutral or basic electrolytes with a specific capacitance of only 5–7 F g^{-1},[83] Chung *et al.* showed that capacitance could be tuned to over 100 F g^{-1} by optimization of the porosity and crystallinity in electrodeposited hierarchical porous Fe_3O_4 thin films, highlighting the potential of nanoscopic, 3-D constructions.[90] During preparation, Fe(II)/Fe(III) hydroxysulfate (green rust 2) was anodically deposited onto a Pt substrate in the presence of ammonium ions as a buffering and complexing agent, followed by chemical oxidation with a dilute basic solution. The normal growth of Fe_3O_4 protrusions on the substrate led to an interconnected thin film structure with nano-thick walls and adjustable porosity as shown in Fig. 6, providing a large available surface area for electrolyte penetration and charge-transfer reactions. In Na_2SO_3 aqueous electrolyte, Fe_3O_4 may provide specific adsorption sites that facilitate the subsequent redox reactions for SO_3^{2-}, leading to a specific capacitance of 170 F g^{-1}.[85] The highest specific capacitance of 510 F g^{-1} for Fe_3O_4 was obtained for carbon black nanostructured co-precipitates with a Na_2SO_3 aqueous electrolyte at a scan rate of 2 mV s^{-1}.[83] However, the charge-transfer mechanism and reliability of this composite formulation requires further investigation.

Vanadium oxides and molybdenum oxides containing corner and/or edge shared MO_6 octahedral units that form two-dimensional (2-D) sheet structures have shown excellent ion storage capability in rechargeable batteries and supercapacitors,[91–102] exhibiting high capacitances of up to 400 F g^{-1}.[103,104] Other alternatives such as Fe_2O_3,[105–107] TiO_2[108–111] and SnO_2[55,112,113] also deserve attention because of their promising additional functionality such as photocatalytic activity, photoelectrochemical activity, electroluminescence and optical transparency as well as low cost and non-toxicity. Nonetheless, their charge storage capability is severely hindered by their insulating nature or poor electrical conductivity, and their potential for supercapacitor electrodes lies primarily in doped or complex systems *i.e.* ternary oxides and composites. Complex metal oxides might offer the potential for multi-electron transfer reactions with more chemical valence states within the accessible potential range of an electrolyte. Some of this potential has been explored in primary and rechargeable lithium ion batteries. Spinel ferrites MFe_2O_4 (M = Fe, Co, Ni and Mn) have been studied by Wu *et al.* where nanocrystalline $MnFe_2O_4$ showed the highest specific capacitance of over 100 F g^{-1} at a high power

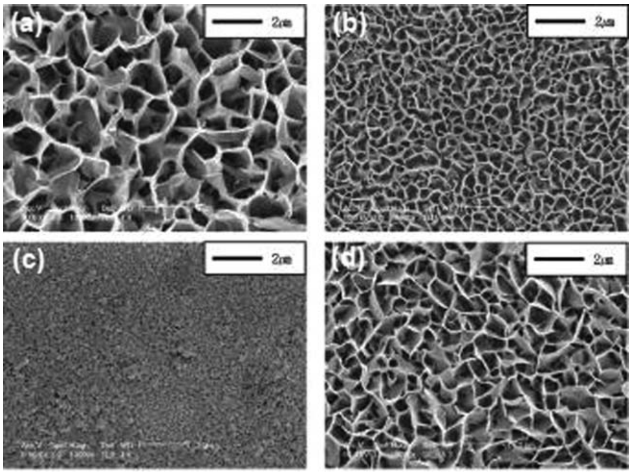

Fig. 6 SEM images of Fe_3O_4 thin films as functions of solution pH and the concentration of $(NH_4)_2SO_4$ for deposition of green rust 2 thin films: (a) pH 7.6, 0.2 M $(NH_4)_2SO_4$, (b) pH 8.1, 0.2 M $(NH_4)_2SO_4$, (c) pH 8.6, 0.2 M $(NH_4)_2SO_4$, (d) pH 7.6, 0.04 M $(NH_4)_2SO_4$. Thin films deposited at −650 mV *vs.* a saturated calomel electrode at room temperature. Reproduced with permission from ref. 90. Copyright 2005 Electrochemical Society.

deliver above 10 kW kg^{-1} in a Li ion electrolyte, associated with charge transfer at both the Mn^{2+} and Fe^{3+} sites.[114] The presence of Fe^{3+} is suggested to inhibit lattice distortion and Mn dissolution during cation/proton insertion/extraction, leading to improved electrochemical stability and cycling life.[114–117]

TiO_2 is of considerable importance in large batteries for power grid applications as TiO_2 exhibits facile lithium ion insertion without the formation of solid electrolyte interface by-products and catastrophic volume changes, which contribute to its high power capacity and long shelf life.[118–122] Aligned or randomly oriented anatase and brookite crystals have been studied as anode materials for hybrid electrochemical cells[109,110] where 3-D TiO_2 nanotube arrays and networks were shown to facilitate redox reactions of many oxides including RuO_2, $Ni(OH)_2/NiO$ and $Co(OH)_2$ in an aqueous electrolyte. These were achieved by promoting an initial effective dispersion of the oxide nanoparticles, and possibly by catalyzing the charge-transfer reactions themselves.[53,56,123,124]

