3D Graphene-Based Anode Materials for Li-Ion Batteries

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Keywords: 3D hybrid anodes; graphene; Li-ion batteries; graphene-metal oxides; nanocomposites

Abstract

Advances in the synthesis and processing of nanocarbon materials particularly carbon nanotubes and graphene have presented the opportunity to design novel Li-ion battery (LIB) anode materials that can meet the power requirements of next-generation power devices. This mini-review presents an overview of recent studies on the electrochemical behavior of three-dimensional (3D) nanostructured anode materials formed by coupling graphene sheets with alloying type active material (metals or metal oxides). A number of promising 3D graphene-based hybrid anodes ranging from sheet-like, core-shaped, to foam-like morphologies are discussed. The significant improvement observed in the LIB performance of the 3D hybrid anodes is largely attributed to the unique properties of graphene and the resulting 3D architecture.

Introduction

Li-ion batteries (LIBs) hold substantial promise as the next-generation power devices due to their high-energy content, rechargeability, low self-discharge, high operating voltage, wide temperature window, and no “memory effect,” [1-3]. The huge interest in LIBs is evident in the rise in its global market value that has nearly doubled from \$11.6 billion in 2012 to 22.5 billion in 2016 [4]. However, current LIBs still lack a favorable combination of high rate capability, high reversible capacity, safety, and long cycle life that is required to meet the energy needs of future technologies especially in consumer appliances and the automotive industry. Therefore, there has been a major thrust to improve the properties of LIB components (electrodes and electrolyte) given the strong dependence of LIB performance (energy capacity, power density, and durability) on the components.

This review focuses on recent advances in improving the negative electrode (anode). Graphite, the current state-of-the-art anode material, is plagued by a variety of problems including relatively low theoretical specific capacity (~ 372 mAh/g), inhomogeneity in the structure, tortuous electrolyte diffusion paths, and high electrical and thermal resistances [5-7]. Also, graphite-based anode materials experience capacity deterioration at high cycling rate [8]. It is clear from the literature [7,9-11] that the current electrode material and design fundamentally limit the energy stored and the deliverable power per unit area, mass, and volume. The long transport distance and low intrinsic diffusivity of Li ions through the solid electrolyte interface (SEI) both contribute to the power density limitation observed in traditional LIBs [7,9,11]. Given the dependence of the storage capacity on the charge/discharge rates, research efforts continue to focus on increasing power density without any tradeoff in attainable storage capacity [12].

Recent efforts to improve the power density of LIBs have focused mainly on the use of nanostructured electrodes with unique architectures to decrease the diffusion distance of Li ions [7,9,11]. The characteristic time constant t for ionic diffusion is approximately proportional to the square of the diffusion distance L ($t \approx \frac{L^2}{D}$) where D is the diffusion constant [12-14]. This means that the use of three-dimensional (3D)

nanostructured electrodes with exceptionally short ion and electron transport distance (L) will result in a significant decrease in the value of t as demonstrated by several studies [9,11,13-20]. In addition, a porous 3D nanostructured electrode design is expected to provide better accommodation of the strain accompanying volume changes during cycling, and improved contact area with the electrolyte thereby increasing the Li ion flux across the interface. The search for higher capacity electrode materials have focused on alloying type materials such as metals and metal oxides (Si, Co_3O_4 , Fe_3O_4 , MoO_2 , SnO_2 , etc.) due to their significantly higher specific capacities in comparison to graphite. However, the use of these materials as anodes is plagued by poor cycling performances due to their poor conductivity, large volume expansion during cycling, and structural degradation via aggregation or pulverization [15,18,20,21].

An effective strategy for resisting the volume expansion of metal or metal oxide anodes during cycling and improving their low intrinsic electrical conductivity is to fabricate hybrid anodes by integrating carbon nanomaterial with the active material. The use of graphene, a 2D hexagonal lattice of sp^2 carbon atoms [22], for the construction of 3D hybrid anodes is a promising route to alleviate these issues. Graphene is known to have outstanding properties, in terms of electronic conductivity, thermal stability, structural flexibility, and surface area that make it well suited as a building block in 3D architectures. The use of 3D graphene architecture as host of metal/metal oxide active materials in anodes has several advantages [23]. Graphene serve as efficient and reliable conductive channels; graphene nanosheets facilitate charge transfer during the cycling process by forming an electrically conductive network with nanoparticles [21]. 3D graphene structure provides void spaces for accommodation of the volume expansion that occurs during Li insertion and extraction. The porosity, favorable geometry, and 3D conductive network provide short path length for Li ion and electron transport that result in high rate capabilities. Pristine graphene exhibit a high reversible capacity of 1264 mAh /g at low current density (50 – 100 mA/g) [24,25], therefore, the use of 3D graphene as host could provide additional Li ion storage. The anchoring of the nanoparticles or active materials on the graphene surface prevents agglomeration of the nanoparticles. However, it should be noted that the high surface area of 3D graphene host structure leads to excess irreversible capacity due to the

