Energy & Environmental Science

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/ees

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Towards superior volumetric performance: design and preparation of novel carbon materials for energy storage

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The volumetric performance of electrochemical energy storage (EES) devices, other than gravimetric performance, is attracting increasing attention due to the fast development of electric vehicles and smart devices. Carbon-based electrodes have advanced the fast development of EES devices while being limited by their low volumetric performance because of their porous structure and the resulting low density. This paper aims to clarify the importance of the volumetric performance and review the most recent progress on advanced EES devices with a high volumetric performance. Strategies for improving the volumetric performance, particularly with carbon-based materials are also proposed here. The transformation of normal low-density carbons to high-density ones through the assembly of different building blocks is highlighted as a promising remedy for this issue, and their applications in next-generation EES devices (Li-S, Li-air, Na-ion, *etc.*) are also discussed.

1. Introduction

The continuous breakthroughs in consumer electronics (CEs) and electric vehicles (EVs) with integrated multifunctionality are revolutionizing our daily life and dramatically improving our work efficiency.[1-3] It goes without saying that these EVs and CEs are ubiquitous and necessary, but their convenience and lifespan are the major issues that concern customers. Thus, the power sources are of great significance to guarantee their performance.[4-6] Electrochemical energy storage (EES) devices, in particular lithium-ion batteries (LIBs), are the most commonly used power source due to their high energy density, safety, long cycle lifespan and environmental friendliness.[7] Other EES devices, including supercapacitors, lithium-sulfur batteries (Li-S), fuel cells and lithium-air batteries, have also gained increasing attentions due to their distinctive features.[3, 8, 9] A common issue that they suffer from is the need for a large weight in order to guarantee long life and convenience.[8, 10, 11] They also need to be recharged frequently, making people always look for a power supply or carry supplementary chargers. Thus, the development trend of EES devices is to be lightweight and thin, to have a long lifespan, to be able to be charged rapidly and to be stable under extreme conditions. In other words, future EES devices need store as much energy as possible with minimum cost, weight and volume. This requires them to have a high energy density and power density in respect to both weight and volume, which are respectively defined as gravimetric performance and volumetric performance.

Gravimetric performance reflects how much and how fast energy can be stored per unit weight of a packed cell, and has been the most important criterion to evaluate an EES device in recent years. It can be described as a critical indicator that reflects the intrinsic energy storage ability of the electrode materials.[12] This issue is especially critical for EVs because outputting enough energy to keep working longer is inevitably at the cost of increasing the overall weight of the vehicles, thus will increase the volume of the battery, which decreases the feasibility and price-performance ratio of commercial EVs. For CEs, including smart phones, ultrabooks, etc., small and flexible batteries that revolutionize the traditional concept of batteries have become the focus of both manufacturers and the marketplace.[13] Most recently, volumetric performance has become the focus over gravimetric performance, since CEs and EVs both require power sources delivering the maximum energy in a very limited space. Volumetric performance reflects how much and how fast energy can be stored in a unit volume of a packed cell, and it is the most important criterion to evaluate EES devices in their future development.[12] A high volumetric performance requires the combination of high performance electrode materials with an effective configuration of the different parts involved. Unfortunately, the current volumetric performance of different types of EES device, especially with novel nanomaterials, is still far from a satisfactory level for practical applications.

Although different types of EES devices have their own specific structures and working principles, it is interesting that what they have in common is the wide use of carbon-based materials as illustrated in Figure 1.[14-16] Graphite can be used as the anode material in LIBs,[17, 18] carbon black is the commercial conductive additive to improve the electrical conductivity,[19, 20] activated carbon (AC) is the commercial electrode material in supercapacitors,[14] a porous carbon framework for active sulfur is used in Li-S batteries, carbon supports for noble metals and carbon-based transparent electrode in various energy devices.[21-23] Generally, the electrode materials of LIBs are graphite as anode and lithium metal oxide as cathode, both of which are of relatively higher density compared with normal carbon materials, thus the material design of carbon-based materials in LIBs is not the main issue. Supercapacitors, as another representative energy storage system, use AC as the main electrode material, and its density (0.3 ~ 0.6 g cm^{-3}), in normal cases, is far lower than that of graphite (~ 2.2 g cm^{-3}).[12, 24] The necessity of using AC rather than graphite in supercapacitors is because graphite delivers little capacitance due to the rejection of ions from its interplanar space since it is the most compact conductive carbon with a low surface area and non-porous structure. Carbon materials also play a significant role in next-generation Li-S batteries, which are believed to be the most promising candidate to substitute for LIBs due to their high energy density (2650 Wh kg^{-1}) and low cost. However, sulfur cannot be used on its own because it is an insulator and a conductive phase must be added to the cathode of Li-S batteries.[3, 25] Generally, the use of carbon materials is essential to improve the conductivity of the sulfur cathode, and the porous structure of carbon can tackle the shuttle effect of polysulfides, leading to a better utilization of active sulfur.[21, 26] Nonetheless, porous carbons usually have a low density (in most cases, 0.3~ 0.6 g cm^{-3}) and the sulfur loading is always restricted to low values to ensure satisfactory cathode performance. These factors result in the low density of most carbon/sulfur cathodes, which further causes the low volumetric performance of packed Li-S batteries, further hindering the advance to compact applications.

Herein we illustrate the significance of the volumetric performance of EES devices and summarize recent progress in the development of carbon-based electrode materials with high volumetric performance. Remarks on the design of their structure and production also indicate the need to consider the relationship between microstructure and electrochemical properties. We also highlight the possible development of next-generation EES devices including Li-S, Na-ion and Li-Se batteries. The improvement of volumetric performance involves system engineering and embraces materials science, electrochemistry and device fabrication to realize the upgrading of EES devices.

2. Present focuses on design of carbon materials for EES devices

Materials design is important in the fabrication of functional nanomaterials for energy storage.[27] Their macroscopic morphology, mesoscopic texture and microscopic infrastructure are of great importance in achieving high energy storage performance, as does their surface chemistry. For instance, carbon materials are responsible for the electrochemical performance of supercapacitors, and a carbon electrode with an optimized structure is necessary for achieving better performance. Pore structure, surface area and surface chemistry are the three most important properties of carbon materials. A suitable pore structure (i.e. pore volume and size) is responsible for the ion diffusion as well as the rate performance of the supercapacitor,[28] while a high surface area contributes to a high capacitance because of its large number of accessible active sites. The surface chemistry is also important since it can contribute to extra capacitance and determines the wettability of the carbon framework.[14, 15] All these factors help understand the fundamental role of the electrochemical interfaces at the nanoscale. The elimination of macro- and mesopores or tuning the pore size to match the ion size, as well as the pore shape has been demonstrated to have effects on improving the capacitance.[29, 30] The fine tuning of pore size, especially the micropores, for improved electrochemical performance can be realized by chemical activation[31], suitable selection of precursors[32] or a combination of the above two[33]. A hierarchical porous structure has recently been developed to produce a high performance electrode due to its multifunctional pores.[34, 35] For example, macropores serve as the reservoir to accommodate the electrolyte, mesopores can facilitate ion transfer to guarantee a timely ion supply, while micropores dominate the ion adsorption for energy storage.[34] Wu *et al.* developed a series of new strategies for producing porous carbon materials with a high surface area and hierarchical pore structure.[36-39] Gogotsi *et al.* developed a monolithic carbide-derived carbon, which contained micro-, meso- and macropore structures with an extremely high surface area, and showed great potential for energy storage.[40] Our group recently proposed a one-step activation of polymerized glucose spheres for the fabrication of a sheet-like carbon with vertically aligned carbon walls consisting of micropores on the wall and macropores formed by chemical activation. Such a unique carbon has an ultrahigh surface area of 2633 m^2 g^{-1} with excellent capacitive performance, which is attributed to the well-designed hierarchical porous structure.[41]