3.2 Conducting polymers

The pseudo-capacitance of conducting polymers originates from the reversible oxidation and reduction of the conjugated double bonds in polymer networks, which can be described by the following reactions:[42]

$$P_m - xe + xA^- \leftrightarrow P_m^{x+} A_x^- \tag{6}$$

$$P_m + ye + xM^+ \leftrightarrow P_m^{y-} M_y^+ \tag{7}$$

where P_m refers to a polymer with conjugated double bonds, m is the polymerization degree, A^- refers to anions, and M^+ refers to cations. The oxidative *p*-doping reaction takes place in most conducting polymers, and the most extensively studied ones are polyaniline (PANI) and polypyrrole (PPy). In both aqueous and non-aqueous electrolytes, PANI can reach a specific capacitance of 150–190 F g^{-1},[125–127] and PPy a specific capacitance of 80–100 F g^{-1}.[128,129] However, conducting polymers as monolithic electrodes may not meet practical requirements since the pseudo-capacitance of conducting polymers is limited by many factors. These include the percentage of dopant, doping mechanism, redox switching and redox stability. In addition, the exchange of anions between polymer and electrolyte usually has a detrimental effect on electric charge density, switching speed and cyclability. Nanostructured conducting polymers prepared using template methods with a high aspect ratio and controlled orientation can partially address the capacitance and mechanical degradation, and conducting polymers PANI, PPy and poly(3,4-ethylenedioxythiophene) (PEDOT) combined with nanostructured carbon and metal oxides have shown promising rate capability and cycling life.[129–135]

3.3 Carbon composites

Microporous activated carbon is the current material of choice for commercial supercapacitors with a specific surface area of up to 2000 m^2 g^{-1} providing capacitance in excess of 200 F g^{-1} in an aqueous electrolyte, operating at up to 1.2 V. The capacitance in these supercapacitors is provided primarily by electric double-layer capacitance and reviews of carbon in supercapacitors have recently been published,[16,19–22] and further detailed consideration of monolithic activated carbon electrodes is beyond the scope of this review. Here only nanoscale polymorphs of carbon are considered, and in particular where they are used in conjunction with redox active materials to form composite electrodes.

3.3.1 Carbon nanotube based composite electrodes. Approaches to composite electrodes combining metal oxides or conducting polymers with carbon can offer an effective solution to overcome some of the drawbacks of pseudo-capacitive materials, while maintaining a high specific capacitance.

By providing a readily electrical percolating structure with mechanical robustness, carbon nanotubes have exerted a strong influence on research trends in the supercapacitor field. Single-walled carbon nanotubes (SWNTs) have an electrical resistivity of 0.03 to 0.1 mΩ cm, and multi-walled carbon nanotubes (MWNTs) can reach an electrical resistivity of 5.1 $\mu\Omega$ cm, lower than the in-plane resistivity of graphite (0.04 mΩ cm).[136,137] The tensile strength and Young's modulus have been estimated to be 45 GPa and 1.2 TPa respectively for SWNTs, and 150 GPa and 900 GPa respectively for MWNTs.[138–141] The specific surface area of CNTs is dependent on the diameter of the tubes/bundles, and usually lies in the range of 100–2000 m^2 g^{-1} which is moderate compared with activated carbon. However, the interpenetrating network formed by randomly distributed CNTs has been shown in some cases to be more accessible for solvated ions than the micropores existing in activated carbons, leading to a low ESR and a high power density above 8 kW kg^{-1}.[142–144] The specific capacitance of CNTs is mostly derived from double-layer formation but physical and chemical activation can improve the specific capacitance of CNTs by 2–7 times, leading to a capacitance of 20–180 F g^{-1}.[130,145–156] These intriguing properties along with the excellent integrity induced by the van der Waals interactions suggest the use of CNTs as both mechanical binder and conducting enhancer in composite electrodes for supercapacitors, including the potential for free-standing and flexible energy storage devices.[157–161] An example is shown in Fig. 7, illustrating a typical procedure to fabricate solid-state flexible supercapacitors and batteries from chemical vapor deposition (CVD)-grown CNTs.[159] By infiltration of a cellulose and room temperature ionic liquid (RTIL) mixture into vertically aligned CNT arrays, the CNTs could be peeled off from substrates, forming a micron-thick foldable and configurable electrochemical device with RTIL in cellulose as the self-sustaining electrolyte.

In CNT/conducting polymer composites, the π-bonded surface of CNTs can interact strongly with the conjugated structure of conducting polymers through the quinoid ring and facilitates the functionalization of CNT electrodes with various active polymers.[162,163] The percolating network of CNTs provides a large, open surface for the active sites of conducting polymers. The excellent mechanical flexibility of CNTs allows the network to adapt to volumetric changes during charge/discharge cycles restricting the otherwise damaging effects of swelling or cracking of the electrode materials. Composite electrodes in the form of CNT networks coated with conducting polymers have been explored extensively, with specific capacitances of 320–420 F g^{-1} for CNT/PANI composites[131–134] and 200–350 F g^{-1} for CNT/PPy composites[129,130,135] and excellent rate capability and

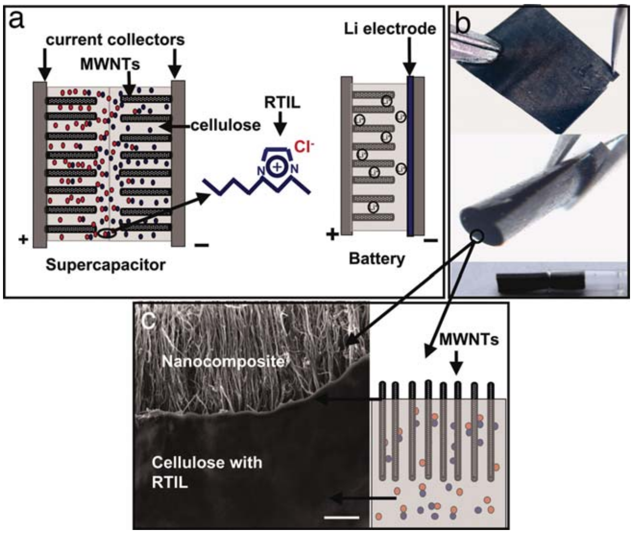

Fig. 7 Fabrication of self-supported CNT composite paper units for supercapacitors and batteries. (a) Schematic of the supercapacitor and battery assembled using nanocomposite film units. The nanocomposite unit comprises a room temperature ionic liquid and MWNT embedded inside cellulose paper. A thin extra layer of cellulose covers the top of the MWNT array. A Ti/Au thin film deposited on the exposed MWNT acts as a current collector. In the battery, a thin Li electrode film is added onto the nanocomposite. (b) Photographs of the nanocomposite units demonstrating mechanical flexibility. Flat sheet (top), partially rolled (middle), and completely rolled up inside a capillary (bottom) are shown. (c) Cross-sectional SEM image of the nanocomposite paper showing MWNTs protruding from the cellulose-ionic liquid thin films (scale bar, 2 μm). The schematic displays the partial exposure of MWNT. Reproduced with permission from ref. 159. Copyright 2007 National Academy of Sciences of the United States of America.

