**Three Dimensional Graphene Electrode for Lithium Ion Batteries: Opportunities and Chalenges**

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# Abstract

Graphene has been considered to be extremely attractive and ideally suited for implementation in energy storage applications and to bring a huge improvement in the performance of lithium ion batteries (LIBs) due to its large electrical conductivity, vast surface area, unique heterogeneous electron transfer and charge carrier rates, widely applicable electro-catalytic activity, and low production costs. Despite the unique properties of 2D graphene, restacking of the graphene sheets has been one of the greatest setbacks in their applications in LIBs. To overcome this, 2D graphene is fabricated into 3D hierarchical frame works, the balanced space organization radically relieves the self-restacking of graphene layers. The 3D materials also inherit intrinsic physical properties of 2D graphene. This study starts with a brief introduction, concept and working principle of LIBs, graphene and highlighting the function of 3D graphene as electrode materials. The preceding sections laid the foundation for the discussion on the review of various electrodes used in LIBs, the issues and efforts to offer solutions to these problems.

**Keywords:** lithium ion battery (LIB), 3D graphene, electrode, energy storage.

# 1.0 Introduction

The ever increasing global energy demands have called for more efficient, sustainable and renewable energy resources and most of the available renewable energy sources are intermittent. To make energy affordable, available in amounts, and at times and places that are different from those when and where one is in need of it, then there is a need for development of electrical energy storage systems. Thus, methods to store and transport energy from place to place can be of great importance. Lithium ion batteries (LIBs), electrochemical capacitors (ECs) (also known as supercapacitors or ultracapacitors) and metal air batteries are the most prominent and fast-growing energy storage devices (Li and Zhi, 2018).

Comparatively, LIBs generally possess higher energy density due to their different energy storage principles (Liu *et al.*, 2018; Li *et al.*, 2017). However, the current lithium-ion battery technology is approaching its limit especially in terms of specific energy (per weight) and energy density (per volume), incapable of satisfying the ever increasing demand for diverse applications in expanded fields such as mobile electronic devices, vehicle electrification and renewable energy integration (Chen *et al.*, 2018). To relieve this situation, a good number of electrode (anode and cathode) materials with theoretically high specific capacities have thus far been widely scanned and/or revisited in recent years in order to enhance the energy density and power density of the LIBs (Fan *et al.*, 2015).

There has been a concerted effort to synthesis advanced electrode materials with tailored structure, composition and morphology. Significantly, engineering the nanostructured active materials into highly conductive matrix offers desirable functionality and great potential to achieve excellent energy storage, high rate capabilities and long lifespan for electrode materials (Cabana *et al.*, 2010; Lee *et al.*, 2011; Zhou *et al.*, 2011; Peng *et al.*, 2012). Among the materials pursued to offer solutions to the limitations and challenges related to these electrode materials for LIBs, recent research has shown that graphene, a type of two-dimensional carbon material, is a promising candidate to overcome these issues owing to its unique physical and chemical properties (Li and Zhi, 2018). Graphene is extremely attractive and ideally suited for implementation in energy storage applications due to its reported large electrical conductivity, vast surface area, unique heterogeneous electron transfer and charge carrier rates, widely applicable electro-catalytic activity, and low production costs (Brownson *et al.*, 2011).

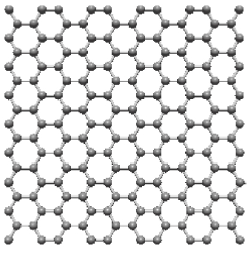
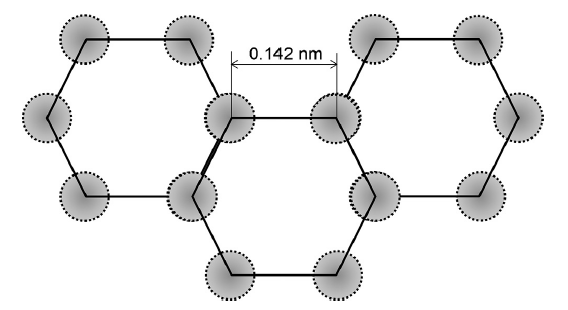
Despite the attracting properties of 2D graphene, restacking of the graphene sheets still occurred in many cases, where a partially-turbostratic structure that reduces the specific capacity forms (Kim *et al.*, 2018). On the other hand, if 2D graphene is fabricated into three-dimensional (3D) hierarchical frameworks, the balanced space organization radically relieves the self-restacking of graphene layers. The 3D materials also inherit intrinsic physical properties of graphene. Through the formation of porous channels, the 3D spongy form of graphene has shown much higher surface area than aggregates of 2D sheets. Especially in energy-related applications, the porosity becomes a determinative advantage for 3D porous graphene networks over its 2D counterparts. To acquire materials for high-performance energy storage, a 3D graphene with an interconnected cellular network is a promising candidate among various porous scaffolds (Xu *et al.*, 2017). The 2D grapheme sheet can be assembled or processed into 3D structures that exhibit desired physical and chemical properties (Ferrer, Mace, Thomas, & Jeon, 2017).

Three dimensional (3D) graphene structures can be synthesised using either template or template-free methods; the template method employs some predetermined structures as the template (Choi, Yang, Hong, Choi, & Huh, 2012; Huang, Sun, Su, Zhao, & Wang, 2014; Shi, Peng, Zhu, Zhu, & Zhang, 2015) while on the other hand, the template-free approach is targeted at modifying the 2D graphene using chemical etching or some other means (Ferrer, Mace, Thomas, & Jeon, 2017; Lee, et al., 2010; Chen & Yan, 2011; Zhang, Chen, Hedhili, Zhang, & Wang, 2012). Template-assisted synthesis methods are attracting more attention basically because morphology and architecture of resulting 3D graphene and its composites are determined by the templates used during the synthesis (Choi, Yang, Hong, Choi, & Huh, 2012; Wen, Zhang, Yan, Zhang, & Shi, 2013). A range of templates has been reported in the literature which are soft and hard templates including polymers, carbon spheres, inorganic particles, micelles, ionic liquids, and nanostructured substrates (Ferrer, Mace, Thomas, & Jeon, 2017; Meng, Wang, Zhang, & Wei, 2013; Choi, Yang, Hong, Choi, & Huh, 2012; Huang, et al., 2014; Huang, et al., 2012). (Fan, et al., 2013). (Zhang & Li, 2018; Losurdo, Giangregorio, Capezzuto, & Bruno, 2011; Cen, Sisson, Qin, & Liang, 2018). hotoanodesde of graphene material, tedly influenced by several factors which may include Therefore, this study briefly underscores the concept and working principle of LIBs and application of 3D graphene-based electrode materials in LIBs. The discussion on the various electrodes used in LIBs, the issues and efforts to offer solutions to these problems are undertaken.

