Graphene to Supplement Conventional Electrode Materials in Lithium-Ion Batteries: Opportunities and Challenges

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Abstract—**Graphene is extracted from graphite and possesses some the ideal characteristics of very light weight, high conductivity, and chemical stability. The conventional materials used as LIB electrodes fail to meet the increasing demand of more efficient, faster, and lighter charge storing cells. This magnifies the role of graphene to be used as supplementary material for achieving higher levels of battery charge capacity, reduced charge losses during discharge, and greater cyclic stability over a longer duration. The researcher has examined graphene as a hybrid or supplementary element with lithium iron phosphate ($LiFePO_4$), manganese oxide, (MnO_2), and cobalt oxide(Co_3O_4), which are currently used as cathode materials, and with lithium titanium oxide ($Li_4Ti_5O_{12}$) and silicon (Si), which are presently used as anode materials.. Graphene as supplementary cathode material exhibited benefits of greater charge capacitance and cyclic stability, while at the anode it exhibited benefits of reduced discharge losses and reduced volumetric expansion. The integration of graphene at anode was met with fewer challenges than at the cathode as anode act as active charge carrier during the charging process and carbon-family elements serve as good charge retainers.**

I. INTRODUCTION

The current energy storage devises need to have higher conductivity, greater flexibility, lighter weight, and stable charging and discharging cycles in order to comply with the next generation electronics. Lithium-ion batteries (LIBs) have attained an edge over several other conventional battery types due to its high energy density, uniform charge-discharge rate, no memory effect, and longer durability [1]. It is for this reason that LIBs have gained much attention over the years and exhibit great potential for further improvement [2]–[4]. The conductivity, charge capacity, and overall cyclic performance of the battery depend on its cathode and anode [3]. The limited conductivity and irreversible losses incurred by the cathode and anode materials limit the overall battery performance [5]. The demand for more efficient energy storage devises augments put stress on the improvement of the cathodes and anodes of LIB so to make it more conductive and stable without increasing its weight.

A chemically and electronically stable material with high electrical conductivity, known as 'Graphene', has been discovered about a decade ago from the ores of graphite, and can be deemed a promising material to be used as LIB's electrode material [6], [7]. It is the lighter weight and high stability of graphene that makes it an ideal material to be used as a supplementary material with the conventional electrode materials [8]. The use of a very small proportion of graphene

has been observed to lessen the pertinent issues with the battery and improve the overall battery performance. The central discussion of the study will remain on the problems or limitations of LIB electrodes and how graphene can be used as a hybrid or supplementary material to overcome those limitations. Researches on graphene are comparatively scarce and also in their infancy stages. Thus, there is a need to compare and analyse multiple researches to justify the use of graphene in LIBs, and whether it can help the battery to sustain its charge capacity for even greater time period.

II. LITHIUM-ION BATTERIES

The charging and discharging capabilities of the lithium ion battery (LIB) is the most essential for its performance, and it is carried out by its power generating compartments called cells [7]. Each cell comprises of a positive electrode (cathode), a negative electrode (anode), and an electrolyte [9]. The most common compounds used for cathode are of lithium cobalt oxide ($LiCoO_2$) and lithium manganese oxide ($LiMnO_2$) [10]. A number of other chemical compounds of lithium nickel oxide ($LiNiO_2$) and lithium iron phosphate ($LiFePO_4$) have also been tested to be used as cathode materials, but with little success, because of the instability of the compound at extreme temperatures and when ion activity within the electrolyte increases beyond the defined threshold level [11]. The negative electrode i.e. the 'anode' is created from carbon element or carbon allotropes like graphite (allotrope) [12], silicon (Si) [2], and germanium (Ge) [2]. The electrolyte material then varies with the type of compound used as cathode and anode [7]. Figure 1 presents a schematic drawing of a cylindrical LIB, showing its various cell-layers.
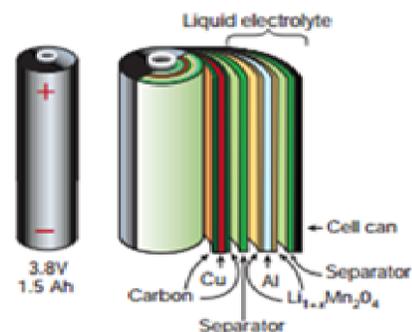