cyclability. Profiting from the solution processability of polymers, CNT/conducting polymer composites can be applied uniformly or locally patterned onto arbitrary substrates by spin-on, spray-on and dip-coating methods, or processed into free-standing buckypapers by filtration and electrospinning approaches.

Design of composite electrodes for supercapacitors can also draw inspiration from recently emerged transparent CNT/conducting polymer composite film systems with interesting electrochromic and electromechanical characteristics.[164–167] Recently developed multifunctional biocompatible organic/CNT hybrid systems could have potential applications in both energy storage and biological fields.[168–170] The introduction of CNTs as an additive into metal oxide nanostructures also significantly improves the charge/electron transport as well as interparticle contact and mechanical integrity during extended cycling. A several-fold increase in specific capacitance was found in TiO_2/CNT and SnO_2/CNT composite electrodes compared with pure TiO_2 and SnO_2 electrodes.[171]

Overall, the incorporation of CNTs into composite electrodes plays three major roles: (1) a percolating network of CNTs avoids the high weight loading associated with conventional conducting additives such as carbon black;[172] (2) self-supporting CNT sheets may eliminate the need for metal foil current collecting substrates, without significantly undermining the ESR and cyclability of electrodes; and (3) CNTs can provide a 3-D scaffold with tunable macro/mesoporosity for supporting redox-active pseudo-capacitive materials.

Das *et al.* prepared porous CNT buckypapers by filtration using 200 nm polystyrene (PS) spheres as a template to control porosity in CNT films.[173] After removal of the template, these macroporous (diameter >50 nm) CNT sheets supported RuO_2 nanocrystallites and attained a specific capacitance of 1715 F g^{-1}, which was very close to the theoretical maximum (Fig. 8[173]). Manganese oxide/CNT and vanadium oxide/CNT composite electrodes prepared by wet chemistry deposition or electrodeposition of MnO_2 or Mn_3O_4 and V_2O_5 nanostructures onto CNT substrates also displayed enhanced electrochemical properties.[174–179] For example, an amorphous MnO_2/CNT composite film exhibited an attractive combination of energy density of 100 Wh kg^{-1} at a power density of 5 kW kg^{-1} in a Li ion electrolyte.[180] Using electrodeposition of a very thin $V_2O_5 \cdot xH_2O$ layer onto CNTs to minimize ion diffusion distances, an amorphous $V_2O_5 \cdot xH_2O$/CNT composite attained an energy density of 851 Wh kg^{-1} at a power density of 125 kW kg^{-1} in a Li ion electrolyte, exceeding both the energy and power capability of conventional Li ion batteries.[181,182] An ultrahigh specific capacitance of 1701 F g^{-1} been reported for NiO_x deposited on a CNT based substrate in an aqueous electrolyte, when normalized to the NiO_x content.[183] CoOOH/CNT multilayer films prepared by alternating electrodeposition of CoOOH nanoflakes and CNTs reached a specific capacitance of 802 F g^{-1} at 10 mV s^{-1} in an aqueous electrolyte.[184]

The idea of direct deposition of pseudo-capacitive metal oxides onto CNT networks has been extended to vertically aligned CNT arrays in order to promote charge transfer and decrease ESR.[185,186] CVD-grown CNT arrays have been utilized as

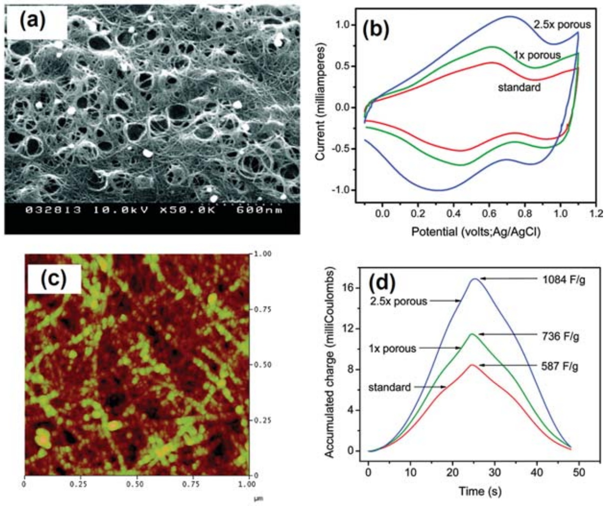

Fig. 8 (a) SEM image of an etched porous SWNT film, (b) cyclic voltammograms for RuO_2/SWNT electrodes of standard, 1×, and 2.5× underlying SWNT film porosity at a scan rate of 50 mV s^{-1} in 1 M H_2SO_4, (c) AFM image of RuO_2 electrodeposited onto a standard dense SWNT film, (d) integrated current *vs.* time plots for each RuO_2/SWNT electrode in cycling in the voltage range of 0–1.2 V *vs.* Ag/AgCl reference electrode. Reproduced with permission from ref. 173. Copyright 2009 American Chemical Society.

substrates for the nucleation of metal oxides during wet chemistry synthesis, and the intimate contact at the vertically aligned CNT and current collector interface has shown to benefit the ionic and electrical conductivity compared with randomly distributed CNTs. A high specific capacitance of 784 F g^{-1} with excellent cyclability was achieved in γ-MnO_2 loaded CNT arrays, when normalized to the MnO_2 content.[187]

