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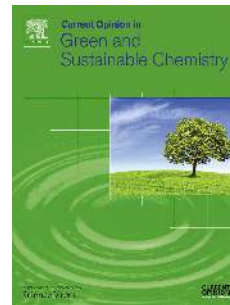
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Graphene-based supercapacitor electrodes: addressing challenges in mechanisms and materials

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Abstract

Electric double layer supercapacitors are a class of energy storage device whose strengths are long lifespan and high power handling. They have a niche to fill in the gradual transition to fully-electric transport systems, and are expected to have future applications in textile-based energy storage and flexible electronics. Relatively new electrode materials, based on graphene, offer an opportunity for improvement over the existing commercial standard of activated carbon, however challenges still lay ahead to bring more of these materials to market. In this review we discuss the scientific challenges in the development of novel electric double-layer supercapacitor electrodes, and present some recent highlights.

Keywords: graphene, supercapacitor, surface area, pore structure, electric double layer, pseudocapacitance.

1 Introduction

Supercapacitors (SCs) are a unique class of energy storage device that lie somewhere in between electrochemical batteries and traditional dielectric capacitors. They possess the capacity to be fully charged in seconds to minutes, and to release the stored electrical energy similarly quickly when required by their given application. SCs are known interchangeably as ultracapacitors, and electric double layer capacitors. They typically employ a layered construction consisting of two electrodes, separated mechanically by a thin porous membrane that is permeated by an electrolyte. The electrode materials are backed by a conductive current collector. The components are then stacked or rolled and packaged into individual cells, which may then be repeated in series or parallel to form modules.

In comparison to batteries, SCs are known for their high power density, low energy density and long lifecycle, characteristics which position SCs to complement lithium-ion batteries (LiB) in a growing global market. Many commercial SCs are specified with ratings of over one million cycles. In comparison, LiBs suffer around 20% loss after as few as 500-2000 low power cycles, depending on the exact chemistry employed (1-4). In terms of energy, an LiB may typically last around 20 times longer than an SC, when subjected to a low power discharge. For comparison of power handling, SCs may be charged and discharged at more than 100 times greater current density than LiBs, without detrimentally affecting the device (5).

The growing demand for *high power* electrical energy storage creates a strong opportunity for supercapacitors. There is considerable interest in the future use of SC energy storage for wearable and textile-based electronics (2, 6), as well as next-generation flexible electronics (7-10). Aside from these novel endeavours, transport-related applications are one of the most significant emerging markets. In use since 2006, the Capabus public transport network in Shanghai, China, is powered solely by supercapacitors (11). SCs are frequently

used in regenerative braking systems where they are able to recapture kinetic energy greater than 20% more efficiently than batteries (12-14). Another emerging example of market demand is as the low-impedance component of maximum-power-point-transfer systems for solar energy harvesting (15).

Presently, the major barriers to widespread SC uptake originate from their relatively poor energy density and *perceived* high cost (16). Interestingly, a significant literature already exists reporting on graphene-based electrode materials whose performance far exceeds the existing commercial benchmarks, (17-19) yet there appear to be few examples of these materials having matured to the stage of being market-viable. Factors contributing to this include: overlapping fundamental mechanisms, a wide variety of means to report performance making comparison challenging, as well as the intrinsic challenges of developing novel materials that are able to match or exceed the commercial scalability of the current standard. This brief review aims to introduce the mechanisms of charge storage in SC's and attempts to clarify some measurement issues, before specifically highlighting some achievements in the development of graphene-based devices.

2. Operation of SCs and electrode testing

The charge storage mechanism of SCs is different to that of batteries, or (polarised) dielectric capacitors. Similar to batteries, SCs employ an electrolyte, meaning there are mobile charge carriers between the electrodes. However, within an *ideal* SC only surface-localised fast-proceeding physical processes occur at the electrode-electrolyte interface. Batteries, on the other hand, employ slower redox reactions to store and release charge throughout the bulk of their active electrode materials. The resulting thermal and mechanical stresses are understood to be principal causes of LiB degradation (20). Additionally, high power cycling of LiBs may lead to increased cell impedance which in-turn further diminishes