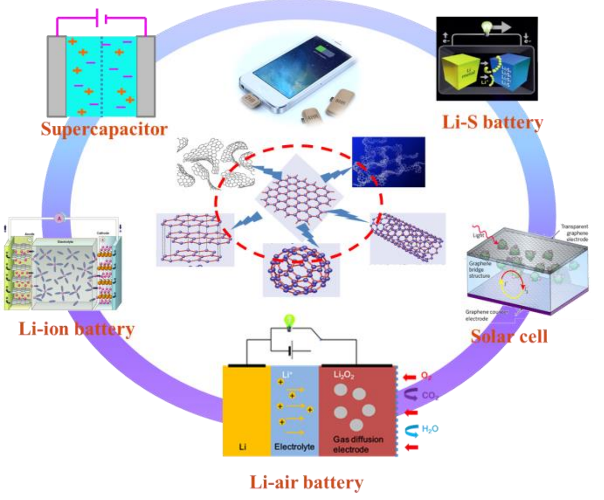

Figure 1. An overview of carbon materials used in EES devices, including lithium-ion batteries, supercapacitors, lithium-sulfur batteries, solar cells and lithium-air batteries. Reprinted with permission.[5, 6, 23]

On the whole, the design of carbon materials should aim at the optimization of ion and electron transfer by nano-engineering or pore structure design.[42] The high performance of a carbon-based electrode can be readily controlled by materials design with function-oriented microstructures. Microstructure design at the nanoscale or microscale concentrates on intrinsic electrochemical behaviour, outputting extraordinary gravimetric performance. However, nanomaterials have to be

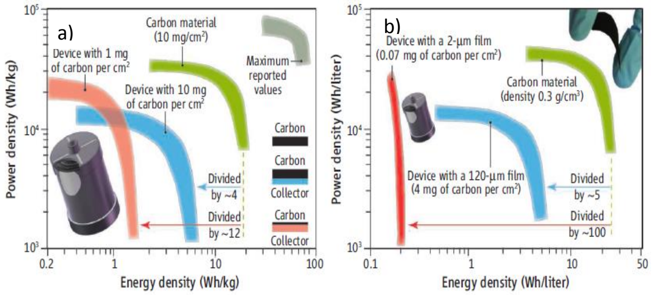

Figure 2. Ragone plots for an electrochemical capacitor. a) Plot based on the gravimetric basis and b) plot based on the volumetric basis. The plots show that excellent properties of carbon materials will not translate to medium- or large scale-devices if thin-film and/or low density electrodes are used. Reprinted with permission.[43]

considered as bulk materials when they are used in real applications, so their mesoscale texture is of equivalent importance for the overall electrochemical performance of an electrode, especially for the volumetric performance. As illustrated in Figure 2,[43] owing to the large surface area, porous structure of carbon materials, addition of conductive additives and the small amount of active material loaded on the electrode, the gravimetric performance of a packed device both for energy density and power density decreases by orders of magnitude compared to that of a high performance carbon electrode if the fraction of carbon in the electrode decreases. This phenomenon can be extended to the volumetric performance of a packed device, whose energy and power densities will drop dramatically with a decrease of the fraction of carbon in the electrode. For instance, the volumetric energy density of a packed device with a 120-μm carbon film is one fifth of that uses pristine carbon materials, which means that there is a big gap between the performance of the carbon electrode materials and the real device. Thus, an exploration of carbon electrodes with high electrochemical values is not sufficient. Novel carbons need to be developed to revolutionize the traditional carbon systems used in EES devices to obtain both high gravimetric and volumetric performance of a real device.

3. Parameters influencing the volumetric performance

The volumetric performance of a packed cell of EES device is very important for the real applications especially for ones in CEs and EVs, which is related specifically to the practicality of use where a high storage capacity is needed in limited space, resulting in a low-volume, high-capacity cell.

Generally, the volumetric performance refers to the performance of an electrode material or the performance of a packed device. Materials scientists have focused on the volumetric capacity of a material because this parameter reflects the intrinsic volumetric energy storage ability of a material. The volumetric capacity of a material is related to its pore structure, density, surface area and surface chemistry. Based on the materials, the electrode, which consists of the materials, binders, conductive additives, suffered from a high pressure compression, and has a totally different microstructure from the pure active materials, thus, the volumetric performance of an electrode depends on the active materials, the amount of binder and additives, and also the thickness of the electrode. For a chemical engineer or manufacturer, the volumetric performance of a packed cell is of far more importance than that of an isolated electrode, because it includes the volume of the electrode consisting of active material, conductive material, binder, current collector, separator, electrolyte and battery case. The volumetric performances of materials, electrodes and cells are interdependent. And the materials performance is the basis for all the devices. Thus the development of advanced electrode materials with high volumetric capacity is urgently needed as is optimization of the packing process to improve the volumetric performance of the devices.

For a better understanding, we propose simplified equations to illustrate the key parameters determining the volumetric performance of an EES device. The volumetric energy density of a device can be expressed as follows:

$$\mathrm{E}_v = \frac{U \times Q}{V} \qquad (1)$$

Where E_v is the volumetric energy density of the device, U is the average discharge voltage and V is the total volume of the device (including electrode, current collector, separator, electrolyte, and battery case). All the parameters here are simplified with no quantitative relations.

$$\mathrm{Q} = C_g \times \mathrm{M} \qquad (2)$$

$$\mathrm{M} = \rho \times V_e \qquad (3)$$

Where Q is the electricity stored in the electrode. C_g and M are the gravimetric specific capacity and mass of the whole electrode (including active materials, binder and additives), respectively. ρ and V_e is the electrode density and volume of the whole electrode (including active materials, binder and additives) respectively.

Combining the above equations, the discharge voltage U and gravimetric capacity C_g are determined by the intrinsic nature of selected active materials (binders and additives do not contribute to the capacity), which can be considered as constant factor. V_e and V are determined by the battery configuration and process, which can influence the volumetric performance, but generally these two factors are constant for manufacturers to meet the industry standard. More importantly, ρ as the electrode density of the whole electrode, is a vital factor concerning the volumetric performance of the device.[44] And the density of the active materials is mainly responsible for ρ, since we cannot get a high-density electrode if the carbon used possesses a very low density even with a high compression process. Thus, the density of the active materials dominates the final electrode density, further determining the volumetric performance of devices. Therefore, our review gives some comments mainly from the viewpoint of materials science on how to achieve practical device applications.