# 2.0 Graphene: Fundamental and its Energy Storage Applications

Fascination with graphene has been growing very rapidly in recent years and the science of graphene is now becoming one of the most interesting and fast-moving topics in material science (Aoki and Dresselhaus, 2014). The horizon of graphene is ever becoming wider, where physical concepts go hand in hand with advances in experimental techniques. On the other hand, graphene attributed properties such as high surface area, excellent transparency, light absorption, and charge transport properties have significantly aroused interest from different research fields concerned with energy conversion and environmental pollution remediation (Tahir, et al., 2016).

Graphene is the first truly 2D crystal ever observed in nature and this is remarkable because the existence of 2D crystals has often been doubted in the past mainly due to Mermin-Wagner theorem stating that a 2D crystal loses its long-range order, and thus melts, at any small but non-zero temperature as a result of thermal fluctuations (Fuchs and Goerbig, 2008). According to Zhen and Zhu (2018), graphene is an allotrope of carbon in the form of a 2D, atomic-scale, hexagonal lattice in which one atom forms each vertex with sp2 hybridization as shown in Figure 2.

(b)

Figure 2 (a) Two-dimensional (2D) graphene (Wong & Akinwande, 2011) (b) Hexagonal lattice of graphene (Zhen & Zhu, 2018)

The unit structure of graphene is a hexagonal carbon ring with an area of 0.052 nm2, carbon-carbon bond length is about 0.142 nm and a stable hexagonal structure is formed through strong connections by three σ bonds in each lattice (Zhen & Zhu, 2018; Harris, 2018). In graphene, each carbon atom uses 3 of its 4 outer orbital electrons to form 3 sigma bonds 1200 apart with 3 adjacent carbon atoms in the same plane, leaving the 4th electron free to move, therefore, electrons in graphene behave just like massless relativistic particles without crystal lattices restrictions (Wei, et al., 2018; Stankovich S. , et al., 2006; Li & Kaner, 2008). As such, graphene possesses excellent electrical conductivities in two dimensions at room temperature (more than 200,000 cm2 V−1 s−1) (Si & Samulski, 2008).

As a 2D material, graphene has zero band gap with a single molecular layered structure (Wei, et al., 2018); the electrical conductivity of graphene is mostly attributed to the π bond located vertically to the lattice plane (Zhen & Zhu, 2018). Graphene’s stability is ascribed to its tightly packed carbon atoms and a sp2 orbital hybridization — a combination of orbitals s, px, and py that constitute the σ-bond. The final pz electron makes up the π-bond. The π-bonds hybridize together to form the π-band and π\*-bands. These bands are responsible for most of graphene’s notable electronic properties, via the half-filled band that permits free-moving electrons (Zhen & Zhu, 2018). Moreover, graphene is known for its tranparancy in the visible region which is attributed to its extreme thinness, this is found useful in DSSC’s conductive substrate (Chae, et al., 2017; Nair, et al., 2008; Britnell, et al., 2013).

3D

# 3.0 Lithium Ion Battery (LIB): Concept and Working Principle

Lithium-ion battery (LIB) typically consists of anode (negative electrode), cathode (positive electrode), electrolyte and separator. The basic components and principle of a LIB is illustrated in Figure 1.

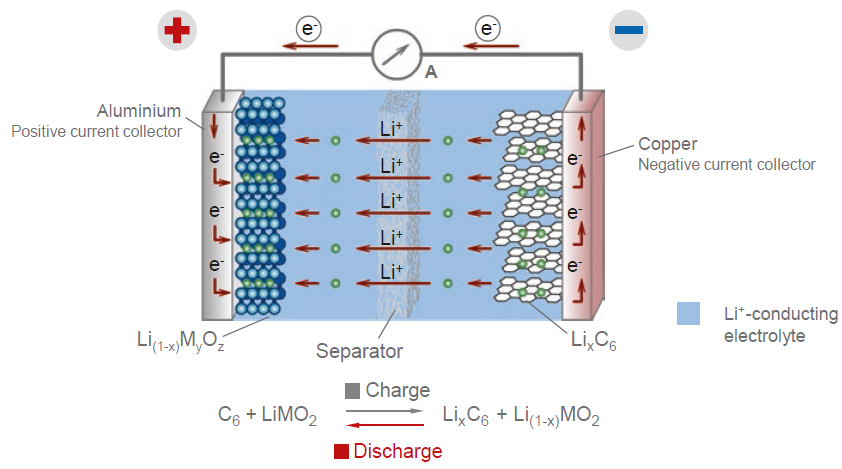


Figure 1: Scheme of lithium-ion battery: discharging process (Leuthner, 2018)

The most widely used anode materials are graphite and other carbon materials, this is due to their high abundance, low cost, and stable performance in Li storage while Li metal oxides (LiCoO2, LiMn2O4), and Li metal phosphates (LiFePO4) are common cathode materials. The electrolyte is usually a solution containing lithium hexafluorophosphate (LiPF6) dissolved in carbonate-based solvents such as a mixture of ethylene carbonate and dimethyl carbonate (Feng, et al., 2018; Vuorilehto, 2018). Separator is a porous membrane (a layer of Li ion permeable membrane) that prevents the direct contact between anode and cathode i.e. it electrically isolates the two electrodes from each other, LIB separators are mostly based on polyolefins (Weber & Roth, 2018). The ion-conducting electrolyte (containing a dissociated lithium conducting salt) is situated between the two electrodes (anode and cathode) with the separator isolating the two electrodes from each other. The anode is relatively at lower potential with respect to Li+/Li while cathode is at higher potential. Lithium is intercalated into anode materials (graphite and amorphous carbon compounds). The electrode materials are powders that are applied as coatings on current collectors, resulting in composite electrodes. The positive current collector is aluminum foil, typically 15 to 20 μm thick. Aluminum has a high conductivity and it is rather stable even at the high potential of the positive electrode. The negative current collector is copper foil, typically 8 to 18 μm thick. Aluminum would be lighter and cheaper but it cannot be used at the low potential of the negative electrode due to parasitic formation of a lithium/aluminum alloy (Vuorilehto, 2018).

During charging and discharging process, there is a back and forth migration of Li+ between the electrodes as well as intercalation and de-intercalation of the Li+ into the electrode materials. Figure 1 illustrate discharging process of Li-ion battery, during discharging Li is de-intercalated from the anode and electrons are released to copper which functions as current collector and at the same time, the Li+ (lithium ions) migrate from the anode through the electrolyte and the separator to the cathode. The released electrons (current electricity) migrate from the anode via an outer electrical connection (cable) to the cathode through aluminum which also functions as current collector. During charging, this process is reversed: Li ions migrate from the cathode through the electrolyte and the separator to the anode (Leuthner, 2018).