increased edge sites that bind strongly to Li and promote decomposition of electrolyte to form SEI layer [26]. Current strategies to decrease the irreversible capacity include introducing additives to common LiF₆-based electrolytes to enhance the stability of the resulting SEI layer [27], using pre-lithiated electrode materials to store extra Li ions before 1st cycle [28], and plugging the micropores of electrodes by Li₂CO₃ (the main component of SEI layer) to reduce the surface area of SEI [29]. Another issue with 3D graphene-based structures is the relatively low volumetric capacity due to the low packing density of active materials in the highly porous host structure. To increase the loading density of active materials, the use of compressible 3D graphene-based aerogel [30] or shrinkable holy graphene-based hydrogel [31] have been explored.

In this review, we present an overview on the electrochemical behavior of 3D nanostructured anode materials formed by the coupling of graphene and alloying type active material. Based on theoretical calculations by Landi *et al.* [32], dramatic enhancement in LIB performance of over 50% is anticipated for 3D nanocarbon electrodes. In the following, the anode design, synthesis process, and LIB performance of promising 3D graphene-based anode materials are discussed; the hybrid materials can broadly be classified in terms of their structure and composition: sheets-like, core-shell shaped, and foams. A comparison of the electrochemical performance of representative 3D graphene-based anodes is summarized in Table 1.

Sheets-like 3D graphene-based anodes synthesized via in situ and ex situ methods

The sheet-like shaped graphene-based anodes have become the most common 3D architectures for LIBs. The graphene sheets and the active materials (usually in the form of nanoparticles) are combined, resulting in nanoparticles deposited on the sheets that tangle together to form unique 3D anode materials. The sheet-like 3D graphene-based anodes are synthesized via either in-situ or ex-situ assembly of nanomaterials on graphene sheets. A widely used in situ assembly method is hydrothermal process, which yields stronger interactions between the nanoparticle and the graphene sheets. In addition, the synthesized porous 3D nanocomposites are well adapted to accommodate the volume expansion during cycling. As an example, Rai *et al.* [21] used a urea-assisted auto-combustion method to fabricate Co₃O₄ nanoparticles/graphene

nanosheets as shown in Figure 1a. The process resulted in a nanocomposite containing 25 – 50 nm Co_3O_4 and CoO nanoparticles deposited on the graphene nanosheets. The nanocomposite electrode delivered an initial charge capacity of 890 mAh/g and exhibited 90% capacity retention after 30 cycles while the reversible capacity of the pure Co_3O_4 nanoparticles anode fades continuously, showing a capacity retention of only 60% after 30 cycles. The observed difference in LIB performance is attributed to the 3D porous structure of $\text{Co}_3\text{O}_4/\text{CoO}/\text{graphene}$ nanocomposite (Figure 1b) and the intimate contact between the nanoparticles and graphene sheets. In the case of the pure Co_3O_4 nanoparticles, there is severe nanoparticle aggregation (Figure 1c) that is detrimental to LIB performance. Other studies [20,23] have observed similar trends whereby the 3D graphene/metal oxide nanoparticle anodes have consistently shown significantly better LIB performance than the pure nanoparticle anode. 3D graphene-based electrodes involving diverse cobalt sulfide compounds (CoS_2 , CoS , Co_9S_8) and Fe_2O_3 synthesized by various hydrothermal methods have also been reported to show excellent cycling durability and high rate capability [33,34]. Besides parallel graphene-based sheet anodes discussed so far, vertically aligned graphene sheets on a Cu current collector for LIB anode has been fabricated by microwave plasma-enhanced chemical vapor deposition as shown by Xiao *et al.* [35]. Owing to the direct transport of electrons and ions from the current collector to the electrolyte along aligned graphene sheets, aligned anodes are expected to exhibit significantly improved rate capability. As examples, after in-situ deposition of Si or Sn nanoparticles on the aligned graphene sheets, the resulting anodes exhibited outstanding rate capability and higher specific capacity; Figure 2 shows images of pristine vertically aligned graphene (VAGN) and the well-dispersed Sn-encapsulated graphene on VAGN (Sn@GS-VAGN), as well as the excellent rate capability of the Sn@GS-VAGN [36,37].