the power handling of the cell and ultimately reduces its lifespan (21). Thus it is the difference in charge storage mechanisms that underpins the difference in cell characteristics, with particular reference to power handling and lifespan. The different mechanisms are schematically illustrated in figure 1 below.
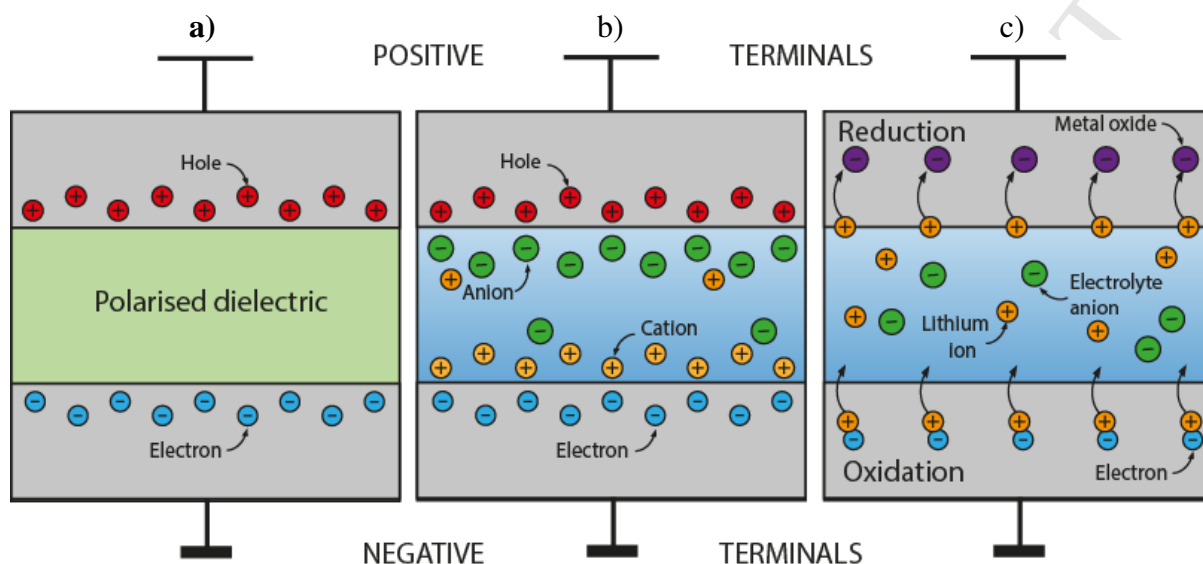
Figure 1: *A depiction of various electrical charge storage mechanisms with a) dielectric capacitance with wide charge separation, b) Electric double layer (EDL) type capacitance with much closer charge separation, and c) a Li-ion type redox battery. During **discharge** electrons will flow from the negative terminals through an external circuit and **either** recombine with holes (capacitive charge storage), or participate in a cathodic reduction reaction (battery storage). With permission from (16).*

In a real SC, some electrochemistry may occur at the surface, producing an effect known as pseudocapacitance. Pseudocapacitance in SCs is a surface localised phenomenon and so is a process that is not highly limited by insertion of ions into the bulk (it may proceed at high speed), but in every other way resembles the mechanism of rechargeable redox batteries. Therefore, pseudocapacitance generally reduces the lifecycle of devices, as compared to supercapacitors operating as purely electric-double-layer devices (22).

Differentiating pseudocapacitive effects from electric double layer (EDL) capacitance remains a challenge as in many ways it represents another middle ground between batteries