The performance of LIB is largely defined by its nominal capacity, electric energy and power. Capacity describes the amount of electric charge a power source can deliver under specific discharge conditions. This depends on the discharging current, the cut-off voltage, the temperature, and the type and amount of active electrode materials, and the unit is Ah (Leuthner, 2018). The energy of LIB is calculated as the product of capacity and average discharge voltage, the unit is Wh. Specific energy refers to the mass of the LIB and its unit is Wh/kg. Energy density refers to the volume of the LIB and its unit is Wh/l (Leuthner, 2018). The power of LIB is Power is the product of current and voltage calculated during discharging and its unit is W. The efficiency of the battery is gotten by the energy released divided by the energy stored during charging (Leuthner, 2018).

# 4.0 3D Graphene Electrode for Lithium-Ion Batteries

Lithium-ion batteries being hi-tech devices are made of complex materials. The basic components of the device feature different materials for their composition. This review highlights the use of 3D graphene network in the LIB application.

## 4.1 Graphene Cathode for LIB

Nitta *et al.* (2015) described a cathode or an intercalation cathode as a solid host network, which can store guest ions; the solid host network creates a platform for the insertion and removal of the guest ions from the host network reversibly. In LIBs, the host network compounds could be metal chalcogenides, transition metal oxides, and polyanion compounds while the guest ion is Li+ (lithium ion). Some metal chalcogenides which have been studied as possible cathode materials include TiS3, NbSe3 and LiTiS2; out of various chalcogenides, LiTiS2 is more attractive owing to its high gravimetric energy density combined with long cycle life (1000+ cycles) (Nitta, Wu, Lee, & Yushin, 2015; Whittingham, 2004). Recently, transition metal oxide and polyanion compounds have been the focus of current LIB cathode research due to their higher operating voltage and the resulting higher energy storage capability (Nayak, et al., 2018; Whittingham, 2004; Nitta, Wu, Lee, & Yushin, 2015). Based on different crystal structures, cathode materials are grouped into four classes in this work namely layered, spinel, olivine, and tavorite.

### 4.1.1 Layered Cathodes

Layered Cathodes can be layered chalcogenide such as TiS3, NbSe3 and LiTiS2 as well as layered transition metal oxides. Nayak *et al.* (2018) and Graf (2018) noted that layered lithiated transition metal oxides is the most frequently examined system of cathode materials. These materials consist of layered oxides with the chemical formula LiMO2 (M = Co and/or Ni and/or Mn and/or Al) and they are probably most widely used cathode materials. Examples of that layered transition metal oxides include lithium cobalt oxide (LiCoO2, LCO) (Cho, Kim, Kim, Lee, & Park, 2003), LiNiO2 (LNO), LiMnO2 (LMO), LiNi0.33Mn0.33Co0.33O2, LiNi0.8Co0.15Al0.05O2, and Li2MnO3. Layered transition metal oxide compounds are very attractive and probably the most widely used cathode materials because of their relatively high theoretical specific capacity, high theoretical volumetric capacity, low self-discharge, high discharge voltage, and good cycling performance (Nitta, Wu, Lee, & Yushin, 2015). However, LCO suffers drawbacks such as high cost (because of the high cost of Co), low thermal stability, and fast capacity fade at high current rates or during deep cycling; pure LNO cathodes are not favourable because the Ni2+ ions have a tendency to substitute Li+ sites during synthesis and delithiation, blocking the Li diffusion pathways (Rougier, 1996), it also suffers from thermal instability (Arai, 1998); and the cycling performance of LMO is still not satisfactory because its layered structure has a tendency to change into spinel structure during Li ion extraction (Gu, 2012) and also Mn leaches out of LMO during cycling (Nitta, Wu, Lee, & Yushin, 2015).

Continuous research efforts on improving the cathode materials has led to the doping of the layered transition metal oxide resulting to the development of layered transition metal oxide analog materials (composite layered cathode) (Nayak, et al., 2018). Nevertheless, these materials is yet to meet the required electronic conductivities for high battery performance. Of the materials sought to fulfil this purpose, graphene is considered very attractive, due to its relative high conductivity, to play a critical role in composite cathode materials which is believed to fundamentally enhance the electrochemical performance of the LIB, though graphene is not to be a direct replacement of the existing cathode materials (Akbar, Rehan, Haiyang, Rafique, & Akbar, 2018; Guan, Li, Li, & Ren, 2017). The utilisation of graphene in LIB have been found beneficial in terms of cycling and rate capability (Nayak, et al., 2018; Goosey, 2012). Li et al (2017) used graphene with LiNi1/3Mn1/3Co1/3O2 as a composite cathode in LIB, the result showed an improved specific capacity over ordinary LiNi1/3Mn1/3Co1/3O2 cathode. Venkateswara et al. (2011) similarly observed that the composites exhibited higher rate capability, longer cycle performance, and improved specific capacity.

### 4.1.2 Spinel (LiM2O4; M=Mn, Co, Ni) Cathodes

In exploring alternatives for commonly used toxic and expensive LiCoO2, LiMn2O4 compounds (lithium manganese oxide, LMO spinel) were developed and these materials crystallize in the spinel type structure which pose less safety hazard and characterised with ease of synthesis. However, due to the presence of John–Teller effect in lattice during the charge/discharge, its structure is prone to distort, resulting in the rapid decay of the capacity, especially at higher temperatures (Wu, Liu, & Guo, 2014; Lee, Cho, Song, Lee, & Cho, 2012). LiMn2O4 and its doping variants are attractive because of their easy availability and abundance but their low electrical conductivity brings about a low rate capacity (Zhang, et al., 2012; Akbar, Rehan, Haiyang, Rafique, & Akbar, 2018). However, many research advances have pointed towards graphene as viable operators for enhancing the rate capacity and conductivity of spinel cathode materials. The use of LiMn2O4 graphene composite as LIB cathode materials has reportedly showed enhanced electrochemical characteristics of the cathode (Akbar, Rehan, Haiyang, Rafique, & Akbar, 2018; Nitta, Wu, Lee, & Yushin, 2015).

### 4.1.3 Olivine (LiMPO4; M = Fe, Mn, Co, Ni) Cathodes

Olivine cathode materials are sometimes referred to as phosphate cathode in the literature (Graf, 2018). Olivine cathode material was introduced in 1997 and crystallizes like the natural mineral lithiophilite in the olivine structure (Graf, 2018; Padhi, Nanjundaswamy, & Goddenough, 1997). It is a polyanionic material, the polyanions ((PO4)3-) occupy lattice positions and increase cathode redox potential while also stabilizing its structure (Nanjundaswamy & al., 1996). Lithium ferrous phosphate (LiFePO4; LFP) is probably most researched cathode material with olivine structure, owing to its high theoretical capacity (170 mAh g-1), acceptable operating voltage (3.4 V vs.Li+/Li), good cycling stability, low toxicity, good thermal stability, and low cost (Doughty & Rother, 2012; Graf, 2018; Nitta, Wu, Lee, & Yushin, 2015; Wu, Liu, & Guo, 2014). Other olivine materials such as LiMnPO4 (lithium manganese phosphate; LMP) has been developed, this material offers about 0.4 V higher average voltage compared to olivine LFP, resulting to higher specific energy, but at the expense of lower conductivity. LiCoPO4, LiNi1/2Co1/2PO4, and LiMn1/3Fe1/3Co1/3PO4, (LCP, NCP, MFCP) also exhibit relatively high operating voltage and good capacity, but further improvements are required in terms power, stability and energy density (Nitta, Wu, Lee, & Yushin, 2015; Li, Mu, vanAken, & Maier, 2013).