Critical to progress the use of CNTs from the laboratory to the commercial market is the development of scalable process technology. For example, a spray-on technique that can be operated at atmospheric pressure and temperature for upscaling the fabrication of fully printable and flexible supercapacitor electrodes has been developed.[188] Uniform sheet electrodes with thickness of 100 nm to 10 μm have been produced in a well-controlled manner by feeding and atomizing aqueous/organic suspensions of active materials into fine droplets through a single nozzle, and then depositing onto a variety of substrates while simultaneously driving off the liquid solvent. Metal oxide, conducting polymer and CNT based thin film electrodes prepared *via* this approach have shown excellent capacitive behaviour, cycling performance as well as mechanical flexibility and durability.[89,189] The scale-up of the spray-on technique has been demonstrated for 1 m length CNT flexible films deposited onto polyethylene terephthalate (PET) substrates, as shown in Fig. 9. This type of roll-to-roll deposition and other emerging patterning strategies, such as ink-jet printing,[165,190–192] nanoimprint lithography[193–195] and transfer printing[196–200] on flexible substrates represent drastic increases in process throughput compared with traditional replication processes.

Nonetheless, despite attention devoted to metal oxide/CNT scaffold composite systems, the high cost of CNTs remains a major barrier to the widespread uptake of CNT based supercapacitor technology. As CNTs prices fall, quality (purity) issues are addressed, and assuming potential environmental concerns surrounding CNTs are allayed, it is likely CNT based energy storage devices will become commercially viable in certain applications.

3.3.2 Graphene based composite electrodes.

3.3.2 Graphene based composite electrodes. Graphene, a 2-D aromatic monolayer of graphite presents another attractive carbon material for energy storage. Recent studies have demonstrated that graphene combines a low electrical resistivity of 5.1 $\mu\Omega$ cm, a high tensile strength of 35 to 41.8 GPa, and a high surface area up to 100s m^2 g^{-1} (2630 m^2 g^{-1} for single layer of graphene).[201–208] Current methods to produce graphene include pyrolysis of suitable precursors, arc evaporation of silicon carbide, thermal exfoliation of graphitic oxide at high temperature, chemical reduction of graphene oxide using different reducing agents, typically hydrazine either in solution or vapor phase, and exfoliation in organic solvents.[209–212] However, these methods may lead to a degree of aggregation and surface defects that disrupt the electrical conductivity or specific surface area of the final products. Exfoliation in the liquid-phase using organic solvents such as N-methylpyrrolidone has been proven to be effective producing <5 layer graphene flakes with conductivity up to 6500 S m^{-1} after annealing in reductive atmosphere, whereas the yield is considerable low (0.01 mg ml^{-1}) and aggregation can be observed upon removal of solvent.[213]

Fig. 9 Optical images of spray deposited CNT thin film on PET webs.

Although high specific capacitances of 190–205 F g^{-1} have been reported for graphene paper in an aqueous electrolyte,[214,215] commonly quoted values are generally much lower and are strongly dependent on the graphene processing routes, the number of graphene layers, the surface area, the porosity and the surface functional groups.[209,216,217] In order to overcome the aggregation problem of graphene and maintain the high surface area upon drying, various approaches have been exploited, among which delamination of graphene sheets through physical intercalation of metal or metal oxide nanoparticles are very efficient.[218–220] Platinum nanoparticles have been used as a ‘spacer’ in between graphene sheets, resulting in an increased surface area of 862 m^2 g^{-1} for a graphene/Pt composite compared to dried graphene sheets with a surface area of 44 m^2 g^{-1}.[221] Graphene sheets have also been re-assembled in the presence of carbon nanotubes and fullerenes, allowing for tuning of the interlayer space of graphene sheets and a doubling of Li ion storage capability.[222,223]

One attractive attribute of graphene in supercapacitors is that the robust and flexible 2-D graphene sheets can be used to encapsulate nanostructured materials to inhibit pulverization and then isolate fragments during charge/discharge cycling, as illustrated in Fig. 10.[224] This approach has been studied for Li ion batteries as well as supercapacitors utilizing pseudo-capacitive materials.[225–231] Wang *et al.* reported a free standing graphene/PANI composite electrode prepared *via in situ* anodic electrodeposition that achieved a specific capacitance of 233 F g^{-1} without apparent degradation over 1500 cycles (Fig. 11[232]). This composite “paper” electrode showed a high volumetric capacitance of 135 F cm^{-3} due to the efficient accommodation of PANI between the nanoscale thin layers of graphene, outperforming other carbon composite-based free-standing electrodes. Similarly, *in situ* polymerization of aniline monomers in the presence of a graphene/graphene oxide suspension produced composites with high capacitances exceeding 1000 F g^{-1} in aqueous electrolytes.[233–235]

3.3.3 Carbon framework based composite electrodes. Synthesis of carbon frameworks with controllable pore sizes and volume fractions using “hard” templates such as silica,[236–239] non-silica metal oxides,[240–244] polymer beads[245,246] and AAO membranes[247] provides a more economical route than the use of CNTs or graphene. Conventional preparation of carbon from carbonization of natural or synthetic precursors is usually characterized by a broad and non-controllable pore size

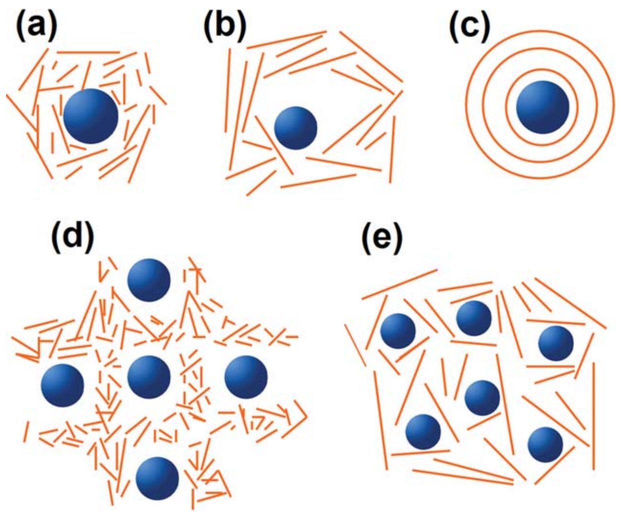

Fig. 10 Schematic illustration of active materials encapsulated by graphene with various structures and alignments. Reproduced with permission from ref. 224. Copyright 2009 Royal Society of Chemistry.