and electrolytic capacitors, i.e. between b) and c) in figure 1. Gogotsi et al. recently discussed some confusion that surrounds pseudocapacitance (23), suggesting that the difference in cyclic-voltammetry (CV) between storage mechanisms aides in determining the appropriateness of applying a capacitor storage metric, Farads (*F*) or battery-like storage metric, milli-Amp hours (mAh), to a material. This difference in CV testing loops is illustrated in figure 2. The letter criticises the use of pseudocapacitance as an excuse to classify battery-like materials as capacitive, and also encourages previously suggested naming conventions such as "oxide-supercapacitor" to avoid confusion with conventional (EDL-based) SCs (24-27).
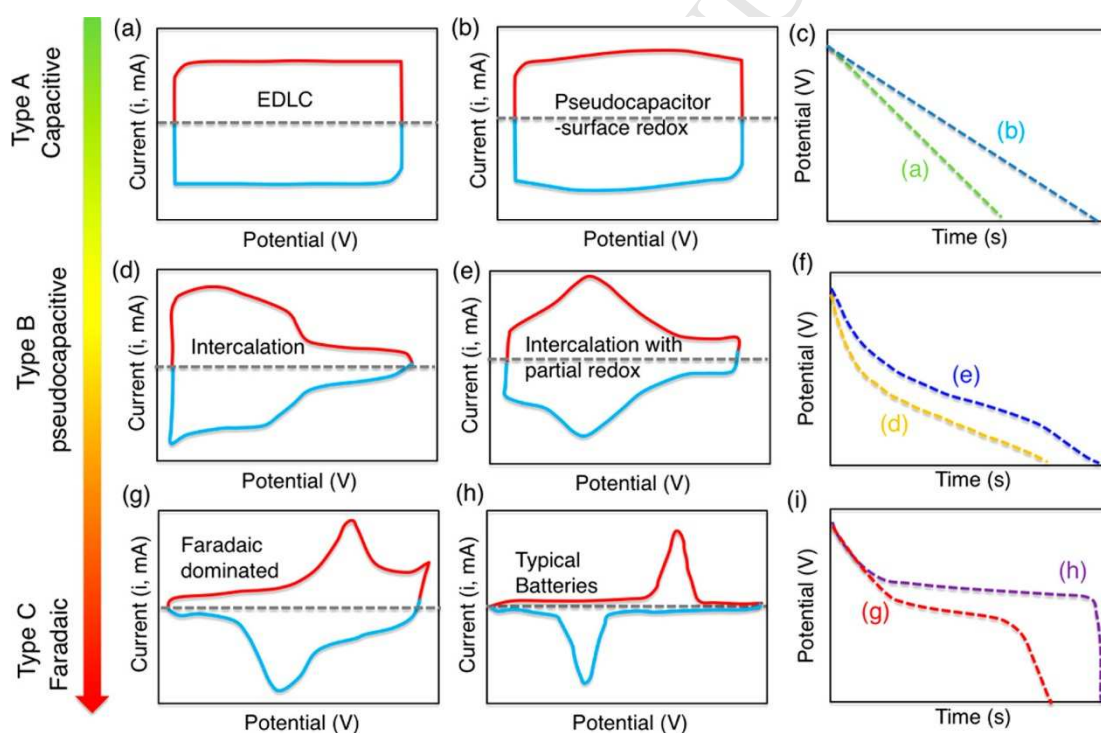
*Figure 2: Cyclic voltammogram schematic diagrams shown in a,b,d,e,g,h) and their respective galvanostatic discharge curves in c,f,i). Type A materials are distinctly capacitive and charge storage should be expressed in Farads. For Type C materials showing battery-like response, an appropriate battery metric should be used, e.g. mAh. Pseudocapacitive materials as with Type B are diffusion and/or intercalation limited and typically do not show current response that is independent of potential, and therefore arguably should also be classified as battery-like. Type A materials where storage is enhanced by **fast, surface**

localised pseudocapacitance, are to be clearly identified as such, for example by naming them as oxide-supercapacitors. Reprinted with permission from (23). Copyright 2018 American Chemical Society.

The difficulty presented by Gogotsi is that type A materials may present some contribution from pseudocapacitance (as with Figure 2b), however the current vs time response of such materials is *not* noticeably limited by diffusion or intercalation (of ions), and this makes them challenging to distinguish from purely EDL materials (as with Figure 2a). One may expect a slightly higher energy density and shorter life-span from materials like those in Figure 2b, however asserting that *all* other testing parameters have been held constant in a comparison study to a Figure 2a type material, is difficult. Distinguishing Type B materials as battery-like is somewhat more practical; Chen et al show that the intercalation and diffusion limited components of charge storage contribution can be separated from the capacitive contribution by plotting the total charge stored against $v^{-1/2}$, where v is the scan rate applied in CV testing (28).

When examining *capacitive* materials, their performance can be expressed using a number of metrics. The most frequently observed parameter in reporting of electrode material development is the electrode material capacitance (C_e) where the subscript e denotes 'electrode'. Most commonly seen are gravimetric/specific capacitance, volumetric capacitance, and electrode areal capacitance. These different normalisations can make direct comparison of results difficult, or even impossible if the parameters necessary for conversion are omitted. In addition, as will be discussed in section 3, peak results in any expression of C_e do not necessarily coincide with the performance of the material in a complete cell that has been constructed for *peak energy density* – the end goal in SC improvement.

Another factor impacting the comparison of related research, is the chosen methodology of testing electrodes, for example via three-electrode lab cells compared to two-electrode constructed cells. For a more detailed discussion of this and other lab-scale testing

issues, the reader is referred to Stoller et al. (29). The following section only cites performance data obtained from constructed test cells, i.e. two-electrode configuration, and also aims to clearly differentiate between *electrode material* figures and *constructed cell/device* performance data, where in the latter, the performance is normalised to the mass or volume of all cell components (separator, electrolyte, current collectors, and packaging).

3. Graphene-based electrode development

Presently, in the majority of commercial devices, highly porous activated carbons possessing specific surface area (SSA) values of around 1000 m²/g, are employed as the electrode active material (30). Typically, when using activated carbon as an electrode active material, a conductivity additive such as carbon black is combined with the active component in a range between 10-50 %wt. ratio, and a binder is added, between 10-40 %wt. of the dry electrode (30, 31).