The biggest benefit of LFP is non-toxic compared to other olivine cathode LiMPO4 (M = Co, Mn, and Ni) but unfortunately, LFP intrinsically exhibits poor electrical as well as ionic conductivity and low average potential which limits its electrochemical performance, especially the rate capability, as cathode in LIBs (Kang, Ma, & Li, 2011; Fisher, Prieto, & Islam, 2008; Andersson, Kalska, Haggstrom, & Thomas, 2000; Wu, Liu, & Guo, 2014). Various approaches have been attempted to improve the both the electrical and ionic conductivities by doping the LFP with other metals ions, reducing the particle size, coating with conductive carbon layer and aliovalent doping (Wu, Liu, & Guo, 2014; Chung, Bloking, & Chiang, 2002; Chung, Jang, Ryu, & Shim, 2004; Xu, Chang, & Gao, 2012). The results show that these approaches have been beneficial somewhat in achieving the aimed intended for but critical improvements are still required. Graphene in the recent times has been pursued as a material of choice to significantly, in combination with LFP, improve the electrochemical performance of LIBs.

It has been noted that 3D graphene-metal oxide structures such as porous graphene films, graphene foams, and graphene ball hybrids are more significant than their 2D in energy storage fields. 3D graphene structures are said to maintain the superior intrinsic properties of graphene sheets which include large surface area and excellent electrochemical properties; the addition of metal oxides can further improve the functions of these structures (Choi, Lee, & Kang, Three-dimensional porous graphene-metal oxide composite microspheres: Preparation and application in Li-ion batteries, 2015; He, et al., 2013; Cao, Yin, & Zhang, 2014; Huang, et al., 2014; Cao X. H., et al., 2014). More importantly, a 3D graphene structure with porous morphology allow easy electrolyte penetration and fast Li+ diffusion for Li-ion batteries (LIBs). Thus, 3D graphene-metal oxide composites are said to exhibit excellent electrochemical properties for a wide range of energy storage applications (Cao, Yin, & Zhang, 2014). Yang *et al.*, (2013) used LFP/3D graphene composite in LIB cathode, the result showed that the conducting 3D graphene nano-network, enables both Li+ and electrons to migrate and reach each of LFP particles, hence realizing the full potential of the active materials which in return led to an enhanced electrochemical performance of the device. Similarly, 3D graphene LFP composite was developed by Zhou et al. (2011) as a Li-ion battery cathode material withexcellent high-rate capability and cycling stability. The composite was prepared with LiFePO4nanoparticles and graphene oxide nanosheets by spray-drying and annealing processes. It was reported that the presence of abundant voids between the LiFePO4 nanoparticles and graphene sheets was beneficial for Li+ diffusion. The composite cathode material was able to deliver a capacity of 70 mAh g-1 at 60C discharge rate and showed a capacity decay rate of <15% when cycled under 10C charging and 20C discharging for 1000 times (Zhou, Wang, Zhu, & Liu, 2011).

### 4.1.4 Tavorite Cathodes

Another type of cathode materials is tavorite-sructured cathodes such as Li3V2(PO4)3 (LVP) and LiFeSO4F (LFSF). Tavorite-sructured cathode materials are another attractive cathode materials owing to their high cell voltage and reasonable specific capacity. Electrochemically active lithium iron sulfate fluoride (LiFeSO4F) with tavorite structure was first reported in 2010 by These materials are said to hold promise for the future of LIB cathode materials (Nitta, Wu, Lee, & Yushin, 2015; Masquelier & Croguennec, 2013).

## 4.2 Graphene LIB Anode

Materials for LIB anode are required to exhibit certain characteristics such as high lithium storage capability and robust structure for repeated charge/discharge cycles (Mao, Lu, & Chen, 2015). Carbon-based materials especially graphite are most widely used as anode in Li-ion (Sobkowiak, 2015). Graphite anodes possess a high electronic conductivity and high practical capacity of approximately 350 mAh/g i.e. maximum one Li atom can be stored per six C atoms (LiC6) based on the intercalation of Li, which give a theoretical maximum capacity of 372mAh/g (Campbell, et al., 2016; Ferrer, Mace, Thomas, & Jeon, 2017). In addition, the crystalline carbon allotrope graphite is almost exclusively utilized due to a much flatter cycling curve profile, and low operation voltage averaging about 0.125 V vs. Li/Li+. Interestingly, using graphene as anode, two Li atoms can be stored per six C (Li2C6) because both sides of graphene are able to store lithium ions, giving a theoretical capacity of 744 mAh/g; and more Li atoms can be intercalated in defective sites and edges of graphene, which could lead to even higher capacity than 744 mAh/g (Ferrer, Mace, Thomas, & Jeon, 2017; Bonaccorso, et al., 2015; Zhu, Yin, Yan, & Zhang, 2014; Sun, Wu, & Shi, 2011).

On the other hand, many alternative non-carbon based materials have been demonstrated as potential anode materials for LIBs due to their high specific capacities. The alternative non-carbon based anode materials that have attracted considerable attention recently are Li-alloys with different p-block elements, LixM, (M = Si, Sn, Sb, Al, etc.) (Croguennec & Palacin, 2015; Li & Dahn, 2007; Obrovac & Chevrier, 2014; Mao, Lu, & Chen, 2015) as well as conducting polymers such as polypyrrole (ppy) (Xia, Chao, Zhang, Shen, & Fan, 2015). These materials possess theoretical capacities of up to ten times higher than that of the carbon materials, for instance, Sn exhibits 981 mAh/g, SnO2 exhibits 1491 mAh/g, and Si exhibits 4200 mAh/g compared with those of carbon-based materials (372 mAh/g for graphite) (Mao, Lu, & Chen, 2015). However, non-carbon based anodes suffer from significant capacity degradation, volume change (expansions and contractions) during Li+ insertion/extraction cycles, which causes the pulverization of the anodes and electrical detachment of the active materials from the current collector (Sobkowiak, 2015; Mao, Lu, & Chen, 2015). The issues of volume changes during lithiation and delithiation, and extensive internal stresses have limited their utilization as anode materials despite the high theoretical capacity.

Various attempts have been made in using the graphene/non-carbon based electrode nanocomposite with the view to facilitate the transport of electrons and ions, and reduce the stress of the collective electrode during lithiation and delithiation process. Yet, most of the reported composites either with reduced graphene oxide (rGO) or 2D graphene framework are far from practically serving as anodes due to low Coulombic efficiency in the first cycle and unsatisfactory cycling performance (Mao, Lu, & Chen, 2015). Restacking of rGO or 2D graphene due to the van der Waals forces can significantly reduce the surface area and limit electron and ion transport. 3D graphene eliminates restacking issues and provide a large specific surface area, porous structure, and fast electron transport (Chen, et al., 2011; Han, Wu, Li, Zhang, & Feng, 2014).