distribution on the surface of the carbonaceous powder. In spite of the complex synthetic methodology and relatively high cost of synthetic templated carbon frameworks, their use can significantly enhance electrochemical performance balancing the overall area and pore diameter distributions. Similarly to CNTs, the 3-D porous architectures that can be engineered provide shorter diffusion pathways for ions, an increased number of active sites for possible charge-transfer reactions, good electrical conductivity along interconnected walls, and an ideal support scaffold for pseudo-capacitive materials.[17,241,248,249]

Zhang *et al.* reported a 3-D ordered macroporous carbon (3DOMC) framework fabricated with silica spheres which was then employed as a substrate for electrochemical polymerization of aniline, as shown in Fig. 12.[249] By optimizing the fraction of deposited PANI in order not to isolate the carbon frame, a specific capacitance of 352 F g^{-1} was attained in carbon/18 wt% PANI composites with only 15% degradation over 1000 cycles, and specific capacitances of nearly 1500 g^{-1} were obtained when normalized to the PANI content.

Pseudo-capacitive nanostructures confined in mesoporous/microporous carbon with high surface area and electrolyte accessibility are a good example of the trend in which strategies for enhanced energy density for supercapacitors using composite electrodes in asymmetric arrangements converge with those strategies emerging for batteries with enhanced power density.[250–252]

3.4 Three-dimensional current collectors

The current collector is responsible for the transfer of electric charge to and from the electrode material and consequently should have high electrical conductivity and low interfacial electrical resistance to the active electrode material. Additionally, the current collector must be passive in contact with the electrolyte; provide structural robustness for the electrode; be thin

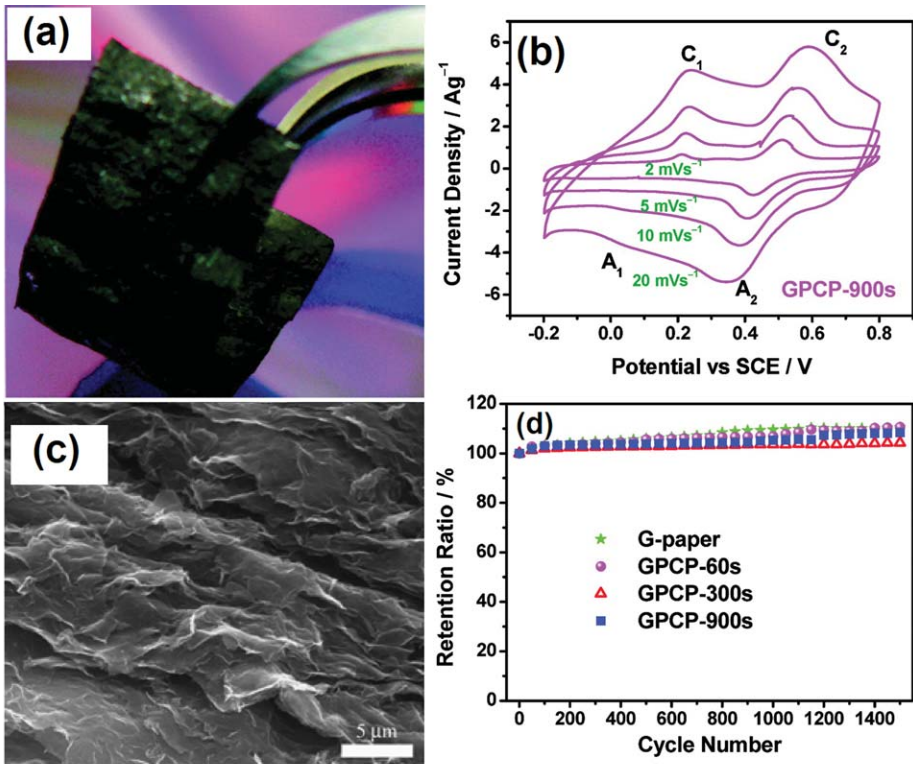

Fig. 11 (a) Optical image of a flexible graphene paper, (b) cyclic voltammograms for graphene/PANI composites at scan rates from 2 to 20 mV s^{-1} in 1 M H_2SO_4, (c) SEM image of graphene/PANI composites showing the stacked layer-by-layer structure, (d) cycling stability of graphene/PANI composites with different fractions measured at 50 mV s^{-1}. Reproduced with permission from ref. 232. Copyright 2009 American Chemical Society.