Over the last decade, attention has been devoted to high SSA graphene-based materials including electrochemically exfoliated graphene (32), and in particular, various preparations and treatments of graphene oxide (GO) (33, 34) which are subsequently used to produce reduced graphene oxide (rGO) (35, 36), and doped rGO (37, 38). Graphene-based materials, defined by having a higher proportion of sp2 bonded carbons than sp3, show strong prospects as electrodes. Electrodes constructed from these materials have been shown not to require conductivity additive or binder (1, 39). Exploiting the electrical and mechanical advantages of these materials, in combination with rationally optimised pore structures that enable access to the maximum available SSA, will be of significant importance for further improvements in SC device performance. Table 1 below shows some recent highlights in graphene-based electrode material development.

Author & reference	Year	Electrode Description	Electrolyte	Current Collector	Areal load (mg/cm^2)	C_{grav} (F/g)	C_{areal} (F/cm^2)	Voltage (V)

Pan (40)	2018	BNP-HGH	EMIMBF4 in AN	Pt foil	10	316		3.5
Rasul (36)	2017	rIGO(hydrothermal) /w Nafion	1M H_2SO_4	glassy carbon		274		1
Pan (41)	2017	MnO$_2$@CNTs@3DGA-3.9 /w Ppy@CNTs@3DGA-1.92	Na$_2$SO$_4$ /w PVA	Au on polyimide	3.9 & 1.92	200	0.95	1.8
Wang (42)	2016	blade coated rGO	H_2SO_4 /w PVA	Au on polyimide	0.23	185	0.05	0.8
Wang (42)	2016	sprayed rGO	H_2SO_4 /w PVA	Au on polyimide	0.27	122	0.037	0.8
Yang N (43)	2016	Mg-rGO /w PTFE & carbon black	2M KOH	Nickel mesh	4	367.7		1
Yang Q (39)	2016	MWCNTs - ecrGO	1M HCL	Pt plate	1.8	177		0.8
Mei (37)	2015	MnO$_2$-N-rGO /w PTFE	1M Na$_2$SO$_4$	Nickel foam	3.6	275.2		1
Liu (44)	2013	Ultrasonically exfoliated graphene	H_3PO_4 /w PVA	Au on glass			0.000713	1.2

Table 1: *Summary of recent results on supercapacitors as a function of the electrode and electrolyte material. Uncommon and unused abbreviations in order of appearance are as follows, boron-nitrogen-phosphorus (doped) holey graphene hydrogel (BNP-HGH), 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4), acetonitrile (AN), carbon nanotubes (CNTs), 3D graphene aerogel (3DGA), polypyrrole (Ppy), polyvinyl alcohol (PVA), polytetrafluoroethylene (PTFE), multi-wall CNTs (MWCNTs).*

We want to draw particular attention to some of the results presented in Table 1, which demonstrate the implications of fabrication technique for the large-scale adoption of graphene-based electrodes.