Several composites combining 3D graphene with various non-carbon based high-capacity anode materials have been demonstrated to be promising in LIB. The non-carbon based anode materials include Sn (Qin, et al., 2014), SnO2 (Huang, et al., 2013), Si (Luo, et al., 2012; Zhu, Zhang, Xu, Yan, & Xue, 2014), Fe3O4 (Chang, et al., 2013), Fe2O3 (Cao X. H., et al., 2014; Cao X. , et al., 2014), MnO (Lee, Choi, Lee, & Kang, 2014), MnO2 (Li, Zhang, Zhu, Wei, & Shen, 2014; Zhu, Zhang, Xu, Yan, & Xue, 2014), TiO2 (Jiang, et al., 2014; Shen, Zhang, Li, Yuan, & Cao, 2011), NiO (Choi, Ko, Lee, & Kang, 2014), MoO2 (Choi & Kang, 2014), V2O5 (Choi & Kang, 2014), Co3O4 (Choi, et al., 2012), CoO (Ma, et al., 2014), MoS2 (Xu, Lin, Huang, Liu, & Duan, 2013; Wang, et al., 2014), Ni3S2, (Zhao, et al., 2014)186 Ge (Ma, et al., 2014), S (Wang, et al., 2014), and also conducting polymers (Xia, Chao, Zhang, Shen, & Fan, 2015).

For instance, Qin et al. (2014) employed 3D graphene/Sn composite as a LIB anode through CVD technique, the composite anode exhibited good capacities of 1022 mAh/g at 0.2 C, 865 mAh/g at 0.5 C, 780 mAh/g at 1 C, 652 mAh/g at 2 C, mAh/g at 5 C, and 270 mAh/g at 10 C, where 1 C is 1 A/g. Long cycling stability was also and maintaining approximately 96.3% after 1000 cycles. The result demonstrated that the anode pecific capacity and good capacity retention surpass many other carbon/Sn composites (Mao, Lu, & Chen, 2015; Li, Dhanabalan, Gu, & Wang, 2012; Xu, et al., 2013). The observed enhanced electrical conductivity was ascribed to the porosity, high electrical conductivity, large surface area, and high mechanical flexibility of the graphene/Sn composite structure.

Another study carried out by Huang et al. (2013) obtaining 3D graphene/SnO2 composites through a two-step assembly method indicated a large surface area, several macropores, and a low mass density. The the result showed that the composite provided multidimensional channels for electron transport and electrolyte access, and enabled the rapid diffusion of lithium ions from the electrolyte to theelectrode. A high capacity of 830 mAh/g for up to 70 charge/discharge cycles at 100 mA/g with good cyclingstability was achieved. The composite have been reportedly doped by other workers in order to either tune the electronic properties of the composite or improve the lithium storage properties (Mao, Lu, & Chen, 2015; Wang, Xu, Sun, Gao, & Yao, 2014).

# 5.0 Conclusion and Perspective

The revolution in the landscape of the battery technology through the invention of LIBs and the continued development of the materials via intensive research has been a monumental feat. The success of LIBs have affected our everyday life positively ranging from portable electronics to the large-scale energy-storage devices, such as electric vehicles. The present LIB technology could boast of high energy density, high cycle life, and good efficiency, yet there is a need to push the boundaries of cost, energy density, power density, cycle life, and safety in order to meet the ever increasing demand for the enhanced energy storage devices. To achieve this, this will require inexpensive high capacity electrode materials with good electrical/ionic conductivity as well as cyclic stability, environmental benignity and excellent lithium storage properties. 3D graphene networks has been demonstrated to be a promising candidate due to its unique properties such as excellent mechanical strength, large specific surface area, desirable flexibility, and good electronic conductivity.

Presently, the 3D graphene composite as electrode material is considered as suitable strategy to practically improve LIB performance; the electrochemical performance can be improved due to availability of more active sites, the porosity of the 3D graphene networks can facilitate the ion diffusion, issues of safety and of cyclic stability can be addressed with 3D graphene composite electrode. However, there are still notable concerns related to the high cost and synthesis of 3D graphene composite electrode which have to be addressed to make the LIBs using 3D graphene composite electrode commercially viable. Future work should be directed towards reducing the current high cost of production with focus on mass producing high-quality 3D graphene composite electrode. In addition, effective synthesis design is essential to maximise LIB performance, structure and morphology of the composite which has to be environmentally benign, simple, affordable and scalable.

# REFERENCES

Akbar, S., Rehan, M., Haiyang, L., Rafique, I., & Akbar, H. (2018). A brief review on graphene applications in rechargeable lithium ion battery electrode materials. *Carbon Letters, 28*, 1-8.

Andersson, A. S., Kalska, B., Haggstrom, L., & Thomas, J. O. (2000). Lithiumextraction/insertion in LiFePO4: an X-ray diffraction and Moss bauer spectroscopy study. *Solid State Ionics, 130*(1-2), 41–52. doi:10.1016/S0167-2738(00)00311-8

Arai, H. (1998). *Solid State Ionics, 109* (3), 295.

Bonaccorso, F., Colombo, L., Yu, G., Stoller, M., Tozzini, V., Ferrari, A. C., . . . Pellegrini, V. (2015). Graphene, related two-dimensional crystals, andhybrid systems for energy conversion and storage. *Science, 347*, 6217.

Britnell, L., Ribeiro, R. M., Eckmann, A., Jalil, R., Belle, B. D., Mishchenko, A., . . . Novoselov, K. S. (2013). Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films. *Science, 340*(6138), 1311-1314. doi:10.1126/science.1235547

Cai, M., Thorpe, D., Adamson, D. H., & Schniepp, H. C. (2012). Methods of graphite exfoliation. *J. Mater. Chem., 22*, 24992–25002.

Campbell, B., Ionescu, R., Tolchin, M., Ahmed, K., Favors, Z., Bozhilov, K. N., . . . Ozkan, M

. (2016). Carbon-coated, diatomite-derived nanosilicon asa high rate capable Li-ion battery anode. *Scientific Report, 6*, 33050.

Cao, X. H., Yin, Z. Y., & Zhang, H. (2014). Three-dimensionalgraphene materials: Preparation, structures and applicationin supercapacitors. *Energy Environ. Sci., 7*, 1850–1865.

Cao, X. H., Zheng, B., Rui, X. H., Shi, W. H., Yan, Q. Y., & Zhang, H. (2014). Metal oxide-coated three-dimensional grapheneprepared by the use of metal–organic frameworks as precursors. *Angew. Chem. Int. Ed, 53*, 1404–1409.