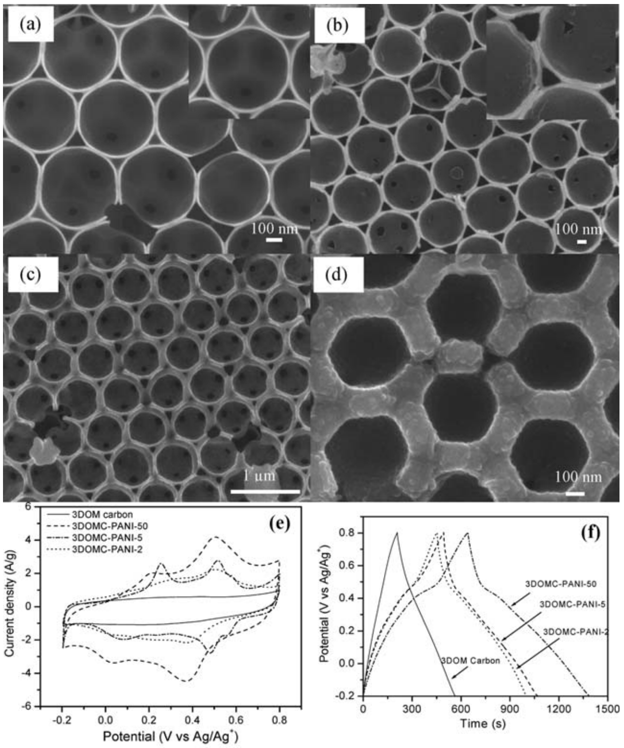

Fig. 12 SEM images of (a) 3DOMC-PANI-2, (b) 3DOMC-PANI-5, (c) 3DOMC-PANI-5 and (d) 3DOMC-PANI2-16. (e) Cyclic voltammograms for 3DOM carbon and 3DOMC-PANI composites at the scan rate of 5 mV s^{-1} in 1 M H_2SO_4, (f) constant current charge-discharge performance of 3DOM carbon and 3DOMC-PANI composites at 0.5 A g^{-1}. Reproduced with permission from ref. 249. Copyright 2010 American Chemical Society.

enough to minimize current collector mass; and flexible enough to allow handling and assembly into different device topologies. In 2-D planar geometry supercapacitors, total device mass can be dominated by the substrate and other inactive components, and thus undermines the practically realizable volumetric or geometric energy and power density.[253–256] Recent innovations in the area of micro/nanofabrication, particularly the rapid advancement of microelectromechanical systems (MEMS)-fabrication techniques[257,258] has opened up the possibility of creating 3-D mesoscopic current collectors. A variety of top-down and bottom-up approaches such as lithography, etching, micromachining, self-assembly, epitaxial engineering and probe microscopy provide a suite of (largely) laboratory tools for building 3-D current collectors for supercapacitors. These current collectors may possess small areal 2-D footprint, high 3-D specific surface area, short ion-diffusion pathways and can provide concomitant increases in specific energy and power density when the total device mass is considered. Nevertheless, high rate/high volume batch fabrication of 3-D nanostructured energy storage devices poses a challenge for economic production, along with consideration of their long-term reliability, calendar life and defect tolerance.

In terms of supercapacitors that are usually charged/discharged under more stringent high power conditions than batteries, reductions in internal resistance are important in minimizing electrode polarization and ohmic heating, that otherwise diminish the energy density and lead to potentially disastrous failure and possibly fire. The previously discussed self-supported 3-D monolithic carbon frameworks, CNT or fabric nanostructures have been suggested as 3-D current collectors because they offer low internal resistance and high chemical resistance. Heat treated carbonaceous aerogel,[259–261] and polymer networks[262] can also serve as 3-D supports for metal oxide nanoparticles or deposited pseudo-capacitive layers.

In addition to 3-D carbon collectors, rigid or flexible Ni and stainless steel current collectors in the form of porous foams or meshes are capable of enhancing the specific capacitance and long-term cycling performance of pseudo-capacitive materials in the absence of binder and conducting additives.[263,264] For example, 3-D thin film supercapacitors that are fully compatible with microelectromechanical systems have been fabricated by coating PPy onto Ti current collectors supported on ion etched or milled nanoscopic Si wafers.[265,266] These supercapacitors have been suggested to replace, or to be coupled with, a microbattery or energy harvester to provide peak power in future electronic applications (Fig. 13[265]). However, metal current collectors contribute to the inactive, "overhead" mass and packaging more dramatically than carbon-based current collectors.

4 Nanostructured asymmetric hybrid supercapacitors

Aqueous alkaline, acid or neutral solution electrolytes offer particular advantages over organic electrolytes in terms of higher ionic conductivity, lower cost, lower volatility and lower hazard. In particular, the lower sensitivity to moisture and O_2 has the potential to simplify the production of aqueous supercapacitor electrodes and devices, their in-service support, and their end-of-life disposal, offering an overall cost saving *versus* higher voltage, higher performing non-aqueous electrolytes. An asymmetric hybrid supercapacitor incorporating a pseudo-capacitive or battery-type electrode with an EDLC-type electrode can overcome the comparatively narrow stable potential window and limited energy density of aqueous electrolytes and permits an operating voltage that may approach twice that of EDLCs.

A hybrid supercapacitor is usually where a battery-type electrode (energy source) is combined with an EDLC-type electrode (power source) in an attempt to provide an increased energy density while maintaining a high power density. Hybrid supercapacitors based on alkaline battery-type positive electrodes *e.g.* PbO_2 and NiOOH with carbon negative electrodes in aqueous electrolytes were initially developed in Russia, providing an energy density in excess of 10 kW kg^{-1} in an operating potential

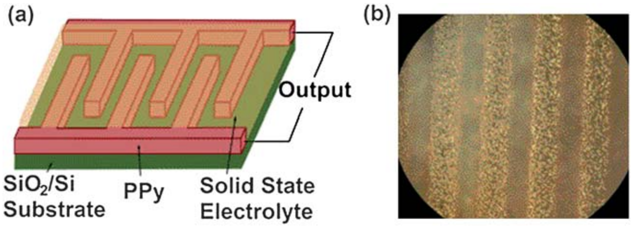

Fig. 13 (a) Schematic and (b) optical image of 3-D supercapacitor after polymerization. Reproduced with permission from ref. 265. Copyright 2009 Elsevier.

range of 0.7–1.8 V.[35,42] Since carbon shifts the hydrogen evolution towards potentials below the nominal thermodynamic value, when coupled with pseudo-capacitive metal oxides possessing high oxygen over-potential such as RuO_2 and MnO_2, the resulting electrochemical stability windows can be widened to *ca.* 2 V.[267–269] Qu *et al.* achieved a promising energy density above 20 Wh kg^{-1} at 2 kW kg^{-1} with excellent cycling life by combining one-dimensional (1-D) MnO_2 or V_2O_5 nanostructured cathodes with activated carbon anodes in a K_2SO_4 aqueous electrolyte,[82,270] while a hierarchical porous supercapacitor comprising nanostructured NiO cathodes and carbon anodes attained an impressive energy density of 10 Wh kg^{-1} at a high power density of 10 kW kg^{-1}.[271]