Wang et al. applied a blade coating approach to produce electrode films from viscous solutions of liquid-crystal oriented GO (42), and compare this blade coating approach to a spray deposition method. Both methods produce additive-free electrodes, directly deposited onto Au coated polyimide current collectors. The blade coating approach is appealing as it is aligned to current supercapacitor manufacturing processes, and is readily scalable for films up to metres in size. The spray deposition is interesting for its simplicity, and for the fact that it is extremely easy to scale up to any size.
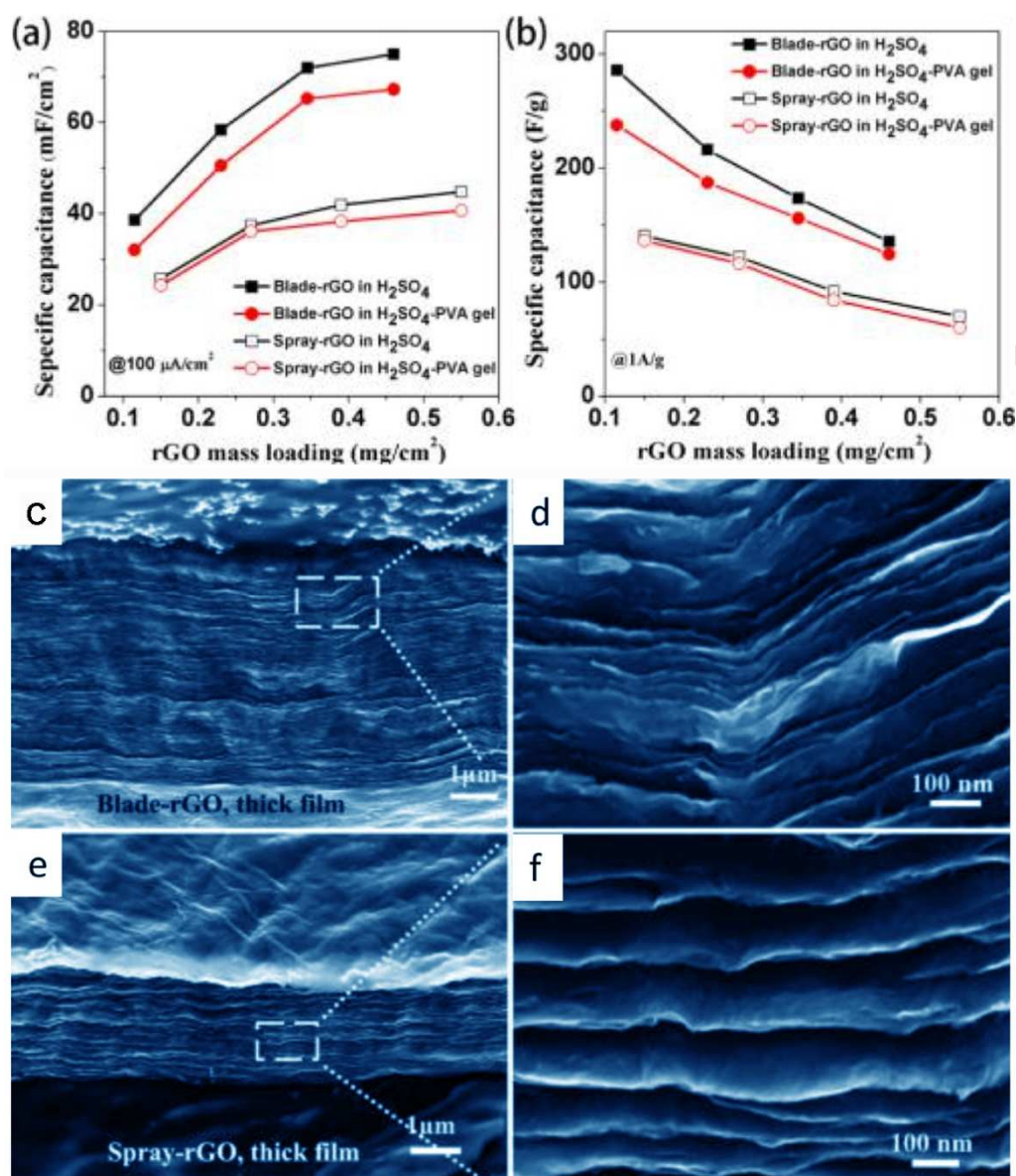
Figure 3: *Variation of specific capacitance of blade-rGO films vs spray-rGO films, with increasing mass loading. a) Areal specific capacitance. b) mass specific capacitance. (c-e) Field emission scanning electron microscopy (FE-SEM) images showing the cross sections of rGO films. (c and d) Blade-rGO film. (e and f) Spray-rGO film. Comparing panel d and f, a larger spacing between layers can be noticed for the spray coated film, a partial explanation for its lower volumetric capacitance. Adapted with permission from (42), American Chemical Society.*

Both the spray deposited and blade-coated films in the study were reduced hydrothermally, and the authors found that the latter outperforms the prior in every aspect (Fig 3a). The blade-coated films possess around 400 Ω/sq. lower sheet resistivity than the spray coated variant. This characteristic, joined to a higher packing density (as visible in

Figure 3c and 3d) ultimately lead to around double the *electrode* specific capacitance (F/g) for H_2SO_4 electrolyte and low film loading, when compared to the spray coated material (Figure 3b). However, Figure 3b also shows that increasing the areal loading (thickness) of a film reduces its gravimetric capacitance. Comparing Figure 3b and 3a, which both use the same x-axis values, it can be seen in Figure 3a that the *areal capacitance* will increase up to some plateau. This is of critical importance for moving novel materials beyond lab-scale work. Obtaining high specific capacitances for a given material by using very thin films, can be relatively straightforward. However in the context of a built device, if all other components (separator, current collectors etc.) were to remain of fixed dimensions, a thin film would contribute less mass to the device than a thicker film. Therefore it is around the plateau in areal capacitance vs areal loading (around $0.45 mg/cm^2$ in Figure 3a) where the greatest *device* energy density may be expected to be found. In the above case, reporting greatest device energy density could result in citing electrode material capacitance around 135 F/g, as opposed to the larger value of around 290 F/g that was achieved with thinner films (Figure 3b).