A second approach that has been used to synthesize sheet-like 3D graphene-based anodes is *ex situ* assembly of graphene and metal/metal oxide nanomaterials. A typical *ex situ* method involves a two-step process of synthesis of nanoparticles, followed by their deposition on graphene sheets, usually via vacuum filtration. As examples, Liu *et al.* [38] synthesized a free-standing, binder-free CuO

nanosheets/graphene hybrid lamellar paper while Kim *et al.* [39] synthesized a gold-coated silicon nanowire/graphene (Au-SiNWs/G) hybrid film anode by vacuum filtration using an anodic aluminum oxide membrane. The CuO nanosheets/graphene sample demonstrated excellent cyclic retention with the specific capacity of 736.8 mAh/g after 50 cycles (Figure 3). The binder-free Au-SiNWs/G composite with the unique 3D structure showed higher energy density (reversible capacity of 1520 mAh/g) than the binder-based composites and pure SiNWs.

Recent reports on the synthesis of 3D sandwich-type architecture involving graphene have focused on Co-based materials. Du *et al.* [40] details a facile and low-cost method to embed Co₃S₄ porous nanosheets in graphene sheets (Co₃S₄-PNS/GS) via freeze drying and subsequent hydrazine treatment (Figure 4a). The resulting Co₃S₄-PNS/GS benefits from the synergistic effect of the two components (Figures 4b and c), evidenced by the outstanding rate capability and cycling stability (showed a specific capacity of 710 mAh/g after 200 cycles). The improved LIB performance of Co₃S₄-PNS/GS anode is attributed to the enhanced electron and Li ion kinetics, larger surface area, and mechanical flexibility provided by the graphene nanosheets in the composites.

3D core-shell fabrication by layer-by-layer assembly

An effective strategy for resisting the volume expansion of Si anodes during cycling and improving the low intrinsic electrical conductivity is to integrate carbon nanomaterial with Si nanoparticles. The combination of graphene and Si nanoparticles in a 3D architecture has been shown to improve the cycling stability of the anodes [41-43]. For example, Zhu *et al.* [43] adopted the electrostatic self-assembly method to wrap negatively charged graphene on the positively charged silicon nanowires. The resulting Si-graphene hybrid with a core-shell structure enhances the conductivity of Si nanowires, diffusion of ions and electrons, and the accommodation of the Si expansion during cycling. Another approach that has been used to integrate graphene and Si is layer-by-layer assembly followed by in situ magnesiothermic-reduction. Due to its unique structural features, the 3D core-shell SiO₂ microspheres-graphene network exhibited significantly enhanced LIB performance (specific capacity, cycling stability and rate capability) compared to the bare Si

spheres [41]. Graphene-wrapped electrode active materials have been encapsulated in graphene sheets via several methods. A promising example is graphene nanoscrolls consisting of roll-up graphene nanosheets with a unique tubular structure, which has been touted as an excellent substrate for electrode active materials, as the tubular cavities can provide pathways for ion transport while the outermost graphitic layer can facilitate efficient electron transport [44-46]. The nanoscrolls are characterized by scrolled conformation, porous structure, adjustable interlayer distance and ends/edges that are open-ended cylindrical structure [46]. The effective use of graphene-based nanoscroll geometry with TiO₂ (B) nanowires to achieve improved LIB performance has been demonstrated by Li *et al.* [44].

3D graphene foams

We note that an advantage of integrating graphene with electrode active materials in composites is that it inhibits the inevitable agglomeration and restacking of graphene sheets due to the strong π - π interactions and van der Waals forces; this problem significantly reduces the specific surface area and lowers the electron and ion transport [47-49]. Recent efforts to exploit the outstanding properties of graphene in LIB anodes have also focused on depositing electrode active materials on 3D graphene foams. Studies [50-53] have shown that 3D graphene aerogel foams can overcome the restacking issue associated with graphene to some extent and provide a porous structure with large surface area and fast electron transport kinetics due to the continuous graphene backbone. As examples, the synthesis of 3D graphene foams via templated-assisted and gel-assisted approaches is discussed. In the case of templated-assisted method, 3D graphene is grown on various templates such as polymer microspheres, carbon skeletons, or metal/metal oxide foams. In Huang's work [54], binder-free MoO₂ nanoparticles were uniformly anchored on the surface of graphene/Ni foam *via* a facile CVD process as shown in Figure 4a. The enhanced capacity and rate performance of MoO₂/graphene foam compared to bulk MoO₂ and pure graphene foam can be ascribed to the synergistic effect between MoO₂ nanoparticles and graphene layers. For the gel-assisted method, Wang *et al.* [55] developed a solvothermal-induced self-assembly process for the synthesis of a macroscopic SnO₂/N-doped 3D graphene foam; the electrode exhibited extraordinarily prolonged cycling stability at

high current densities. A bottom-up strategy assisted by atomic layer deposition was utilized by Luo *et al.* [18] to synthesize a 3D graphene foam/ Fe_3O_4 composite (Figures 5a and b) that exhibited a high reversible capacity and excellent rate capability even at a high C-rate of 60C (Figures 5c and d).