Cao, X., Zheng, B., Rui, X., Shi, W., Yan, Q., & Zhang, H. (2014). *Angew. Chem., Int. Ed.,, 124*, 1428–1433.

Cen, Y., Sisson, R. D., Qin, Q., & Liang, J. (2018). Current Progress of Si/Graphene Nanocomposites forLithium-Ion Batteries. *Journal of Carbon Research, 4*, 1-14. doi:10.3390/c4010018

Chae, S., Jang, S., Choi, W. J., Kim, Y. S., Chang, H., Lee, T. I., & Lee, J. -O. (2017). Lattice Transparency of Graphene. *Nano Letters, 17*(3), 1711-1718. doi:10.1021/acs.nanolett.6b04989

Chang, Y., Li, J., Wang, B., Luo, H., He, H., Song, Q., & Zhi, L. (2013). *Journal of Materials Chemistry A, 1*, 14658—14665.

Chen, W., & Yan, L. (2011). In situ self-assembly of mild chemical reduction graphenefor three-dimensional architectures. *Nanoscale, 3*(8), 3132–3137.

Chen, Z., Ren, W., Gao, L., Liu, B., Pei, S., & Cheng, H. -M. (2011). *Nat. Mater., 10*, 424–428.

Cho, J., Kim, Y. -W., Kim, B., Lee, J. -G., & Park, B. (2003). A Breakthrough in the Safety of Lithium Secondary Batteries by Coating the Cathode Material with AlPO4 Nanoparticles . *Angewandte Chemie International Edition, 42*(14), 1618 - 1621. doi:10.1002/anie.200250452

Choi, B. G., Chang, S. J., Lee, Y. B., Bae, J. S., Kim, H. J., & Huh, Y. S. (2012). *Nanoscale, 4*, 5924–5930.

Choi, B. G., Yang, M., Hong, W. H., Choi, J. W., & Huh, Y. S. (2012). 3D macroporousgraphene frameworks for supercapacitors with high energy and powerdensities. *ACS Nano, 6*(5), 4020–4028.

Choi, S. H., & Kang, Y. C. (2014). *ChemSusChem, 7*, 523–528.

Choi, S. H., & Kang, Y. C. (2014). *Chem. – Eur. J., 20*, 6294–6299.

Choi, S. H., Ko, Y. N., Lee, J. K., & Kang, Y. C. (2014). *Scientific Report, 4*, 5786.

Choi, S. H., Lee, J. -K., & Kang, Y. C. (2015). Three-dimensional porous graphene-metal oxide composite microspheres: Preparation and application in Li-ion batteries. *Nano Research, 8*(5), 1584–1594.

Chung, H. -T., Jang, S. -K., Ryu, H. W., & Shim, K. -B. (2004). Effects of nanocarbonwebs on the electrochemical properties in LiFePO4/Ccomposite. *Solid State Communications, 131*(8), 549–554.

Chung, S. Y., Bloking, J. T., & Chiang, Y. M. (2002). Electronically conductivephospho-olivines as lithium storage electrodes. *Nature Materials, 1*(2), 123–128.

Croguennec, L., & Palacin, M. R. (2015). Recent Achievements on Inorganic Electrode Materials for Lithium-Ion Batteries. *Journal of the American Chemical Society, 137* (9), 3140–3156.

Doughty, D., & Rother, E. P. (2012). *Electrochem. Soc. Interface, 21*(2), 35.

Fan, Z., Yan, J., Ning, G., Wei, T., Zhi, L., & Wei, F. (2013). Porous graphene networks ashigh performance anode materials for lithium ion batteries. *Carbon, 60*, 558–561.

Feng, K., Li, M., Liu, W., Kashkooli, A. G., Xiao, X., Cai, M., & Chen, Z. (2018). Silicon-Based Anodes for Lithium-Ion Batteries: FromFundamentals to Practical Applications. *Small, 1702737*, 1-33. doi:10.1002/smll.201702737

Ferrer, P. R., Mace, A., Thomas, S. N., & Jeon, J. -W. (2017). Nanostructured porous graphene and its composites for energy storage applications. *Nano Convergence, 4*(29), 1-19. doi:10.1186/s40580-017-0123-0

Fisher, C. A., Prieto, V. M., & Islam, M. S. (2008). Lithium batterymaterials LiMPO4 (M = Mn, Fe Co, and Ni): insights into defectassociation, transport mechanisms, and doping behavior. *Chemistry of Materials, 20*(18), 5907–5915. doi:10.1021/cm801262x

Goosey, M. (2012). short introduction to graphene and its potential interconnect applications. *Circuit World, 38*, 83-86.

Graf, C. (2018). Cathode materials for lithium-ion batteries. Ninu R. Korthauer, *Lithium-Ion Batteries: Basics and Applications* (oju ewe 29 - 43). Ber;lin, Germany: Springer-Verlag.

Gu, M. (2012). *ACS Nano, 7*(1), 760.

Guan, X., Li, G., Li, C., & Ren, R. (2017). Synthesis of porous nano/micro structuredLiFePO4/C cathode materials for lithium-ion batteries byspray-drying method. *Transactions of Nonferrous Metals Society of China, 27*(1), 141 - 147. doi:10.1016/s1003-6326(17)60016-5

Han, S., Wu, D., Li, S., Zhang, F., & Feng, X. (2014). *Advanced Materials, 26*, 849–864.

Harris, P. J. (2018). Transmission Electron Microscopy of Carbon: A Brief History. *Journal of Carbon Research, 4*(4), 1-17. doi:10.3390/c4010004

He, Y. M., Chen, W. J., Li, X. D., Zhang, Z. X., Fu, J. C., Zhao, C. H., & Xie, E. Q. (2013). Freestanding three-dimensionalgraphene/MnO2 composite networks as ultralight and flexiblesupercapacitor electrodes. *ACS Nano, 7*, 174–182.

Huang, X., Qian, K., Yang, J., Zhang, J., Li, L., Yu, C., & Zhao, D. (2012). Functionalnanoporous graphene foams with controlled pore sizes. *Advanced Materials, 24*(32), 4419–4423.

Huang, X., Sun, B., Su, D., Zhao, D., & Wang, G. (2014). Soft-template synthesis of3D porous graphene foams with tunable architectures for lithium-O2 batteries and oil adsorption applications. *Journal of Materials Chemistry A, 2*(21), 7973–7979.

Huang, X., Yu, H., Chen, J., Lu, Z. Y., Yazami, R., & Hng, H. H. (2014). Ultrahigh rate capabilities of lithium-ion batteries from 3D ordered hierarchically porous electrodes with entrappedactive nanoparticles configuration. *Adv. Mater., 26*, 1296–1303.

Huang, Y. S., Wu, D. Q., Han, S., Li, S., Xiao, L., Zhang, F., & Feng, X. L. (2013). *ChemSusChem, 6*, 1510—1515.