4. Improving the volumetric performance—the way promoting the practical use of carbon nanomaterials

As mentioned above, the use of carbon-based nanomaterials in energy storage is based on their excellent conductivity, high surface area and porous structure. But the inevitably low density of carbon nanomaterials is an obstacle hindering their practical use on a large scale. Thus, improving the volumetric performance of carbon-based EES devices is the most effective way to realize the practical value of carbon nanomaterials. As we discussed above, two strategies can effectively improve the volumetric performance, i) improving the volumetric capacity of the electrode materials; ii) simplifying the configuration to reduce the volume of the packed cell. In this section, efforts are made mainly concerning the first approach since the design and fabrication of novel carbon nanomaterials with high volumetric capacity is a kind of bottom-up approach to solve the current limitations, while the second approach is a problem for engineers and manufacturers.

4.1 Carbon electrode

Carbon materials have different functions in an energy storage device, and are commonly used as the electrode, conductive additives and sometimes even as functional separators.[45] As electrode materials, carbon materials are responsible for the overall performance of the whole device. In this section, we pay attention to the design and fabrication of carbon electrodes with a high volumetric performance.

Graphite and porous carbon are the most commonly used carbon materials in energy storage systems. Graphite is the commercial anode material for LIBs owing to its layered structure that allows the intercalation of Li^+ and provides stable charge-discharge plateaus. However, graphite cannot be used in supercapacitors or Li-S batteries because of its compact layer structure that prevents the access of ions into the interplanar space. Even if the packing density of graphite decreases from 2.2 to 1.1 g cm^{-3}, the interplanar space of 0.67 nm is not accessible to most ions.[46, 47] Although a high packing density can be reached in the cell fabrication process, its intrinsic low energy density also results in an unsatisfactory volumetric performance.

Porous carbons have a high surface area and a porous structure that provide sufficient charge storage sites, and their unique structure is favourable for use in supercapacitors or Li-S batteries.[35, 48] Some studies have explored their use for high volumetric performance electrode.[49-53] For instance, ordered mesoporous carbon nanospheres are fabricated via a soft-template method with a hierarchical porous structure and a high mass density, delivering a relatively high volumetric capacitance (107 F cm^{-3}).[49] For CNTs or carbon fibres, hybridization or regulating their alignment is normally used to reach high volumetric performance.[52, 53] Various non-carbon materials are hybridized with them to synergistically improve the density and capacity of the hybrid electrode. Although some advances have been made for improving the volumetric performance of these porous carbons, ultimately they are hardly used for high volumetric performance EES devices due to the low density ascribed to the intrinsic porous structure even under high pressure compression, such as the micropores in ACs and the internal space in CNTs. Thus reaching a high volumetric performance by bottom-up designing novel porous carbons or modifying existing porous carbons is of great significance.

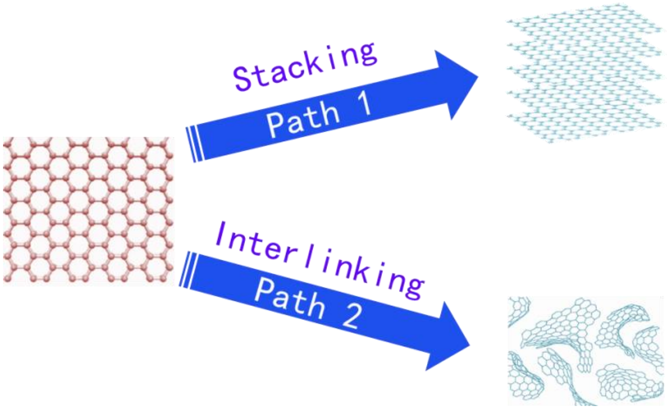

Figure 3. Two typical extreme models of the assembly of graphene or functionalized graphene sheets into other carbon architectures

Nanocarbon materials can be used as the building blocks of bulk carbon by the bottom-up design strategy. Graphene has a 2D sheet-like and flexible structure. It has been widely investigated as an electrode material, and more importantly, is believed as an ideal building block for constructing various carbon materials as shown in Figure 1.[54, 55] Thus, we mainly use graphene as the model material discussed here, to illustrate the general principle that how we improve the volumetric performance of carbon-based materials. Graphene-based 1D fibres, 2D membranes and 3D foams have been fabricated and their promising use in energy storage systems have been widely explored in recent years.[24, 46, 56-65] But most graphene-based assemblies still suffer from a low volumetric performance. To obtain a high volumetric performance, an apparently contradictory high density and porous structure must exist in one material. Thus, the principle of graphene assembly should be first clarified. As illustrated in **Figure 3**, graphene assembly can be considered to have two extremes, face-to-face parallel stacking (Path 1) and edge-to-face or edge-to-edge random packing (Path 2). The first always leads to a dense but non-porous carbon material, while the second usually results in a highly porous carbon with low density.[55, 66]

4.1.1 Strategy 1: face-to-face stacking and its solution

Following Path 1, graphite-like materials can be prepared and they always possess high packing density but insufficient ion transport channels due to the tight stacking sheets. If we want to make full use of the graphene surface in these dense graphite-like materials, a slightly enlarged interlayer spacing is indispensable for better ion diffusion or creating nanochannels in or across the layers. Li *et al* pioneered the assembly of graphene as an electrode material for supercapacitors with ultrahigh volumetric performance. They prepared a series of chemically converted graphene membranes by vacuum filtration similar to Path 1 as shown in Figure 4.[46] They used a liquid-mediated approach to avoid the tight restacking of graphene layers, and a porous yet highly dense graphene membrane with a surface that was easily accessible to ions and with a low ion transport resistance was formed by the capillary compression of adaptive graphene gel film in the presence of a liquid electrolyte as spacer. A high density of 1.33 g cm^{-3} was obtained, almost double that of traditional porous carbons, and the material showed a tremendous electrochemical performance with a maximum volumetric energy density of 59.5 Wh L^{-1}. This study pioneered and accelerated the research on the volumetric performance of carbon-based electrodes.

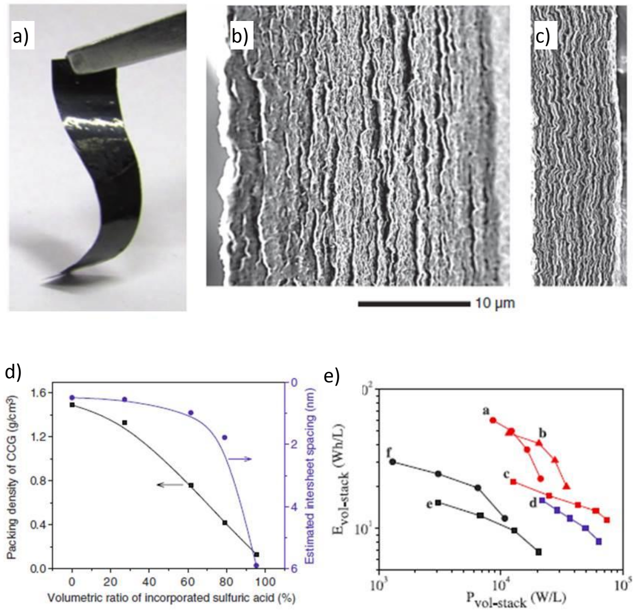

Figure 4. Characterization of a liquid electrolyte-mediated chemically converted graphene film (CCG). a) Photograph of the flexible film. b) and c) SEM images of the cross section of the CCG film with different contents of liquid electrolyte (78.9 27.2 vol % of H_2SO_4). d) Relationship between the packing density and the interlayer spacing versus H_2SO_4 content. e) Ragone plot of the film. Reprinted with permission.[46]