Given the enhancement in cycle life and Li storage capacity observed in N-doped graphene [56], the use of doped graphene in 3D architectures has also been explored. Chemically derived methods [57,58] and a chemical vapor deposition technique [59] have been developed to produce heteroatom-doped graphene with stable reversible capacity at high discharging and charging rate. The SnO_2 /N-doped 3D graphene foam mentioned above is an example of doped 3D graphene-based hybrid anodes. Also, using 7, 7, 8, 8-tetracyanoquinodimethane as nitrogen precursor, Wang *et al.* [60] synthesized N-doped graphene- SnO_2 sandwich paper that exhibited very high capacity, high rate capability and outstanding cycling stability. The performance is attributed to several factors including nitrogen doping that creates surface defects, short transport distance of Li ions and electrons, and the huge elastomeric space to accommodate volume changes during cycling. Other 3D N-doped hybrid anodes with high LIB performance that have been reported include Fe_3O_4 /N-doped graphene foam and MnO /N-doped graphene nanosheets [61,62].

Perspective

Although 3D nanocarbon-based electrodes hold great promise in improving LIB performance, the challenges associated with their synthesis, dimensional control, and high electrode–electrolyte surface area that induces the high irreversible capacity have continued to hinder their widespread application in LIBs. In addition, there is little mechanistic understanding of the complex interactions within the multicomponent 3D electrode system (current collector, active material, and electrolyte). Consequently, there is currently a complete lack of guidelines for the rational design and synthesis of high-performance 3D nanostructured electrodes. The seminal review paper on 3D nanostructured electrodes by Rolison *et al.* [11] describes the major barrier limiting the innovative synthesis of complex 3D nanostructured electrodes for energy storage and conversion applications as “understanding the physical, chemical, and electrochemical interactions within multicomponent nanoscale systems.” Future computational and experimental studies are required to

illuminate the interrelationships between the properties (structural and chemical) of 3D nanocarbon-based electrodes and the LIB performance. As examples, density functional theory (DFT)-based first principle calculations can be applied to predict delithiated and lithiated phases, average lithium intercalation voltage, charge distribution, phase stability and transformation, and lithium diffusion kinetics [63,64] while pair distribution function (PDF) analysis is a powerful approach for understanding the local structural changes that occur in the electrode during cycling [65]. Advances in nanocarbon materials particularly carbon nanotubes and graphene have presented the opportunity to design novel energy storage materials that can meet the power requirements of next-generation power devices. However, there are still fundamental challenges in the characterization of the complex 3D morphology. Electron tomography could become a powerful technique for 3D imaging and compositional mapping of 3D electrodes. The combination of electron tomography and gas physisorption data may yield a complete picture of the aperiodic 3D electrode structure. In this review, we have summarized recent progress in the development of 3D graphene-based hybrid anodes for rechargeable LIBs. A selection of promising anodes with sheet-like, core-shaped or foam morphologies have been discussed. The improved LIB performance observed for the 3D hybrid anodes is attributed to several factors including high Li-ion flux across the interface, short diffusion pathways for both Li ions and electrons, abundant active sites for Li storage, and high freedom for volume change during charging/discharging.

Acknowledgements

This material is based upon work supported by the National Science Foundation under Award No. EPS-0903806 and matching support from the State of Kansas through the Kansas Board of Regents.

References and recommended reading

Papers of particular interest, published within the period of review have been highlighted as:

- of special interest
- of outstanding interest

References Cited

1. Tarascon JM, Armand M: **Issues and challenges facing rechargeable lithium batteries**. *Nature* 2001, **414**:359-367.
2. Mukherjee R, Krishnan R, Lu T-M, Koratkar N: **Nanostructured electrodes for high-power lithium ion batteries**. *Nano Energy* 2012, **1**:518-533.
3. Ji L, Lin Z, Alcoutlabi M, Zhang X: **Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries**. *Energy Environ. Sci.* 2011, **4**:2682-2699.
4. Young A: **Market For Lithium-Ion Batteries Seen Doubling Through 2016 to Over \$22 Billion**. In *International Business Times*. Edited by. New York; 2013.
5. Broussely M, Biensan P, Simon B: **Lithium insertion into host materials: the key to success for Li ion batteries**. *Electrochim. Acta* 1999, **45**:3-22.
6. de las Casas C, Li W: **A review of application of carbon nanotubes for lithium ion battery anode material**. *J. Power Sources* 2012, **208**:74-85.
7. Long JW, Dunn B, Rolison DR, White HS: **Three-Dimensional Battery Architectures**. *Chem. Rev.* 2004, **104**:4463-4492.
8. Kim S-S, Kadoma Y, Ikuta H, Uchimoto Y, Wakihara M: **Electrochemical Performance of Natural Graphite by Surface Modification Using Aluminum**. *Electrochem. Solid-State Lett.* 2001, **4**:A109-A112.
9. Arthur TS, Bates DJ, Cirigliano N, Johnson DC, Malati P, Mosby JM, Perre E, Rawls MT, Prieto AL, Dunn B: **Three-dimensional electrodes and battery architectures**. *MRS Bull.* 2011, **36**:523-531.
10. Candelaria SL, Shao Y, Zhou W, Li X, Xiao J, Zhang J-G, Wang Y, Liu J, Li J, Cao G: **Nanostructured carbon for energy storage and conversion**. *Nano Energy* 2012, **1**:195-220.
11. Rolison DR, Long JW, Lytle JC, Fischer AE, Rhodes CP, McEvoy TM, Bourg ME, Lubers AM: **Multifunctional 3D nanoarchitectures for energy storage and conversion**. *Chem. Soc. Rev.* 2009, **38**:226-252.
- This is a comprehensive review on 3D nanoarchitectures.
12. Hayner CM, Zhao X, Kung HH: **Materials for Rechargeable Lithium-Ion Batteries**. *Annu. Rev. Chem. Biom. Eng.* 2012, **3**:445-471.
13. Zhang H, Yu X, Braun PV: **Three-dimensional bicontinuous ultrafast-charge and -discharge bulk battery electrodes**. *Nat. Nanotechnol.* 2011, **6**:277-281.
14. Roberts M, Johns P, Owen J, Brandell D, Edstrom K, El Enany G, Guery C, Golodnitsky D, Lacey M, Lecoeur C, et al.: **3D lithium ion batteries-from fundamentals to fabrication**. *J. Mater. Chem.* 2011, **21**:9876-9890.
15. Dong X-C, Xu H, Wang X-W, Huang Y-X, Chan-Park MB, Zhang H, Wang L-H, Huang W, Chen P: **3D Graphene-Cobalt Oxide Electrode for High-Performance Supercapacitor and Enzymeless Glucose Detection**. *ACS Nano* 2012, **6**:3206-3213.
16. Dunn B, Long JW, Rolison DR: **Rethinking Multifunction in Three Dimensions for Miniaturizing Electrical Energy Storage**. *Interface* 2008, **17**:49-53.
17. Haag JM, Pattanaik G, Durstock MF: **Nanostructured 3D Electrode Architectures for High-Rate Li-Ion Batteries**. *Adv. Mater.* 2013, **25**:3238-3243.

18. Luo J, Liu J, Zeng Z, Ng CF, Ma L, Zhang H, Lin J, Shen Z, Fan HJ: **Three-Dimensional Graphene Foam Supported Fe₃O₄ Lithium Battery Anodes with Long Cycle Life and High Rate Capability**. *Nano Lett.* 2013, **13**:6136-6143.
 •• This paper reports a new strategy to couple bicontinuous Fe₃O₄ nanostructures on 3D graphene foams to form 3D electrodes that show high reversible capacity and high rate capability.
19. Maruyama B, Durstock MF, Pierce NA, Carlin PS, Pattanaik G, Haag JM, Hooper D, Sargent G, Amama PB, Rao R: **Electrochemical Energy Storage Materials**. Edited by: Air Force Research Lab, Wright-Patterson AFB, OH - Materials and Manufacturing Directorate (AFRL-RX-WP-TR-2012-0349); 2012.
20. Wang G, Wang B, Wang X, Park J, Dou S, Ahn H, Kim K: **Sn/graphene nanocomposite with 3D architecture for enhanced reversible lithium storage in lithium ion batteries**. *J. Mater. Chem. A* 2009, **19**:8378-8384.
21. Rai AK, Gim J, Anh LT, Kim J: **Partially reduced Co₃O₄/graphene nanocomposite as an anode material for secondary lithium ion battery**. *Electrochim. Acta* 2013, **100**:63-71.
 •• A simple and rapid urea-assisted, auto-combustion approach for the synthesis of high-performance Co₃O₄/graphene nanocomposite anode is reported.
22. Avouris P, Dimitrakopoulos C: **Graphene: synthesis and applications**. *Mater. Today* 2012, **15**:86-97.
23. Lian P, Zhu X, Xiang H, Li Z, Yang W, Wang H: **Enhanced cycling performance of Fe₃O₄-graphene nanocomposite as an anode material for lithium-ion batteries**. *Electrochim. Acta* 2010, **56**:834-840.
24. Lian P, Zhu X, Liang S, Li Z, Yang W, Wang H: **Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries**. *Electrochim. Acta* 2010, **55**:3909-3914.
25. Pan D, Wang S, Zhao B, Wu M, Zhang H, Wang Y, Jiao Z: **Li storage properties of disordered graphene nanosheets**. *Chem. Mater.* 2009, **21**:3136-3142.
26. Omichi K, Ramos-Sanchez G, Rao R, Pierce N, Chen G, Balbuena PB, Harutyunyan AR: **Origin of Excess Irreversible Capacity in Lithium-Ion Batteries Based on Carbon Nanostructures**. *J. Electrochem. Soc.* 2015, **162**:A2106-A2115.
27. Lu W, Chen Z, Joachin H, Prakash J, Liu J, Amine K: **Thermal and electrochemical characterization of MCMB/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ using LiBoB as an electrolyte additive**. *J. Power Sources* 2007, **163**:1074-1079.
28. Libich J, Vondrak J, Sedlarikova M, Maca J, Frk M: **Suppressing of Irreversible Capacity in Lithium-ion Batteries**. *Portugaliae Electrochim. Acta* 2013, **31**:297-306.
29. Mukai SR, Hasegawa T, Takagi M, Tamon H: **Reduction of irreversible capacities of amorphous carbon materials for lithium ion battery anodes by Li₂CO₃ addition**. *Carbon* 2004, **42**:837-842.
30. Cao H, Zhou X, Deng W, Liu Z: **A compressible and hierarchical porous graphene/Co composite aerogel for lithium-ion batteries with high gravimetric/volumetric capacity**. *J. Mater. Chem. A* 2016, **4**:6021-6028.
31. Wang X, Lv L, Cheng Z, Gao J, Dong L, Hu C, Qu L: **High-Density Monolith of N-Doped Holey Graphene for Ultrahigh Volumetric Capacity of Li-Ion Batteries**. *Adv. Energy Mater.* 2016, **6**:n/a-n/a.
32. Landi BJ, Cress CD, Raffaella RP: **High energy density lithium-ion batteries with carbon nanotube anodes**. *J. Mater. Res.* 2010, **25**:1636-1644.
33. Huang G, Chen T, Wang Z, Chang K, Chen W: **Synthesis and electrochemical performances of cobalt sulfides/graphene nanocomposite as anode material of Li-ion battery**. *J. Power Sources* 2013, **235**:122-128.