This areal loading issue has been highlighted in other studies as well. Pan et al acknowledge it in their work on a novel material comprising carbon nanotubes (CNTs) that are grown via chemical vapour deposition onto their fabricated 3D rGO aerogel (3DGA) material (41). This produces a high surface area interconnected foam-like material, denoted CNTs@3DGA, which is then functionalised by MnO_2 and poly-pyrole (Ppy) to produce all solid-state asymmetric supercapacitors (AASC) with electrodes that were loaded up to 10 mg/cm^2, comparable with current commercial devices. High loading is achievable because the foam-like material can be cut into slices of arbitrary thickness, and pressed to form electrodes. Peak results are reported for the *complete device* denoted AASC-3.9 (MnO2@CNTs@3DGA-3.9 with Ppy@CNTs@3DGA-1.92 where the suffix numbers refer

to the areal loading in mg/cm^2). A volumetric capacitance of 8.56 F·cm^{-3} at up to 1.8 V results in *device energy density* of 3.85 Wh/L.

This result demonstrates a method by which high loading of novel materials can be achieved. However these devices were enhanced by pseudocapacitance in their charge storage, as evidenced by examining the CV and galvanostatic charge/discharge curves in the full paper. In line with the recommendations of Simon et al. (45) these devices fit the profile of those that may be referred to as *oxide-supercapacitors*. Nevertheless, Pan and colleagues have continued to advance research in the use of rGO based hydrogels for electrodes that can reasonably be described as more purely EDL in their charge storage mechanism (40). In particular, they have explored various combinations of dopants on "holey" graphene hydrogels, which contain etched holes for improved porosity, and compare these against regular graphene hydrogels. Numerous types of device architecture are employed, including the use of organic electrolytes comparable to the existing commercial standard. For fully packaged symmetric cells with electrode materials ~150 μm thick and 10 mg/cm^2, they report *a device* energy density of 38.5 Wh.kg^{-1} / 57.4 Wh.L^{-1}, combined with power density of 83 kW.kg^{-1} / 55 kW.L^{-1}. If plotted onto a Ragone chart, such as in (5), it can be seen just how exceptionally promising this result is; it places the devices on-par with lead acid batteries for energy density, while maintaining the other desirable SC characteristics of high-power and long-life.

4. Conclusion

In this review we analysed how the structure and the chemical composition of electrode materials influences the energy density in SCs. While there are many examples throughout the literature of novel materials with capacitive (*F*) performance figures exceeding that of the current generation of supercapacitors, close scrutiny may reveal limitations in translating those figures to larger scale, or to commercial devices that maintain

the desirable characteristics of electric double layer supercapacitors. Amongst other reasons, this can stem from conflating of mechanisms and metric, extrapolating results obtained on bare electrodes to full scale devices without appropriate consideration, or from practical difficulties in scaling-up manufacturing processes.

Notwithstanding the challenges that remain, researchers have recently been paying particular attention to the abovementioned issues. Meanwhile genuine progress can be found in the development of novel nanomaterials, in particular graphene and graphene oxide. Given the overall advances in supercapacitor electrode construction, there is a strong opportunity for these devices to have far wider applications in the next generation of electronics and electrical energy storage such as in portable devices, automotive applications, and even household storage of solar energy.

5. Acknowledgements

6. References

1. Liu J, Mirri F, Notarianni M, Pasquali M, Motta N. High performance all-carbon thin film supercapacitors. Journal of Power Sources. 2015;274:823-30.
2. Huang C, Zhang J, Young NP, Snaith HJ, Grant PS. Solid-state supercapacitors with rationally designed heterogeneous electrodes fabricated by large area spray processing for wearable energy storage applications. Scientific reports. 2016;6.
3. Technologies M. The New K2 3.0V/3000F Cell. http://wwwmaxwellcom/products/ultracapacitors/k2-3-series. 2017;Acessed 2017/12/14.
4. Wieczorek M, Lewandowski M. A mathematical representation of an energy management strategy for hybrid energy storage system in electric vehicle and real time optimization using a genetic algorithm. Applied Energy. 2017;192:222-33.

5. Simon P, Gogotsi Y. Charge storage mechanism in nanoporous carbons and its consequence for electrical double layer capacitors. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences. 2010;368(1923):3457-67.

6. Aboutalebi SH, Jalili R, Esrafilzadeh D, Salari M, Gholamvand Z, Aminorroaya Yamini S, Konstantinov K, Shepherd RL, Chen J, Moulton SE. High-performance multifunctional graphene yarns: toward wearable all-carbon energy storage textiles. ACS nano. 2014;8(3):2456-66.