This liquid-mediated approach produces unimpeded ion transport channels in the X-Y plane direction, which is parallel to the graphene sheets. Vertical ion transport channels are also needed to facilitate ion diffusion since the planar graphene sheets block ion transport along the Z-axis. Hu *et al* used a simple thermal treatment of commercially available graphene in air to produce holey graphene on a large-scale.[67] The holey graphene is easier to manipulate than the as-received graphene, and a 2D film with strong mechanical strength, a holey structure, high density and easy processability was fabricated by a vacuum filtration method. The fabricated film exhibited good ion diffusion in the Z-direction, while retaining high density. A remarkably improved volumetric capacitance with about a 700% increase compared with the as-received graphene was demonstrated in a supercapacitor and this was ascribed to the unique structure. Holey graphene can also construct a 3D framework, followed by compression into a dense film, and this produces a high capacitive performance and volumetric energy density.[68] Fan *et al* adopted a strategy that combined the above two methods, in which a holey graphene-carbon nanotube (CNT) sandwiched film featured fast cross-plane and in-plane ion diffusion.[69] The high density resulting from the macro-structure and the fast ion transport due to the micro-structure are finely balanced by the incorporation of interlayered CNTs and the abundant holes in the graphene. As a result, the binder-free flexible carbon film showed an ultrahigh volumetric performance of 26 Wh L^{-1} and 331 F cm^{-3}. Graphene-CNT fibres or graphene-porous carbon hybrids were also fabricated with a high capacitive performance.[70, 71]

Modification of a graphene film effectively improves the electrochemical performance to produce a high volumetric performance, but ion diffusion in the interlayer spaces is still in the direction perpendicular to the electric field. Based on the parallel packing of graphene sheets, Lee *et al* subtly fabricated a dense vertically alignment of graphene sheets for compact supercapacitors as illustrated in Figure 5.[72] This study combines the materials in an electrode structure design with a vertically aligned and open-edged reduced graphene oxide (rGO) with an appropriate interlayer distance that allowed fast ion diffusion, which is suitable for use in compact supercapacitors. The hybridization of rGO with single-walled CNTs (SWCNTs) prevented the tight layer-by-layer stacking and a high packing density of 1.18 g cm^{-3} was obtained with a high volumetric capacitance of 171 F cm^{-3} in this system. Such a simple fabrication of graphene-based materials with controllable tuning of sheet orientation provides another way of facilitating fast ion transport and maintaining a high packing density. It also provides the possibility for the large-scale use of graphene in commercial energy storage systems.

Thus, the assembly of graphene by Path 1 modified with a better ion diffusion can contribute to a high volumetric performance for carbon-based EES devices.

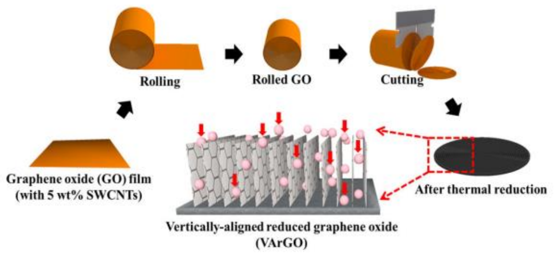

Figure 5. Schematic illustration of the fabrication of vertically aligned rGO. Reprinted with permission.[72]

4.1.2 Strategy 2: edge-to-edge or edge-to-face interlinking and its solution

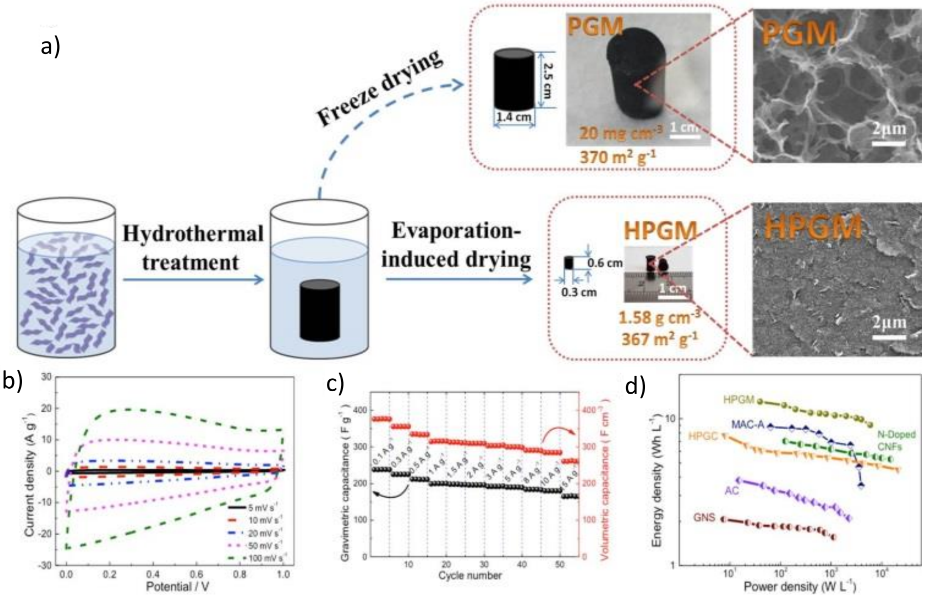

Figure 6. a) Schematic of the self-assembly formation of the highly dense but porous graphene-based monolith (HPGM). b) CV curves of the HPGM at different scan rates. c) Rate performance of HPGM. d) Ragone plot of HPGM compared with other carbon materials. Reprinted with permission.[24]

Path 2 represents the edge-to-edge or edge-to-face randomly stacking of graphene sheets into a hard carbon-like structure, which normally possesses low packing density but sufficient ion transport channels due to the abundant void in the 3D assembly. Li's work created a larger interlayer spacing for fast ion transport in a highly dense carbon film fabricated by Path 1, and it seems impossible to produce a porous material with a high density harmoniously by Path 2. However, our group developed a novel route to realize these two contradictory purposes using the method illustrated in Figure 6.[24] A 3D graphene hydrogel was first prepared by a self-assembly of graphene oxide (GO),[55] followed by the controlled removal of water. The key in this work is that the totally different ways of water removal result in totally different microstructures. By freeze-drying, a low-density graphene foam was obtained due to the fast fixing of the shape, and the transformation of water to ice led to the phase separation between ice crystals and graphene sheets.[73] With the same precursors, a carbon monolith with a density as high as of 1.58 g cm^{-3}, nearly 70% of graphite, was fabricated by an evaporation-induced drying, in which the evaporation of water exerts a ‘‘pulling force’’ on the graphene sheets and results in the shrinkage of the 3D network since there is strong interaction between water and graphene sheets, and it was found that a highly dense but porous graphene monolith (HPGM) was constructed by compactly interlinked graphene sheets. The two different products possess similar specific surface areas and gravimetric capacitances for supercapacitors, but their volumetric capacitances are totally different due to their different densities. The HPGM delivered a high volumetric capacitance of 376 F cm^{-3} in an aqueous electrolyte, which is amongst the highest values reported so far. Such a carbon is mouldable and has an acceptable conductivity and unimpeded ion transport channels for use in supercapacitors. This study demonstrates that spatial interlinking with the appropriate elimination of solvent can result in a highly porous carbon with finely tuned density, and it provides us new insight into the graphene-based materials. More importantly, a new class of hard graphene-based monolith is proposed to be applicable to broader fields.