34. Cao K, Jiao L, Liu H, Liu Y, Wang Y, Guo Z, Yuan H: **3D Hierarchical Porous α -Fe₂O₃ Nanosheets for High-Performance Lithium-Ion Batteries.** *Adv. Energy Mater.* 2015, **5**.
35. Xiao X, Liu P, Wang JS, Verbrugge MW, Balogh MP: **Vertically aligned graphene electrode for lithium ion battery with high rate capability.** *Electrochem. Commun.* 2011, **13**:209-212.
36. Li N, Jin S, Liao Q, Cui H, Wang CX: **Encapsulated within graphene shell silicon nanoparticles anchored on vertically aligned graphene trees as lithium ion battery anodes.** *Nano Energy* 2014, **5**:105-115.
- This paper reports the direct growth of vertically aligned graphene on current collectors that serve as supports for subsequent introduction of the active material (SnO₂ nanoparticles); the resulting composite structure provides short diffusion distance for ions and electrons and an ultra-thin, flexible graphene sheet to accommodate the structural changes during cycling.
37. Li N, Song H, Cui H, Wang C: **Sn@graphene grown on vertically aligned graphene for high-capacity, high-rate, and long-life lithium storage.** *Nano Energy* 2014, **3**:102-112.
38. Liu Y, Wang W, Gu L, Wang Y, Ying Y, Mao Y, Sun L, Peng X: **Flexible CuO nanosheets/reduced-graphene oxide composite paper: binder-free anode for high-performance lithium-ion batteries.** *ACS Appl. Mater. Interfaces* 2013, **5**:9850-9855.
39. Kim H-J, Lee SE, Lee J, Jung J-Y, Lee E-S, Choi J-H, Jung J-H, Oh M, Hyun S, Choi D-G: **Gold-coated silicon nanowire-graphene core-shell composite film as a polymer binder-free anode for rechargeable lithium-ion batteries.** *Physica E* 2014, **61**:204-209.
40. Du Y, Zhu X, Zhou X, Hu L, Dai Z, Bao J: **Co₃S₄ porous nanosheets embedded in graphene sheets as high-performance anode materials for lithium and sodium storage.** *J. Mater. Chem. A* 2015, **3**:6787-6791.
- This article reports a facile and low-cost approach for the synthesis of Co₃S₄ porous nanosheet integrated with graphene sheets in a unique 3D sandwich-like architecture via freeze drying and subsequent hydrazine treatment that shows improved LIB performance.
41. Wu P, Wang H, Tang Y, Zhou Y, Lu T: **Three-dimensional interconnected network of graphene-wrapped porous silicon spheres: in situ magnesiothermic-reduction synthesis and enhanced lithium-storage capabilities.** *ACS Appl. Mater. Interfaces* 2014, **6**:3546-3552.
42. Ji J, Ji H, Zhang LL, Zhao X, Bai X, Fan X, Zhang F, Ruoff RS: **Graphene-Encapsulated Si on Ultrathin-Graphite Foam as Anode for High Capacity Lithium-Ion Batteries.** *Adv. Mater.* 2013, **25**:4673-4677.
43. Zhu Y, Liu W, Zhang X, He J, Chen J, Wang Y, Cao T: **Directing silicon-graphene self-assembly as a core/shell anode for high-performance lithium-ion batteries.** *Langmuir* 2013, **29**:744-749.
44. Li X, Zhang Y, Li T, Zhong Q, Li H, Huang J: **Graphene nanoscrolls encapsulated TiO₂ (B) nanowires for lithium storage.** *J. Power Sources* 2014, **268**:372-378.
45. Zeng F, Kuang Y, Wang Y, Huang Z, Fu C, Zhou H: **Facile Preparation of High-Quality Graphene Scrolls from Graphite Oxide by a Microexplosion Method.** *Adv. Mater.* 2011, **23**:4929-4932.
46. Zeng F, Kuang Y, Liu G, Liu R, Huang Z, Fu C, Zhou H: **Supercapacitors based on high-quality graphene scrolls.** *Nanoscale* 2012, **4**:3997-4001.
47. Wang R, Xu C, Sun J, Gao L, Lin C: **Flexible free-standing hollow Fe₃O₄/graphene hybrid films for lithium-ion batteries.** *J. Mater. Chem. A* 2013, **1**:1794-1800.
48. Luo J, Jang HD, Sun T, Xiao L, He Z, Katsoulidis AP, Kanatzidis MG, Gibson JM, Huang J: **Compression and aggregation-resistant particles of crumpled soft sheets.** *ACS Nano* 2011, **5**:8943-8949.
49. Luo J, Jang HD, Huang J: **Effect of sheet morphology on the scalability of graphene-based ultracapacitors.** *ACS Nano* 2013, **7**:1464-1471.
50. Gong Y, Yang S, Liu Z, Ma L, Vajtai R, Ajayan PM: **Graphene-Network-Backboned Architectures for High-Performance Lithium Storage.** *Adv. Mater.* 2013, **25**:3979-3984.