7. Liu A, Kovacik P, Peard N, Tian W, Goktas H, Lau J, Dunn B, Gleason KK. Monolithic Flexible Supercapacitors Integrated into Single Sheets of Paper and Membrane via Vapor Printing. Advanced Materials. 2017;29(19).

8. Xiao X, Peng X, Jin H, Li T, Zhang C, Gao B, Hu B, Huo K, Zhou J. Freestanding Mesoporous VN/CNT Hybrid Electrodes for Flexible All-Solid-State Supercapacitors. Advanced Materials. 2013;25(36):5091-7.

9. Xu Y, Lin Z, Huang X, Liu Y, Huang Y, Duan X. Flexible solid-state supercapacitors based on three-dimensional graphene hydrogel films. Acs Nano. 2013;7(5):4042-9.

10. Zequine C, Ranaweera C, Wang Z, Singh S, Tripathi P, Srivastava O, Gupta BK, Ramasamy K, Kahol P, Dvornic P. High Per formance and Flexible Supercapacitors based on Carbonized Bamboo Fibers for Wide Temperature Applications. Scientific reports. 2016;6.

11. Technology A. Ultra Capacitor City Bus. http://wwwaoweicom/en/case_viewphp?typeid=1&id=4. 2017;Accessed 18/12/17.

12. Burke A, Zhao H, editors. Applications of supercapacitors in electric and hybrid vehicles. 5th European Symposium on Supercapacitor and Hybrid Solutions (ESSCAP), Brasov, Romania; 2015.

13. Carignano MG, Costa-Castelló R, Roda V, Nigro NM, Junco S, Feroldi D. Energy management strategy for fuel cell-supercapacitor hybrid vehicles based on prediction of energy demand. Journal of Power Sources. 2017;360:419-33.

14. Deshpande R. Ultracapacitors: Future of Energy Storage: McGraw-Hill Education; 2014.

15. Barrade P, Delalay S, Rufer A. Direct connection of supercapacitors to photovoltaic panels with on–off maximum power point tracking. IEEE Transactions on Sustainable Energy. 2012;3(2):283-94.

16. Horn M, MacLeod J, Liu M, Webb J, Motta N. Supercapacitors: A new source of power for electric cars? Economic Analysis and Policy. 2018.

17. Wang B, Liu J, Zhao Y, Zheng D, Li Y, Sha J. 3D nanoporous graphene films converted from liquid-crystalline holey graphene oxide for thin and high-performance supercapacitors. Materials Research Express. 2018;5(1):015503.

18. Zhao Y, Liu J, Wang B, Sha J, Li Y, Zheng D, Amjadipour M, Macleod JM, Motta N. Supercapacitor Electrodes with Remarkable Specific Capacitance Converted from Hybrid Graphene Oxide/NaCl/Urea Films. ACS Applied Materials & Interfaces. 2017.

19. Zhao Y, Liu J, Wang N, Li Q, Hu M. Rational selection of small aromatic molecules to functionalize graphene for enhancing capacitive energy storage. Journal of Materials Chemistry A. 2018;6(17):7566-72.

20. Vetter J, Novák P, Wagner MR, Veit C, Möller KC, Besenhard JO, Winter M, Wohlfahrt-Mehrens M, Vogler C, Hammouche A. Ageing mechanisms in lithium-ion batteries. Journal of Power Sources. 2005;147(1):269-81.

21. Xu B, Oudalov A, Ulbig A, Andersson G, Kirschen DS. Modeling of Lithium-Ion Battery Degradation for Cell Life Assessment. IEEE Transactions on Smart Grid. 2018;9(2):1131-40.

22. **Simon P, Gogotsi Y. Materials for electrochemical capacitors. Nanoscience And Technology: A Collection of Reviews from Nature Journals: World Scientific; 2010. p. 320-9.

23. **Gogotsi Y, Penner RM. Energy Storage in Nanomaterials – Capacitive, Pseudocapacitive, or Battery-like? ACS Nano. 2018;12(3):2081-3.

24. Xu J, Yang C, Xue Y, Wang C, Cao J, Chen Z. Facile synthesis of novel metal-organic nickel hydroxide nanorods for high performance supercapacitor. Electrochimica Acta. 2016;211:595-

602.

25.   Yan Y, Gu P, Zheng S, Zheng M, Pang H, Xue H. Facile synthesis of an accordion-like Ni-MOF superstructure for high-performance flexible supercapacitors. Journal of Materials Chemistry A. 2016;4(48):19078-85.