The assembly of graphene-based materials has been demonstrated as a very effective way to improve the volumetric performance of carbon electrodes, and Ruoff *et al* compared different processing methods (mechanical compression or vacuum-assisted self-assembly) for the improvement of volumetric performance.[74-76] Even under a high mechanical pressure, the packing density of activated microwave-exfoliated graphene oxide (aMEGO) is still very low (0.75 g cm^{-3}), while it was increased dramatically to 1.15 g cm^{-3} by vacuum-assisted self-assembly. Very high volumetric capacitances of 158 F cm^{-3} and 177 F cm^{-3} for the self-assembled aMEGO were demonstrated in an ionic liquid as electrolyte without sacrificing gravimetric capacitance. The excellent volumetric performance is attributed to the highly dense and well-ordered structure of the aligned aMEGO oriented by the vacuum-assisted self-assembly approach, and the preservation of the nano-sized pores in the electrode facilitates charge storage. This approach is essential to the understanding of the advantage of the self-assembly of nanomaterials into multifunctional nanostructures.

4.1.3 Other strategies

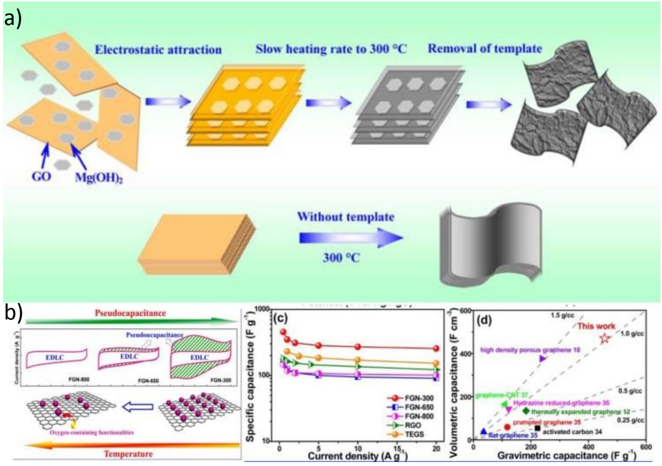

Figure 7. Schematic illustration of the formation of the template-assisted functionalized graphene. Reprinted with permission.[78]

In addition to the above two strategies, some other approaches have also been demonstrated effective in improving the volumetric performance of a carbon-based electrode, including the template-etching of tightly packed graphene sheets, activation, hybridization of different carbon materials, etc.[31, 77-79] Fan *et al* developed a template-assisted synthesis of functionalized graphene with an ultrahigh volumetric performance for supercapacitors.[78] The introduction of $Mg(OH)_2$ nanoparticles prevented the restacking of graphene sheets and created a homogeneous footprint-like structure on graphene sheets as illustrated in **Figure 7.** The obtained graphene had a dented structure without serious aggregation and possessed stable oxygen-containing groups due to the relatively low heating temperature (300 ℃). The large number of accessible surface and resident functional groups provides both a high double layer capacitance and pseudocapacitance. Accompanied by the low pore volume, the functionalized material exhibited ultrahigh gravimetric and volumetric capacitances of 456 F g^{-1} and 470 F cm^{-3} respectively, which are far higher than those of commonly reduced graphene and other carbon materials.[79-81] A high volumetric performance of 27.2 Wh L^{-1} was delivered when the obtained graphene was assembled in a cell and this is amongst the highest values for carbon materials in an aqueous electrolyte. This strategy demonstrates a simple but effective mild heating method with the assistance of a removable template to fabricate dented graphene sheets with a high surface area, abundant active sites and low pore volume. Thus, the functionalization of carbon materials or creating more active sites with more exposed edges is favourable in producing extra capacity for pure carbon.

Huang *et al* developed a novel crumpled graphene ball by a spray drying process, which facilitated the formation of the paper-like crumpled graphene.[82] When it was used as the electrode for a supercapacitor, the gravimetric capacity remained stable due to the highly accessible surface area, elastic structure and fast ion transport even if the mass loading was increased to 16 mg/electrode. This indicated that crumpled graphene may deliver a high volumetric capacitance since more active materials can be compressed into a limited space without sacrificing gravimetric capacitance. In other words, excellent compressibility is an important character for some novel carbon with an intrinsically low density, like crumpled graphene to be up-scaled in real EES applications.

The aforementioned strategies for improving the volumetric performance of EES devices focus on improving the density of the carbon materials in the electrode while maintaining a high active surface and unimpeded ion transport channels. And the highly dense but porous graphene assembly proposed by our group is believed to be a typical example for the improvement of volumetric performance of carbon-based electrode. However, even with these efforts, the gravimetric and the volumetric performance of carbon materials are also limited in the future development due to the intrinsic low energy storage ability. Thus, non-carbon materials with a high capacitance are favourable for improving the overall capacitance or energy density of the electrode materials.

4.2 Hybrid materials

Non-carbon materials including metal, metal oxide or conductive polymers have been widely used in EES devices, delivering superior electrochemical performance to carbon-based materials.[83-88] Thus, the incorporation of these non-carbon materials or doped heteroatoms with a carbon electrode can effectively improve the overall energy density and the synergistic effect may improve the performance of packed cell.[71, 89, 90] As discussed, the self-assembly of graphene into highly dense carbon materials is effective in improving the volumetric performance of EES devices, while the appropriate incorporation of an optimum amount of non-carbon materials with the correct structure may further accelerate our quest to achieve compact devices with a high volumetric performance.

Following the exploration of the self-assembly of aMEGO for ultrahigh volumetric capacitance, Ruoff *et al* fabricated a aMEGO/MnO_2 composite by a redox reaction,[91] because MnO_2 has been demonstrated to be an excellent pseudo-capacitive material with high capacitance. The resulting composite had a 3D structure that retained most of the structural features of aMEGO, and delivered a gravimetric capacitance of 256 F g^{-1} and a volumetric capacitance up to 640 F cm^{-3}, which are both much higher than for self-assembled aMEGO. The uniform size and spatial distribution of MnO_2 on these graphene sheets provides additional pseudocapacitance without increasing the volume of the products, further improving the volumetric capacitance to an extremely high level.

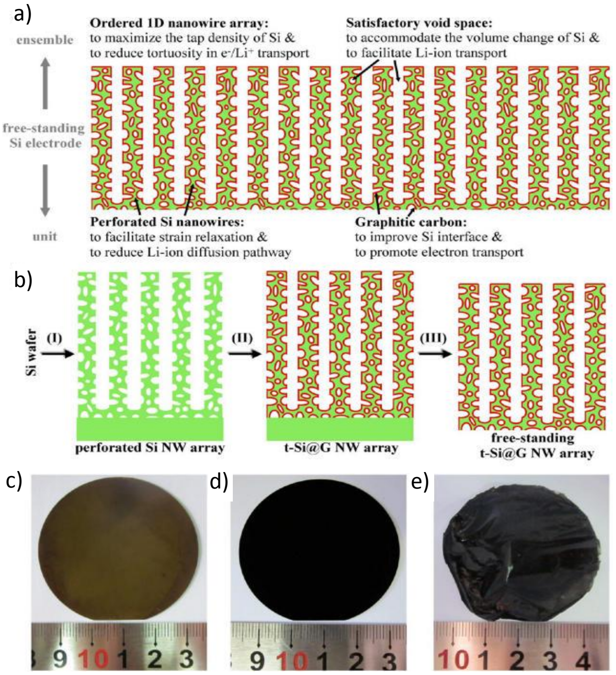

Figure 8. a) Cross-sectional view of a textured silicon@graphitic carbon nanowire (t-Si@G NW) array electrode. b) Schematic of its fabrication process. c), d) and e) Photographs of a perforated silicon nanowire array on a wafer, t-Si@G NW array on a wafer and a free-standing t-Si@G NW array electrode. Reprinted with permission.[95]