- This paper reports the design of 3D porous architectures with graphene sheets as the building block and coated with MoS₂ or FeO_x to form high-performance, additive-free LIB materials.

51. Zhang H, Xie A, Wang C, Wang H, Shen Y, Tian X: **Novel rGO/ α -Fe₂O₃ composite hydrogel: synthesis, characterization and high performance of electromagnetic wave absorption.** *J. Mater. Chem. A* 2013, **1**:8547-8552.
52. Zhang Z, Xiao F, Guo Y, Wang S, Liu Y: **One-pot self-assembled three-dimensional TiO₂-graphene hydrogel with improved adsorption capacities and photocatalytic and electrochemical activities.** *ACS Appl. Mater. Interfaces* 2013, **5**:2227-2233.
53. Qiu B, Xing M, Zhang J: **Mesoporous TiO₂ nanocrystals grown in situ on graphene aerogels for high photocatalysis and lithium-ion batteries.** *J. Am. Chem. Soc.* 2014, **136**:5852-5855.
54. Huang ZX, Wang Y, Zhu YG, Shi Y, Wong JI, Yang HY: **3D graphene supported MoO₃ for high performance binder-free lithium ion battery.** *Nanoscale* 2014, **6**:9839-9845.
55. Wang R, Xu C, Sun J, Gao L, Yao H: **Solvothermal-induced 3D macroscopic SnO₂/nitrogen-doped graphene aerogels for high capacity and long-life lithium storage.** *ACS Appl. Mater. Interfaces* 2014, **6**:3427-3436.
- This paper reports the design of 3D porous architectures with graphene sheets as the building block and coated with MoS₂ or FeO_x to form high-performance, additive-free LIB materials.
56. Li X, Geng D, Zhang Y, Meng X, Li R, Sun X: **Superior cycle stability of nitrogen-doped graphene nanosheets as anodes for lithium ion batteries.** *Electrochem. Commun.* 2011, **13**:822-825.
57. Wu Z-S, Ren W, Xu L, Li F, Cheng H-M: **Doped graphene sheets as anode materials with superhigh rate and large capacity for lithium ion batteries.** *ACS Nano* 2011, **5**:5463-5471.
58. Sahoo M, Sreena K, Vinayan B, Ramaprabhu S: **Green synthesis of boron doped graphene and its application as high performance anode material in Li ion battery.** *Mater. Res. Bull.* 2015, **61**:383-390.
59. Reddy ALM, Srivastava A, Gowda SR, Gullapalli H, Dubey M, Ajayan PM: **Synthesis of nitrogen-doped graphene films for lithium battery application.** *ACS Nano* 2010, **4**:6337-6342.
60. Wang X, Cao X, Bourgeois L, Guan H, Chen S, Zhong Y, Tang DM, Li H, Zhai T, Li L: **N-Doped Graphene-SnO₂ Sandwich Paper for High-Performance Lithium-Ion Batteries.** *Adv. Funct. Mater.* 2012, **22**:2682-2690.
61. Chang Y, Li J, Wang B, Luo H, He H, Song Q, Zhi L: **Synthesis of 3D nitrogen-doped graphene/Fe₃O₄ by a metal ion induced self-assembly process for high-performance Li-ion batteries.** *J. Mater. Chem. A* 2013, **1**:14658-14665.
62. Zhang K, Han P, Gu L, Zhang L, Liu Z, Kong Q, Zhang C, Dong S, Zhang Z, Yao J: **Synthesis of nitrogen-doped MnO/graphene nanosheets hybrid material for lithium ion batteries.** *ACS Appl. Mater. Interfaces* 2012, **4**:658-664.
63. Meng YS, Arroyo-de Dompablo ME: **First principles computational materials design for energy storage materials in lithium ion batteries.** *Energy Environ. Sci.* 2009, **2**:589-609.
64. Zhang T, Li D, Tao Z, Chen J: **Understanding electrode materials of rechargeable lithium batteries via DFT calculations.** *Prog. Nat. Sci.: Mater. Inter.* 2013, **23**:256-272.
65. Yamakawa N, Jiang M, Key B, Grey CP: **Identifying the Local Structures Formed during Lithiation of the Conversion Material, Iron Fluoride, in a Li Ion Battery: A Solid-State NMR, X-ray Diffraction, and Pair Distribution Function Analysis Study.** *J. Am. Chem. Soc.* 2009, **131**:10525-10536.