Fig. 1: Inner layers of a lithium-ion battery [11]

During the charging process, lithium ions are removed from the cathode into the electrolyte and intercalate or add to the carbon-based anode [12]. Electrons flow in a clockwise direction from the external circuit connecting the cathode and the anode. During the discharging process, a reverse procedure occurs, where the lithium ions deposited on the anode de-intercalate and add back to the cathode (figure 2).
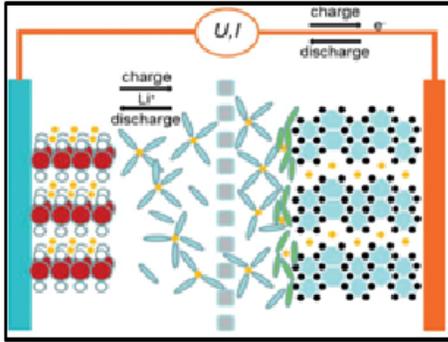

Fig. 2: Schematic diagram of a lithium-ion battery

The battery capacity is determined by the amount of charges that can be obtained and retained by the electrodes during the charging and discharging processes [6]. The theoretical capacity of a LIB can be determined by the following equation:

$$C_0 = 26.8n\frac{m_0}{M} = \frac{1}{q}m_o(Ah) \qquad (1)$$

Where, 'C_o' is the (theoretical) capacity of the battery, 'm_o' is the combined mass of all active chemicals participating in the charging and discharging process, 'M' is the molar weight of the active material, 'n' represents the total number of electrons involved in the reaction, and 'q' is the electrochemical equivalence.

A. Challenges with LIBs

Despite of the lightweight and fast charging and discharging abilities of the LIBs, there still remain some challenges and issues that hinder the true power potential of these batteries [1], [5]. First, the use of hard carbons like graphite often makes the selection of the electrolyte material a challenge [13]. Graphitic carbons do not combine well with an electrolyte compound of propylene carbonate (PC), which is used for faster Li-ion transport [14]. This mismatch between the anode material and the electrolyte causes the graphite carbon to deteriorate and lose capacity with each charging cycles, thus, reducing battery life [14]. One of the major problems with the present LIBs is their shorter life span, which is mainly because of the oxidation of the positive electrodes with the electrolyte [15]. When using delithiated $LiMn_2O_4$, the oxygen loss from the electrode is deposited at the electrolyte, which forms additional oxide layers [15]. This not only slows downs the charging process after some time, but also affects the overall life span of the battery. Moreover, the increasing demand of lightweight electronics is putting further pressure on the manufacturers to further reduce the size and weight of these batteries, which remain unachievable with the current chemical compounds [11], [16].

III. GRAPHENE CHARACTERISTICS

Graphene is one of the newly discovered carbon allotropes that offers great potential to be used in the electronic industry because of its high flexibility, conductivity, and stability [17]. Atabaki and Kovacevic (2013) state that graphene is the thinnest compound known to man, which is one atom thick with a two-dimensional honey-comb structure [8]. Other compounds like graphite have a three-dimensional structure due to which they have greater internal resistance and also take more space in the fabrication process [18]. On the other hand, graphene is a carbon nano-sheet, consisting of sp_2 hybridized carbon atoms with a molecular bond length of 0.142 nanometres [19]. When multiple layers of graphene are stacked on top of each other, it forms a three-dimensional structure, which is called graphite (figure 3).
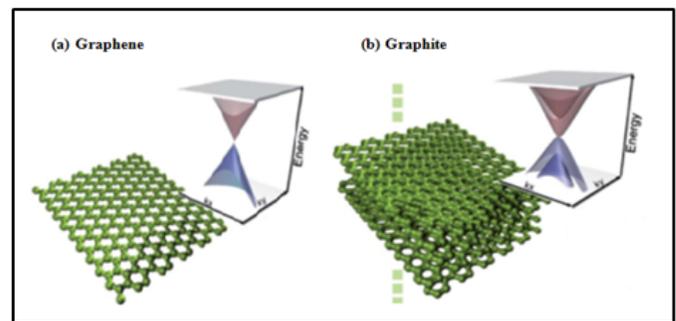