The incorporation of non-carbon materials into carbon hosts can effectively increase the volumetric performance of carbon materials, while the introduction of carbon to a non-carbon host can also modify the interfacial reaction of non-carbon materials, further improving the performance. Si, Sn and some other metal or metal oxide materials usually have to accommodate a damaging volume expansion because of their remarkably high lithium storage ability, and some void space is necessary, resulting in a low density and volumetric performance.[92-94] Zhi *et al* proposed a novel Si-C electrode for LIBs on the basis of nanoscale system engineering.[95] They fabricated an electrode composed of a textured Si@graphitic carbon nanowire array for direct use as a high performance electrode with high volumetric performance as illustrated in **Figure 8.** The ordered 1D nanowires with a perforated infrastructure combined with a graphitic carbon coating synergistically contributed to a high volumetric capacity that remained as high as 1500 mA h cm^{-3} after 200 cycles. More importantly, the nanoscale system-engineering approach could be extended to other emerging high performance non-carbon electrodes with severe volume expansion.

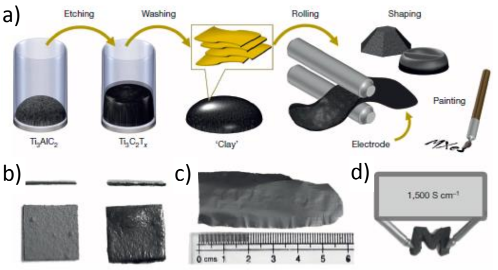

Figure 9. Schematic of MXene clay synthesis and electrode preparation. a) The fabrication and preparation process of MXene. b) Shrinking (left) and swelling (right) of MXene. c) Image of a rolled film and d) Shaped MXene into letter M with high conductivity. Reprinted with permission.[96]

Different from the general concept of hybrid materials that combines carbon and non-carbon materials, a new two dimensional material, titanium carbide (Ti$_3$C$_2$, a member of 'MXene' family) shows appealing properties in energy storage systems. Gogotsi *et al* recently developed a novel approach for the fabrication of Ti$_3$C$_2$, and the obtained hydrophilic material swelled in volume when hydrated, and can be shaped like clay and dried into various shape, from highly conductive solid to rolled thin film of tens micrometres thick as shown in **Figure 9.**[96] When this highly plastic clay-like material was shaped into thin films and serves as supercapacitor electrode in H$_2$SO$_4$ electrolyte, it delivered an extraordinary volumetric capacitance of up to 900 F cm^{-3}, which can be defined as the "first-generation" numbers that will extent the application of the non-oxide two dimensional materials. This kind of carbide materials possesses both high conductivity and excellent clay-like shaping properties, making this carbide suitable for energy storage with high volumetric performance.

The addition of non-carbon materials not only provides additional capacitance, but its intrinsic relatively high density can also contribute to improving the volumetric performance. It should be noted that the key to the fabrication of high performance carbon/non-carbon electrodes is the optimized interaction between different components and the fraction of non-carbon materials must be optimized so that a decreased conductivity or severe volume change is not harmful to the performance of the whole device.

4.3 Construction of micro-devices

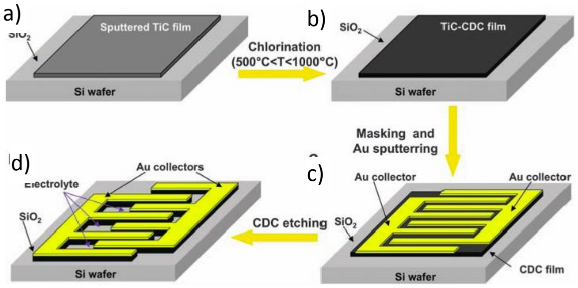

Figure 10. Schematic of the fabrication of a microsupercapacitor integrated onto a silicon chip based on a CDC film. Standard photolithography techniques are used for fabricating a CDC capacitor electrode and the deposition of the gold current collector. Reprinted with permission.[106]

As discussed in equation (1), the battery configuration is also important to the volumetric performance of EES devices, but few breakthroughs have been made. Recently, new techniques for the fabrication of micro EES devices make it possible to realize high volumetric performance, since their use in the micro/nano systems makes them have to deliver high volumetric performance, thus binder and current collector-free electrode is developed and electrolyte is always solid-state, which can minimize the volume of the integrated device. For example, micro-supercapacitors with short ion diffusion paths are considered highly competitive candidates for integrating various micro-electromechanical systems (MEMS) due to their high performance and particularly small size.[97-100] Much effort has been made to fabricate carbon electrodes for micro-supercapacitors and also to develop new techniques for the fabrication of high performance micro-supercapacitors.[101-106] Müllen *et al* proposed an efficient Layer-by-Layer (LBL) assembly and intercalation protocol for the fabrication of large, ultrathin, heteroatom-doped graphene films.[102] A micro-supercapacitor using this co-doped graphene film delivered an ultrahigh volumetric capacitance of 488 F cm^{-3} and an excellent rate performance up to 2000 V s^{-1}. A monolithic carbon film produced by well-controlled etching can also be used as an electrode for microsupercapacitors. Gogotsi *et al* developed a carbide-derived carbon monolithic film with a respectable volumetric capacitance up to 180 F cm^{-3} in TEABF$_4$ and 160 F cm^{-3} in 1 M H$_2$SO$_4$ as shown in **Figure 10.**[96, 106] This strategy provides a framework for the integration of high performance micro-EES devices into a series of devices. Lin *et al* also made great advances on the fabrication of high performance carbon-based microsupercapacitors.[107, 108] Microsupercapacitors based on 3D graphene/carbon nanotube carpets (G/CNTCs) hybrid is fabricated with excellent electrochemical performance. The unique seamless transition structure and water-etching significantly improved the conductivity and capacity, resulting in a high volumetric energy density of 2.42 mWh cm^{-3} in ionic liquid, and a high rate capability of 400 V s^{-1} with a power density of 115 W cm^{-3}. They also developed a one-step and scalable preparation of porous graphene from commercial polymer by a laser irradiation method (Figure 11), which allows for the roll-to-roll manufacturing of polymer written electronic and energy storage devices.