Table 1. Comparison of the electrochemical performance of representative 3D graphene-based anodes in LIBs.

Architectures		Active components	Capacities (mA h/g) (1st- last cycle)	Current density (mA/g)	Cycles	Voltage window (V)	Average discharge potential (~V vs. Li)	Ref.
Sheet-like		Co ₃ O ₄ , CoO	890.44-801.31	21.12	30	0.005-3.0	1.1	21
Parallel alignment of sheets	Vertical alignment of sheets	CoS ₂ , CoS ₂ ,Co ₉ S ₈	1018-954	100	50	0.005-3.0	1.35	33
		CuO	782.3-736.8	67	50	0.01-3.0	1.35	38
		Au,Si	2210-1520	200	20	0.001-3.2	0.25	39
		N- doped MnO	1230-722	100	90	0.01-3.0	0.6	62
		Sn	1910-1005	150	130	0.001-3.0	0.25	37
Core/shell		Si	2142-1335	200	80	0-2.0	0.23	42
SiO ₂	2700-1299.6	210	25	0.01-1.2	0.17	43

		TiO ₂	272-153	3350	300	1.0-3.0	1.25	44
Foams		MoS ₂ (85%)	1300-1200	600	30	0.01-3.0	1.0	50
SnO ₂	1693-1340	500	200	0.01-3.0	0.4	55
		TiO ₂	249-200	100	50	1.0-3.0	1.5	53
		Fe ₃ O ₄	1750-1130	100	200	0.001-3.0	0.85	61

Figure 1. Schematic representation of the synthesis of 3D Co₃O₄/CoO/graphene nanocomposite (a).

FESEM images of Co₃O₄/CoO/graphene nanocomposite (b) and pure Co₃O₄ nanoparticles (c). From Ref. [21], with permission.

Figure 2. Scanning electron microscopy images showing the morphology of pure VAGN (a), Sn@GS-VAGN (b), and the rate capability of Sn@GS-VAGN (c). From Ref. [37], with permission.

Figure 3. Schematic illustration of the preparation of CuO nanosheets/graphene paper with SEM image and cycle performance. From Ref. [38], with permission.

Figure 4. Schematic representation of the synthesis process of the sandwich-type Co₃S₄ porous nanosheets and graphene sheets (Co₃S₄-PNS/GS) via freeze drying and subsequent hydrazine treatment (a). LIB performance of Co₃S₄-PNS/GS: rate capability at different current densities from 0.5 to 20 A/g (b), and cycling performance and corresponding Coulombic efficiency at 0.5 A/g (c). From Ref. [40], with permission.

Figure 5. 3D $\text{Fe}_3\text{O}_4/\text{graphene}$ foam with low magnification SEM image (a), high magnification image (b), cycle performance at 6C and 10C rate (c), and the rate capability at different C-rates from 1C to 60C (d). From Ref. [18], with permission.