Jiang, X., Yang, X. L., Zhu, Y. H., Jiang, H. L., Yao, Y. F., Zhao, P., & Li, C. Z. (2014). *Journal of |Materials Chemistry A, 2*, 11124–11133.

Kang, F. J., Ma, J., & Li, B. H. (2011). Effects of carbonaceous materials onthe physical and electrochemical performance of a LiFePO4cathode for lithium-ion batteries. *New Carbon Mater, 26*(3), 161–170. doi:10.1016/S1872-5805(11)60073-5

Lee, S. H., Kim, H. W., Hwang, J. O., Lee, W. J., Kwon, J., Bielawski, C. W., . . . Kim, S. O. (2010). Three-dimensional self-assembly of graphene oxideplatelets into mechanically flexible macroporous carbon films. *Angewandte Chemie International Edition, 49*(52), 10084–10088.

Lee, S. M., Choi, S. H., Lee, J. -K., & Kang, Y. C. (2014). *Electrochim. Acta, 132*, 441–447.

Lee, S., Cho, Y., Song, H. -K., Lee, K. T., & Cho, J. (2012). Carbon-coatedsingle-crystal LiMn2O4 nanoparticle clusters as cathode materialfor high-energy and high-power lithium-ion batteries. *Angew.Chem. Int. Ed., 51*(35), 8748–8752. doi:10.1002/anie.201203581

Leuthner, S. (2018). Lithium-ion battery overview. Ninu R. Korthauer, *Lithium-Ion Batteries: Basics and Applications* (oju ewe 13 - 19). Berlin, Germany: Springer-Verlag .

Li, C., Mu, X., vanAken, P. A., & Maier, J. (2013). A High‐Capacity Cathode for Lithium Batteries Consisting of Porous Microspheres of Highly Amorphized Iron Fluoride Densified from Its Open Parent Phase. *Advanced Energy Materials, 3*(1), 113-119. doi:10.1002/aenm.201200209

Li, D., & Kaner, R. B. (2008). Graphene-based composite materials. *Science, 320*(5880), 1170-1171. doi:10.1126/science.1158180

Li, J., & Dahn, J. R. (2007). An In Situ X-Ray Diffraction Study of the Reaction of Li with Crystalline Si. *Journal of the Electrochemical Society, 154*(3), A156-A161.

Li, X., Dhanabalan, A., Gu, a. L., & Wang, C. (2012). *Advanced Energy Materials, 2*, 238–244.

Li, X., Zhao, X., Wang, M. S., Zhang, K. J., Huang, Y., Qu, M. Z., . . . Zheng, J. (2017). Improved rate capability of aLiNi1/3Co1/3Mn1/3O2/CNT/graphene hybrid material for Li-ionbatteries. *RSC Advances, 7*, 24359.

Li, Y. Y., Zhang, Q. W., Zhu, J. L., Wei, X. L., & Shen, P. K. (2014). *Journal of Materials Chemistry A, 2*, 3163 – 3168.

Losurdo, M., Giangregorio, M. M., Capezzuto, P., & Bruno, G. (2011). Graphene CVD growth on copper and nickel: Role of hydrogen in kinetics and structure. *Phys. Chem. Chem. Phys., 13*, 20836–20843.

Luo, J., Zhao, X., Wu, J., Jang, H. D., Kung, H. H., & Huang, J. (2012). *J. Phys. Chem. Lett, 3*, 1824–1829.

Ma, J. J., Wang, J. L., He, ,. Y., Liao, X. Z., Chen, J., Wang, J. Z., . . . Ma, Z. F. (2014). *Journal of Materials Chemistry A, 2*, 9200–9207.

Mao, S., Lu, G., & Chen, J. (2015). Three-dimensional graphene-based compositesfor energy applications. *Nanoscale, 7*, 6924–6943.

Meng, Y., Wang, K., Zhang, Y., & Wei, Z. (2013). Hierarchical porous graphene/polyaniline composite film with superior rate performance for flexiblesupercapacitors. *Advanced Materials, 25*(48), 6985–6990.

Nair, R. R., Blake, P., Grigorenko, A. N., Novoselov, K. S., Booth, T. J., Stauber, T., . . . Geim, A. K. (2008). Fine Structure Constant Defines Visual Transparency of Graphene. *Science, 320*(5881), 1308 - 1308.

Nanjundaswamy, K. S., & al., e. (1996). *Solid State Ionics, 92*(1-2), 1.

Nayak, P. K., Erickson, E. M., Schipper, F., Penki, T. R., Munichandraiah, N., Adelhelm, P., . . . Aurbach, D. (2018). Review on Challenges and Recent Advances in the Electrochemical Performance of High CapacityLi- and Mn-Rich Cathode Materials for Li-Ion Batteries. *Advanced Energy Materials, 8*(1702397), 1 - 16. doi:10.1002/aenm.201702397

Nitta, N., Wu, F., Lee, J. T., & Yushin, G. (2015). Li-ion battery materials: present and future. *Materials Today, 18*(5), 252 - 264. doi:10.1016/j.mattod.2014.10.040

Novoselov, K. S., Geim, A. K., Morozov, S., Jiang, D., Zhang, Y., Dubonos, S. A., . . . Firsov, A. (2004). Electric field effect in atomically thin carbon films. *Science, 306*, 666–669.

Obrovac, M. N., & Chevrier, V. L. (2014). Alloy negative electrodes for Li-ion batteries. *Chemical Review, 114*, 11444 – 11502.

Padhi, A. K., Nanjundaswamy, K. S., & Goddenough, J. B. (1997). *J Electrochem Soc, 144*, 1188.

Qin, J., He, C. N., Zhao, N. Q., Wang, Z. Y., Shi, C. S., Liu, E. Z., & Li, J. J. (2014). *ACS Nano, 8*, 1728–1738.

Rho, W. -Y., Song, D. H., Lee, S. H., & Jun, B. -H. (2017). Enhanced Efficiency in Dye-Sensitized Solar Cells by Electron Transport and Light Scattering onFreestanding TiO2 Nanotube Arrays. *Nanomaterials, 7*(345), 1-11. doi:10.3390/nano7100345

Rougier, A. (1996). *J. Electrochem. Soc, 143* (4), 1168.

Shen, L., Zhang, X., Li, H., Yuan, C., & Cao, G. (2011). *Journal opf Physical Chemistry Letters, 2*, 3096–3101.

Shi, J. -L., Peng, H. -J., Zhu, L., Zhu, W., & Zhang, Q. (2015). Template growth of porousgraphene microspheres on layered double oxide catalysts and theirapplications in lithium–sulfur batteries. *Carbon, 92*, 96–105.

Si, Y., & Samulski, E. T. (2008). Synthesis of Water Soluble Graphene. *Nano Letters, 8*(6), 1679-1682. doi:10.1021/nl080604h

Sobkowiak, A. (2015). *LiFeSO4F as a Cathode Material forLithium-Ion Batteries: Synthesis, Structure, and Function.* Uppsala: Uppsala University.