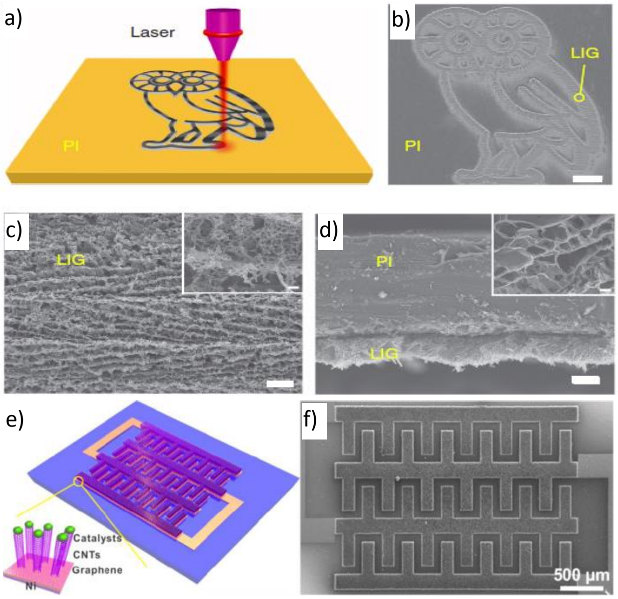

Figure 11. a)-d) Laser-induced graphene formed from commercial PI films using a CO$_2$ laser under ambient conditions. Copyright (2014) Nature Publishing Group. e) and f) Schematic and SEM images of the G/CNTCs based microsupercapacitor. Reprinted with permission.[107, 108]

Related studies on micro-EES devices show that, the volumetric performance is the most important criterion, thus, methods for fabricating the electrode materials used in these micro or flexible devices are critical due to the high standard of these electrodes. More advanced techniques also need to be developed to promote the real applications of micro-devices with high volumetric performance.

5. Next-generation EES devices calling for high volumetric performance of carbon materials

Next-generation EES devices including Li-S batteries, Li-O$_2$ batteries, Li-Se batteries, etc., show great potential in the future development of power sources due to their much higher energy density than current state-of-the-art EES devices.[3, 21, 22, 109-111] The use of new electrode materials is responsible for the revolutionary improved performance. Carbon materials still play an important role in these novel electrode materials, either as a conductive network or as active materials. Thus, the improvement of volumetric performance for the next-generation devices is also as important as in the case of Li-ion batteries and supercapacitors.

Taking Li-S batteries as an example, since a sulfur cathode is insulating and electrochemically unstable, carbon-sulfur hybrids have been used to overcome these obstacles. However, there is a huge gap between the volumetric capacity of a state-of-the-art sulfur-carbon cathode and the theoretical value of pure sulfur (3467 mAh cm^{-3}), and this is hindering the development of highly compact high-energy Li-S batteries. Generally, the use of carbon materials is essential to improve the conductivity of the sulfur cathode, and the porous structure of carbon can tackle the shuttle effect, leading to a better utilization of the active sulfur. Nonetheless, porous carbons usually have a low density and the sulfur loading is always restricted to low values to ensure satisfactory cathode performance. These factors result in a low density for most carbon/sulfur cathodes unless the nano/meso-texture is appropriately tailored. Such a low density causes a low volumetric performance of packed Li-S batteries, further hindering the advance to compact applications. Therefore, exploring an effective solution to the low volumetric capacity of the sulfur cathode is urgently required, and the key point is to construct novel carbon-sulfur assemblies, which combine both excellent electrochemical performance and high density.

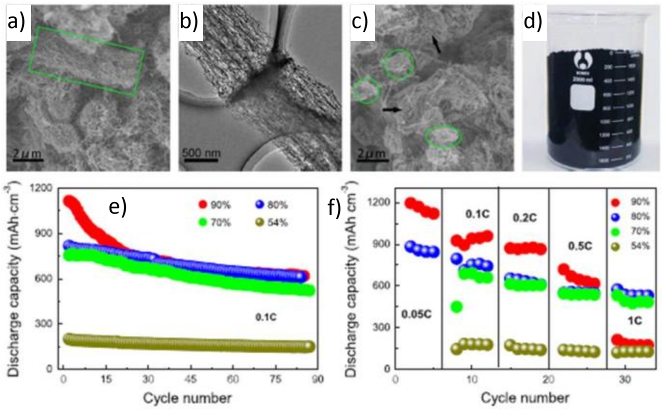

Figure 12. a) SEM and b) TEM of the pristine aligned CNTs. c) SEM and d) photograph of the aligned CNT/S composite. e) and f) cycle performance and rate performance of the aligned CNT/S composite with different sulfur content. Reprinted with permission.[112]

Some efforts have been made to meet the increasing demands for a high volumetric performance of Li-S batteries. One effective approach is to increase the sulfur content in the C/S electrode without sacrificing conductivity by finely controlling the interaction between carbon and sulfur. Zhang *et al* have developed a series of strategies for the industrialization of Li-S batteries.[112-115] They used aligned CNTs as the scaffold with an ultrahigh sulfur loading up to 90 wt % as shown in **Figure 12**. The aligned CNTs used have excellent alignment, a hierarchical pore structure, an extremely high conductivity, low density and low cost. They form an unblocked conductive network for sulfur, so that the sulfur content can be dramatically increased for practical use in Li-S batteries. As a result, a CNT/sulfur hybrid prepared by simple ball milling method had a high density of up to 1.98 g cm^{-3} with an ultrahigh volumetric capacity of 1116 mAh cm^{-3}, which is much higher than that for low sulfur contents. This study indicates a new route for improving the volumetric performance of EES devices through a simple but effective materials design.

Despite using a high sulfur content in the cathode of Li-S batteries to produce an ultrahigh volumetric performance, a more promising strategy is to densify the carbon matrix while maintaining an acceptable sulfur content for a better performance as we discussed above. Our group recently made advances in fabricating a high-density graphene/sulfur cathode for Li-S batteries with a promising volumetric performance as shown in Figure 13.[116] The high performance graphene/S hybrid was fabricated by pre-impregnating sulfur onto the graphene sheets from the redox reaction between H_2S and GO reported previously by our group,[117] which caused a partial reduction of the GO that triggers the spatial assembly of rGO due to the amphiphilic nature of the rGO sheets. Different drying processes were used to tune the microstructure of the as-prepared hydrogel and a high density of ~1.53 g cm^{-3} was reached by the evaporation-induced drying,[24] which is much higher than that produced by freeze drying. The resulting hybrid has a high density with abundant ink bottle-like pores, whose structure is similar to the "shumai" with graphene skin and sulfur stuff and this structure is beneficial for the confinement of sulfur. Such a unique high-density structure is responsible for the much improved volumetric capacity and cyclic stability. Our approach provides an effective solution for the advanced cathode with high volumetric performance in Li-S batteries and future efforts are being made to combine densification of the carbon matrix and increasing sulfur content to obtain a Li-S battery with higher volumetric performance. Similar to our protocal, Zhang *et al* also employed a graphene/sulfur hybrid by post-impregnating sulfur into a high-density graphene monolith,[118] which showed high volumetric performance as cathode materials for Li-S batteries.