The reversibility and cyclability of hybrid supercapacitors is highly dependent on the depth of discharge and capacity retention of the redox-based electrodes. In this sense, the rate capability and cycling performance could be improved considerably upon introduction of CNTs to the pseudo-capacitive materials in hybrid supercapacitors, for example, an aqueous hybrid supercapacitor based on a $Ni(OH)_2$/MWNT composite cathode and activated carbon anode achieved an energy density of 32 kW kg^{-1} at a power density of 1.5 kW kg^{-1} with no apparent degradation over 2000 cycles.[272]

As previously described, the desirability of higher operating voltage (and therefore energy density) for supercapacitors has led to the employment of Li ion based organic electrolytes with an electrochemical stability window of up to 2.5–2.8 V. The slightly sluggish charge-transfer kinetics, lower ionic conductivity and larger size of solvated ions of these organic electrolytes is balanced by the increased operating voltage, with energy capacity able to exceed 50 Wh kg^{-1}. Battery-type cathodes including both lithium-rich compounds with high insertion potentials and layered or tunnel binary metal oxides with more open lattices are emerging as the two major categories of cathodes for these non-aqueous supercapacitors.[273–276] While hybrid designs consisting of nanostructured insertion cathodes and activated carbon or CNT anodes have shown high energy densities comparable with that of conventional Li ion batteries, these arrangements may suffer from a lack of reversibility and cyclability particularly at high charge/discharge rates because of the distortion of the host oxide lattices on Li ion insertion/extraction and the formation of the solid electrolyte interface (SEI), as reported for Li ion batteries.[277–279] In many cases, the theoretical operating voltage and depth of discharge needs to be reduced in practice, at the expense of energy and power density, in order not simply to turn a supercapacitor into a mediocre battery.

As mentioned earlier, one strategy to reduce the damaging insertion strains is the use of 1-D nanowires and nanotubes that accommodate volume changes more tolerably.[159,189,280–286] 3-D ordered mesoporous architectures that have been studied in battery cathodes may offer another solution to suppress the possible lattice transformation of supercapacitor cathodes by ensuring an even contact between the electrode and electrolyte, a short Li ion diffusion path and better accommodation of volume expansion-contraction. Fig. 14 shows an ordered porous MnO_2 structure with highly crystalline walls fabricated by impregnating a $Mn(NO_3)_2$ solution into a mesoporous silica template followed by calcination.[287] The thin walls not only provided high contact area and short diffusion distances for Li ion insertion/extraction, but also inhibited the cooperative Jahn–Teller effect in which the cubic spinel crystalline structure of β-MnO_2 transforms to inactive tetragonal and leads to subsequent capacity fading. The highly ordered porous structure accommodated a large amount of Li ions reversibly as shown in Fig. 13(c) and (d) and therefore could be safely cycled between 4.5–2.0 V.

Titanium oxides represent another group of thermodynamically stable anodes having no passivation layer and thus could be utilized to replace carbon anodes delivering fast Li ion insertion/extraction and eliminating Li plating. Hybrid systems based on a carbon or conducting polymer cathode and a nanostructured $Li_4Ti_5O_{12}$ anode in a Li ion containing electrolyte achieved an energy density of above 20 Wh kg^{-1} along with high reversibility and fast kinetics comparable to that of EDLCs.[288–290] Hybrid supercapacitors with carbon cathodes and brookite TiO_2 anodes boosted the energy density further to 50–80 Wh kg^{-1} in the power density range 240–300 W kg^{-1}.[291]

In view of rapid recent progress in this field, it seems likely, at least at the laboratory scale, that with careful optimization of the hybrid device parameters such as the thickness and mass of active materials, nanostructured hybrid supercapacitors will provide a power-energy density balance that fills the gap between Li ion batteries and conventional EDLCs. Table 2 summarizes various reported aqueous and non-aqueous based nanostructured hybrid supercapacitor arrangements with energy and power densities derived from eqn (4).

5 Conclusions and future perspective

In this review we have described recent advances in pseudo-capacitive nanomaterials for electrochemical supercapacitor

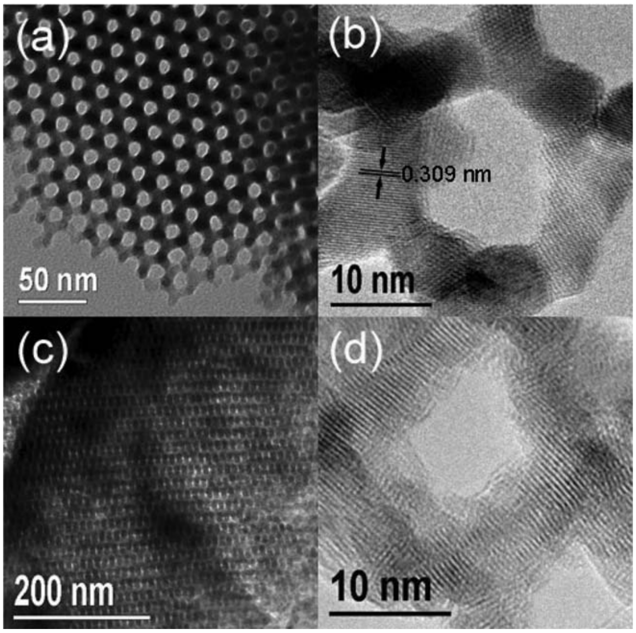

Fig. 14 TEM images of mesoporous β-MnO_2 (a, b) as-prepared and (c, d) after first discharge. Reproduced with permission from ref. 287. Copyright 2007 Wiley.