Stankovich, S., Dikin, D. A., Dommett, G. H., Kohlhaas, K. M., Zimney, E. J., Stach, E. A., . . . Ruoff, R. S. (2006). Graphene-based composite materials. *Nature, 442*, 282-286.

Stankovich, S., Dikin, D., Piner, R., Kohlhaas, K., Kleinhammes, A., Jia, Y., . . . Ruoff, R. (2007). Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon, 45*, 1558–1565.

Sun, Y., Wu, Q., & Shi, G. (2011). Graphene based new energy materials. *Energy Environ. Sci., 4*(4), 1113–1132.

Tahir, A. A., Ullah, H., Sudhagar, P., Teridi, M. A., Devadoss, A., & Sundaram, S. (2016). The Application of Graphene and ItsDerivatives to Energy Conversion,Storage, and Environmental andBiosensing Devices. *The Chemical Record,, 16*(3), 1591–1634.

Venkateswara, R. C., Reddy, A. L., Ishikawa, Y., & Ajayan, P. M. (2011). LiNi1/3Co1/3Mn 1/3O2–graphene composite as a promising cathode for Lithium-ion batteries. *ACS Applied Materials Interfaces, 3*, 2966.

Vuorilehto, K. (2018). Materials and function. Ninu L.-I. B. Applications, *Lithium-Ion Batteries: Basics and Applications* (oju ewe 21 - 27). Berlin, Germany: Springer-Verlag.

Wang, C., Su, K., Wan, W., Guo, H., Zhou, H., Chen, J., . . . Huang, Y. (2014). *Journal of Materials Chemistry A, 2*, 5018–5023.

Wang, J., Liu, J., Chao, D., Yan, J., Lin, J., & Shen, Z. X. (2014). *Advanced Materials, 26*, 7162–7169.

Wang, R., Xu, C., Sun, J., Gao, L., & Yao, H. (2014). *ACS Appl. Mater. Interfaces, 6*, 3427–3436.

Weber, C. J., & Roth, M. (2018). Separators. Ninu R. Korthauer, *Lithium-Ion Batteries: Basics and Applications* (oju ewe 75 - 88). Berlin, Germany: Springer-Verlag .

Wei, L., Chen, S., Yang, Y., Dong, Y., Song, W., & Fan, R. (2018). Effect of Graphene/TiO2 Composite Layer on thePerformance of Dye-Sensitized Solar Cells. *Journal of Nanoscience and Nanotechnology, 18*(2), 976-983. doi:10.1166/jnn.2018.14186

Wen, X., Zhang, D., Yan, T., Zhang, J., & Shi, L. (2013). Three-dimensional graphenebasedhierarchically porous carbon composites prepared by a dualtemplatestrategy for capacitive deionization. *Journal of Materials Chemistry A, 1*(39), 12334–12344.

Whittingham, M. S. (2004). Lithium Batteries and Cathode Materials. *Chemical Review, 104*(10), 4271–4302. doi:10.1021/cr020731c

Wong, H. -S., & Akinwande, D. (2011). *Carbon Nanotube andGraphene Device Physics.* Cambridge CB2 8RU, UK: Cambridge University Press.

Wu, H., Liu, Q., & Guo, S. (2014). Composites of Graphene and LiFePO4 as Cathode Materialsfor Lithium-Ion Battery: A Mini-review. *Nano-Micro Lett., 6*(4), 316–326. doi:10.1007/s40820-014-0004-6

Xia, X. H., Chao, D. L., Zhang, Y. Q., Shen, Z. X., & Fan, H. J. (2015). Three-dimensional graphene and theirintegrated electrodes. *Nano Today, 417*, 1-23. doi:10.1016/j.nantod.2014.12.001

Xu, H., Chang, J. S., & Gao, L. (2012). Graphene-encapsulated LiFePO4nanoparticles with high electrochemical performance for lithiumion batteries. *Materials Letters, 83*, 27–30.

Xu, Y., Lin, Z., Huang, X., Liu, Y. H., & Duan, X. (2013). *ACS Nano, 7*, 4042—4049.

Xu, Y., Liu, Q., Zhu, Y., Liu, Y., Langrock, A., Zachariahand, M. R., & Wang, C. (2013). *Nano Letters, 13*, 470–474.

Yang, J., Sham, T. K., & Sun, X. (2013). LiFePO4/graphene as a superiorcathode material for rechargeablelithium batteries: Impact of stackedgraphene and unfolded graphene. *Energy and Environmental Science, 6*, 1521-1528. doi:10.1039/c3ee24163g

Yu, Q., Lian, J., Siriponglert, S., Li, H., Chen, Y. P., & Pei, S. (2008). Graphene segregated on Ni surfaces and transferredto insulators. *Applied Physics Letters, 93*, 113103. doi:10.1063/1.2982585

Zhang, L., Chen, G., Hedhili, M. N., Zhang, H., & Wang, P. (2012). Three-dimensionalassemblies of graphene prepared by a novel chemical reductioninducedself-assembly method. *Nanoscale, 4*(22), 7038–7045.

Zhang, R., & Li, X. (2018). Multidimensional Assemblies of Graphene. Ninu H. Zhu, Z. Xu, D. Xie, & Y. Fang, *Graphene: Fabrication, Characterizations, Properties and Applications* (oju ewe 27-72). London, United Kingdom: Academic Press.

Zhang, W., Liu, F., Li, Q., Shou, Q., Cheng, J., Zhang, L., . . . Zhang, X. (2012). Transition metal oxide and graphene nanocomposites forhigh-performance electrochemical capacitors. *Physical Chemistry Chemical Physics, 14*, 16331.

Zhao, W., Fang, M., Wu, F., Wu, H., Wang, L., & Chen, G. (2010). Preparation of graphene by exfoliation of graphiteusing wet ball milling. *J. Mater. Chem., 20*, 5817–5819.

Zhao, Y., Feng, J., Liu, X., Wang, F., Wang, L., Shi, C., . . . Mai, L. (2014). *Nature Communication, 5*, 4565.

Zhen, Z., & Zhu, H. (2018). Structure and Properties of Graphene. Ninu H. Zhu, Z. Xu, D. Xie, & Y. Fang, *Graphene: Fabrication, Characterizations, Properties and Applications* (oju ewe 1-12). London, United Kingdom: Academic Press.

Zhou, X., Wang, F., Zhu, Y., & Liu, Z. (2011). Graphene modified LiFePO4 cathode materials for high power lithium ion batteries. *Journal of Materials Chemistry, 21*, 353–3358.

Zhu, J. Y., Yin, Z., Yan, Q., & Zhang, H. (2014). Graphene and graphene-basedmaterials for energy storage applications. *Small, 10*(17), 3480–3498.

Zhu, X., Zhang, P., Xu, S., Yan, X., & Xue, Q. (2014). *ACS Appl.Mater. Interfaces, 6*, 11665–11674.