Considering other energy storage systems, Na-ion batteries have a similar working principle to Li-ion batteries, although graphite is not suitable for the electrode of Na-ion batteries due

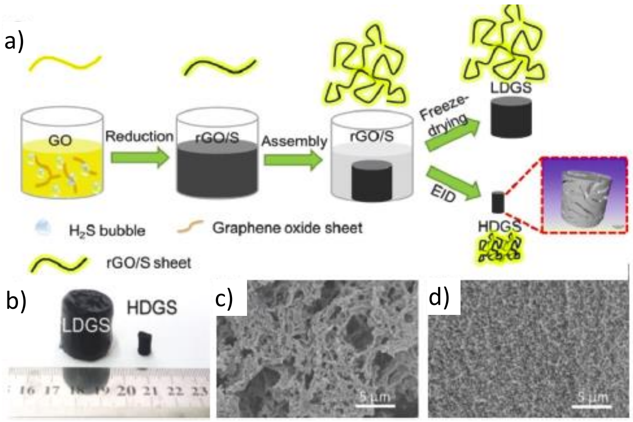

Figure 13. a) Illustration of the formation of HDGS and LDGS. b) Optical photos of LDGS and HDGS. SEM images of (c) LDGS and (d) HDGS. Reprinted with permission.[116]

to the larger ion size of Na^+ compared to Li^+.[110, 119, 120] Thus the carbon used in Na-ion batteries must have a larger interlayer spacing for the diffusion of Na^+. As a result, void space in the electrode is inevitable, and the volumetric performance will be impaired. Thus the fabrication of a novel electrode with both a tight structure and fast ion transport channels is urgently required. Li-air batteries, which convert the energy from oxygen, usually use porous carbons as the catalyst support, and their performance relies on the catalytic activity of the catalyst and the diffusion of O_2. In this case, the use of porous carbon has the same issue that a high diffusion rate is always at the expense of the volumetric performance. Our group developed a graphene/CNT all-carbon electrocatalyst with a hierarchical porous structure for the oxygen reduction reaction (ORR).[121] Electron transfer between graphene and CNTs facilitates the improved ORR catalytic performance and the readily structure tuning can further improve the volumetric performance. The recently developed Li-Selenium batteries are highlighted by their high volumetric performance compared with Li-S batteries due to their better electrical conductivity and intrinsic high density of Se, but porous carbon materials are also necessary to distribute and confine the selenium.[109, 122] The advanced energy storage systems discussed above are of great importance in the future development of large scale applications, and the solution for the volumetric performance is fatal for their broader uses.

6. Summary and Prospects

We have clarified the crucial importance of volumetric performance for the future development of EES devices, which is not limited to the currently commercial LIBs and supercapacitors, but far more important for the next-generation EES devices, such as Li-S, Na-ion batteries, etc. Detailed description of gravimetric and volumetric performance of EES devices is also presented in this review, and volumetric performance is especially crucial for carbon-based electrode materials since porous carbons always have a low density in order to ensure sufficient ion transport channels. The pursuit of high volumetric performance involves both the materials design and the battery configuration. For the materials, the key is to eliminate the redundant pores and maintaining the necessary surface area for energy storage. For the device, the inactive components should be minimized on the premise of structural stability. The design and modification of these porous carbons can effectively improve the volumetric performance from the materials viewpoint. The arise of graphene provides us an opportunity to design carbon and composite materials from the basic unit, and it has been widely used as the most promising building block to realize the construction of function-oriented structures of these carbon materials. Densifying carbons that contain porous channels for easy ion transfer accompanied by the formation of a spatially conductive network has proved to be the most promising route to realize a high volumetric performance of EES devices.

Structure design, interfacial assembly and microstructure control are effective for the fabrication of carbon-based electrode materials with high volumetric performance. Such structures should inherit the pore features of traditional porous carbon and have a high density and be easily manipulated. The assembly of graphene sheets is usually classified into two categories, face-to-face stacking and edge-to-edge or edge-to-face packing. The face-to-face stacking always results in graphite-like structures which have a high density and small interlayer spacing, but fast ion transport is usually limited by the tightly stacked graphene sheets. The spatial interlinking of graphene sheets provides sufficient space for ion transfer while sacrificing the density of the materials. Thus, increasing the interlayer spacing of the face-to-face stacked layers and decreasing the pore volume of the edge-to-edge interlinked graphene sheets can effectively lead to a balance between the high density and the ion transport, resulting in improved volumetric performance of the EES devices. Another important approach is the incorporation of non-carbon components with a high electrochemical capacity. The appropriate content of the non-carbon materials gives rise to a synergistic effect that improves the overall volumetric performance due to the intrinsic high volumetric capacity. The key issue for the incorporation of non-carbon components is the controllable interaction between carbon and non-carbon materials, so that the carbon materials contribute to the high conductivity and facilitate fast ion transport while the non-carbon materials are responsible for improving the overall capacity both from the gravimetric and volumetric aspects.

The battery configuration is also important for improved volumetric performance. A high volumetric performance is particularly required in micro-batteries or flexible batteries which are always used as power sources in nano/micro-systems. Thus, the fabrication of electrode materials with tuneable size, shape and flexibility is of great importance, which comes back to the point of materials design. The systematic exploration of the related components, including the matching of electrolyte, separator *etc* is of critical importance for compatibility with novel electrode materials. Furthermore, the fabrication process of the proof-of-concept batteries also needs innovative development to satisfy future requirements for next-generation smart devices. Among the future concepts, flexible EES devices are the most useful and promising system that is available for the real applications of commercial CEs, and more importantly, high volumetric performance must be emphasized as a requirement for flexible EES devices due to their potential use.

The use of carbon materials as electrodes or conductive additive in next-generation devices is also of great significance. The future applications of these EES devices need much better volumetric performance. Thus, improvement of the volumetric performance is urgently needed for next-generation EES devices. A high density carbon monolith as an effective S scaffold or the high sulfur content with well-designed carbon conductive network is believed to be the ultimate solution to the low volumetric performance of Li-S batteries. The carbons used in Na-ion batteries, Li-air batteries and Li-Se batteries, etc. also need to be fabricated with specific energy storage features.

Thus, the upgrade of EES devices with high volumetric performance is one of the primary tasks for the development of CEs and EVs in the coming years. We believe that the design and construction of novel carbon materials together with new devices structure integration will be of great significance for improving the volumetric performance of EES devices, which will accelerate the commercialization and applications of CEs and EVs.

Acknowledgements

We appreciate support from National Basic Research Program of China (2014CB932400), National Natural Science Foundation of China (Nos. U1401243, 51372167, 51302146 and 51311140260) and Shenzhen Basic Research Project (No. ZDSYS20140509172959981).

Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Towards superior volumetric performance: design and preparation of novel carbon materials for energy storage

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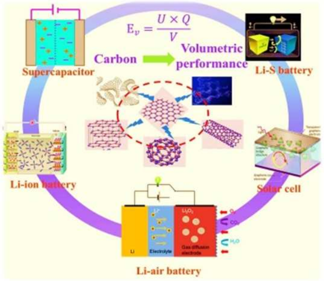
Graphical abstract



Design and fabrication of carbon materials are highlighted for high volumetric performance of EES devices.

Broader Context

Volumetric performance is critically important for electrochemical energy storage (EES) devices and their future development in consumer electronics (CEs) and electric vehicles (EVs). As the key component in EES devices, carbon material decides the applicability of these devices. However, most of carbon materials always bring low volumetric performance because of their relatively low density. In this review, we address the significance of volumetric performance to EES devices, and comprehensively summarize recent progresses to improve the volumetric performance, especially from the viewpoints of materials design and structure control of carbon materials, in which balancing the contradictory high density and suitable porous structure is crucial. The assembly from graphene provides an effective bottom-up strategy to build dense carbons, while hybridization with non-carbon and the construction of micro-devices are also promising for improving the volumetric performance. Next-generation EES devices including Li-S, Na-ion and Li-Se batteries are also commented. The improvement of volumetric performance involves system engineering and embraces materials science, electrochemistry and device fabrication to realize the upgrading of EES devices.