Table 2 Comparative performance of nanostructured asymmetric supercapacitors reported in the literature. NP: nanoparticle; AC: activated carbon; PFPT: poly(fluorophenythiophene); aq: aqueous; EC: ethylene carbonate; DEC: diethyl carbonate; DMC: dimethyl carbonate

Ref	Cathode	Anode	Electrolyte	Voltage (V)	Capacitance (F g^{-1})	Energy Density (Wh kg^{-1})	Power Density (kW kg^{-1})	Cycles
81	MnO_2 NPs	Fe_3O_4 NPs	0.1 M K_2SO_4 aq	0–1.8	21.5	8.1	10.2	5000
81	MnO_2 NPs	AC	0.1 M K_2SO_4 aq	0–2.2	31.0	17.3	19.0	5000
82	δ-MnO_2 nanorods	AC	0.5 M Li_2SO_4 aq	0–1.8	31.0	17	2	23 000
88	Fe_3O_4 NPs	AC	6 M KOH aq	0–1.2	37.9	7.6	0.07	500
268	amorphous MnO_2	AC	1 M KCl aq	0–2	50	20.8–28.8	0.5–8	100
269	amorphous MnO_2	AC	0.1 M K_2SO_4 aq	0–2	21	10	16	195 000
270	hydrous V_2O_5 nanoribbons	AC	0.5 M K_2SO_4 aq	0–1.8	64.4	20.3–29	0.07–2	100
271	NiO nanoflakes	porous carbon	6 M KOH aq	0–1.3	38	10	0.01–10	1000
272	$Ni(OH)_2$/MWNTs	AC	6 M KOH aq	0–1.5	96	32	1.5	2000
286	MnO_2/porous carbon	V_2O_5 nanowires/MWNTs	1 M Na_2SO_4 aq	0–1.6	45	5.5–16	0.075–3.75	100
292	MnO_2/MWNTs	SnO_2/MWNTs	2 M KCl aq	0–1.7	38	20.3	143.7	1000
293	MnO_2	β-FeOOH nanorods	1 M Li_2SO_4 aq	0–1.85	51	15–24	0.45–2	2000
273	$LiNi_{0.5}Mn_{1.5}O_4$	AC	1 M $LiPF_6$/EC/DMC	0–2.8	32	55	—	1,000
274	$LiMn_2O_4$	MnO_2/MWNTs	1 M $LiClO_4$/PC	0–2.5	60	26–56	0.3–2.4	—
275	$LiCoPO_4$ NPs	carbon nanofoam	1 M $LiClO_4$/EC/PC	0–2	21.9	11	0.2	1000
276	$LiMn_2O_4$/AC	$Li_4Ti_5O_{12}$	1 M $LiPF_6$/EC/DMC/DEC	1.2–2.8	59	16	4	5000
289	AC	$Li_4Ti_5O_{12}$	1 M $LiBF_4$/EC/DMC	1.5–3	—	85	—	5000
290	PFPT	$Li_4Ti_5O_{12}$ NPs	1 M $LiPF_6$/EC/DMC	0–3	13	16	2.5	1500
291	AC	TiO_2	1 M $LiPF_6$/EC/DMC	1.2–3.5	44	30–80	0.35	600
109	MWNTs	TiO_2 nanowires	1 M $LiPF_6$/EC/DEC/DMC	0–2.8	11.5	8–12.5	0.3–1.2	600
189	MWNTs	Fe_2O_3/MWNTs	1 M $LiClO_4$/EC/DMC	0–2.8	80	50	1	500

applications and have shown that nanoscale approaches are playing a key role in the progression of the technology. Nanoscale engineering is being applied to achieve elegant material and device configurations that offer a hitherto unachievable balance of energy and power characteristics at the laboratory scale. The beneficial use of nanoscale effects in electrochemical energy storage include: (1) a reduction in the dimensions of electrode materials that increases the electrode/electrolyte contact area per unit mass significantly, providing more ion adsorption sites for double-layer formation and charge-transfer reactions; (2) a reduction in ionic diffusion distances that improves high rate charge/discharge capability, including the use of three-dimensional nano/meso-architectures; (3) a greater tolerance to the otherwise pulverizing volumetric changes upon ion insertion/extraction and other reactions; and (4) the potential to achieve unusual multi-functionality such as low weight, transparency and flexibility.

Amongst pseudo-capacitive redox active materials, metal oxides are predominant. Technologies for well-controlled growth of metal oxide nanostructures have been established and provide the building blocks to construct nanoscale electrode configurations with optimized morphology, porosity, crystallinity and wetting characteristics. In particular, interpenetrated or vertically aligned 1-D wire-like, tubular and 3-D mesoporous topologies offer a low diffusion barrier, a high areal density of active surface sites and a high strain tolerance.

Carbon-based materials are anticipated to continue to be an important component of commercial supercapacitors because they are efficient stabilizers and substrates for pseudo-capacitive materials and are available in a rich variety of morphologies and surface conditions. The technological use of CNTs or even graphene in supercapacitors is likely to first occur as a minority, low volume fraction additive to composite electrodes. Free-standing CNT electrodes can also be envisaged if manufacturing costs can be reduced significantly.

The many device configurations afforded by nanostructured hybrid supercapacitors involving asymmetric and/or organic electrolyte configurations provides a wide scope to develop devices that can compete with commercial supercapacitors and batteries for particular energy density-power density combinations.

The incumbent, industrialized supercapacitor technology based on activated carbon electrodes provides a stiff test for any emerging supercapacitor technology in terms of cost, cyclability and ease of manufacture. Cost-effective processing, assembly and packaging remains a major barrier for practical implementation of nanostructured materials. Therefore, increasing emphasis should be placed on nanoscale *material-process combinations* that offer the potential for cost-effective mass production if market penetration is to be achieved.

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