26.   Yin D, Huang G, Sun Q, Li Q, Wang X, Yuan D, Wang C, Wang L. RGO/Co 3 O 4 composites prepared using GO-MOFs as precursor for advanced lithium-ion batteries and supercapacitors electrodes. Electrochimica Acta. 2016;215:410-9.

27.   Zhu J, Tang S, Wu J, Shi X, Zhu B, Meng X. Wearable High‐Performance Supercapacitors Based on Silver‐Sputtered Textiles with FeCo2S4–NiCo2S4 Composite Nanotube‐Built Multitripod Architectures as Advanced Flexible Electrodes. Advanced Energy Materials. 2017;7(2).

28.   Chen Z, Augustyn V, Jia X, Xiao Q, Dunn B, Lu Y. High-performance sodium-ion pseudocapacitors based on hierarchically porous nanowire composites. ACS nano. 2012;6(5):4319-27.

29.   Stoller MD, Ruoff RS. Best practice methods for determining an electrode material's performance for ultracapacitors. Energy & Environmental Science. 2010;3(9):1294-301.

30.   Pandolfo A, Hollenkamp A. Carbon properties and their role in supercapacitors. Journal of power sources. 2006;157(1):11-27.

31.   Barbieri O, Hahn M, Herzog A, Kötz R. Capacitance limits of high surface area activated carbons for double layer capacitors Problem at nm pore size described. Carbon. 2005;43(6):1303-10.

32.   Liu J, Notarianni M, Will G, Tiong VT, Wang H, Motta N. Electrochemically exfoliated graphene for electrode films: effect of graphene flake thickness on the sheet resistance and capacitive properties. Langmuir. 2013;29(43):13307-14.

33.   Chen J, Yao B, Li C, Shi G. An improved Hummers method for eco-friendly synthesis of graphene oxide. Carbon. 2013;64:225-9.

34.   Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, Alemany LB, Lu W, Tour JM. Improved synthesis of graphene oxide. ACS nano. 2010;4(8):4806-14.

35.   Park S, An J, Potts JR, Velamakanni A, Murali S, Ruoff RS. Hydrazine-reduction of graphite-and graphene oxide. Carbon. 2011;49(9):3019-23.

36.   *Rasul S, Alazmi A, Jaouen K, Hedhili M, Costa P. Rational design of reduced graphene oxide for superior performance of supercapacitor electrodes. Carbon. 2017;111:774-81.

37.   Mei J, Zhang L. Anchoring high-dispersed MnO2 nanowires on nitrogen doped graphene as electrode materials for supercapacitors. Electrochimica Acta. 2015;173:338-44.

38.   Mao J, Iocozzia J, Huang J, Meng K, Lai Y, Lin Z. Graphene aerogels for efficient energy storage and conversion. Energy & Environmental Science. 2018;11(4):772-99.

39.   Yang Q, Pang S-K, Yung K-C. Electrochemically reduced graphene oxide/carbon nanotubes composites as binder-free supercapacitor electrodes. Journal of Power Sources. 2016;311:144-52.

40.   **Pan Z, Zhi H, Qiu Y, Yang J, Xing L, Zhang Q, Ding X, Wang X, Xu G, Yuan H. Achieving commercial-level mass loading in ternary-doped holey graphene hydrogel electrodes for ultrahigh energy density supercapacitors. Nano energy. 2018;46:266-76.

41.   Pan Z, Liu M, Yang J, Qiu Y, Li W, Xu Y, Zhang X, Zhang Y. High Electroactive Material Loading on a Carbon Nanotube@ 3D Graphene Aerogel for High‐Performance Flexible All‐Solid‐State Asymmetric Supercapacitors. Advanced Functional Materials. 2017;27(27):1701122.

42.   **Wang B, Liu J, Zhao Y, Li Y, Xian W, Amjadipour M, MacLeod J, Motta N. Role of Graphene Oxide Liquid Crystals in Hydrothermal Reduction and Supercapacitor Performance. ACS Applied Materials & Interfaces. 2016;8(34):22316-23.

43.   Yang N, Xu X, Li L, Na H, Wang H, Wang X, Xing F, Gao J. A facile method to prepare reduced graphene oxide with nano-porous structure as electrode material for high performance capacitor. RSC Advances. 2016;6(48):42435-42.

44.   *Liu J, Galpaya D, Notarianni M, Yan C, Motta N. Graphene-based thin film supercapacitor
      with graphene oxide as dielectric spacer. Applied Physics Letters. 2013;103(6):063108.
45.   **Simon P, Gogotsi Y, Dunn B. Where do batteries end and supercapacitors begin? Science.
      2014;343(6176):1210-1.