Fig. 3: **(a)** Single layer graphene structure **(b)** Multi-layer graphite structure [5]

A. Methods to Produce Graphene

One of the reasons that graphene could not be adopted as a substitute for a number of low conductive semiconductors in the electronic devices was the high cost involved in producing large scale graphene [9], [19]. However, in the recent years, great efforts have been made towards the production of cheap and stable graphene from graphite ores, which can be used in industrial goods [5], [20] like the lithium ion batteries, as will be discussed in this study. Some of the commonly used methods for extracting graphene are of micro-mechanical ex-foliation [21], chemical vapour deposition (CVD) [22], chemical reduction of graphene oxide (GO) [23], and the ball-milling approach [24].

The methods of micro-mechanical ex-foliation of pyrolytic graphite and CVD produce the most promising results in terms of graphene quality and stability when used in as a semi-conductor [25]. However, these methods are costly and only produce small amount of graphene [25]. For this reason, these methods are limited to applications that require very high quality graphene, whereas in applications demanding bulk production of graphene, these methods are not considered feasible [9]. The ball-milling approach has received great prominence over the years because of the simplicity of the procedure and also a cost-effective high quantity graphene yield [24]. This method does not require graphite to go through structural changes and this is how the complexity of the extraction procedure is minimized [24]. The chemical

reduction of GO is currently the most commonly used method for producing low-cost large-scale graphene [19]. The majority of the applications including battery electrodes production involve graphene extraction and preparation using the GO reduction method [26]. In this method, graphite is oxidized using a solution-based route to produce GO, which then reacted with hydrazine hydrate or other reacting agents to eliminate oxygen and produce graphene [26].

B. Potential benefits of Graphene

There are numerous factors that make graphene one of the ideal materials to be used as the base material for LIB electrodes. The honey-comb structure of graphene takes a surface area of 2600 m^2/G, which can store higher quantity of lithium ions [27]. This surface area is greater than the surface area measurements of activated carbons fabricated in electrochemical double layer capacitors [27]. For all electronic devices, high electron mobility is always desired in order to speed up the charge carrying process [28]. The electron mobility of graphene has been reported to be in the range of 15000 $cm^2/(V.s)$ to 25,000 $cm^2/(V.s)$, which is nearly three times that of graphite [19], [28]. Moreover, graphene has a thermal conductivity of 3000 $W/(mK)$ [19], which makes it one of the perfect material to be used as semi-conductors for high current density. Atabaki and Kovacevic (2013) stated that the weight of graphene is less as compared to that of other hard carbons used as electrodes. This offers a great opportunity to the manufacturers to further reduce the weight and size of the electronic devices, complying with the current demand for compactness and agility [8].

IV. Graphene-Based Electrodes for LIBs

Graphene has the potential to be used as both cathode and anode materials for LIBs. Currently, graphite is used as the active anode material with a theoretical capacity of 372 $mAhg^{-1}$ [4]. This is because of the trigonal structure of graphite, which allows six active atoms to interact with lithium [4]. The advantage with graphene is its ability to accommodate lithium ions on both sides, because of its uniform 2D structure, allowing a two times larger theoretical charge capacity than that offered by graphite and other hard carbon atoms [6]. While anode is the most prominent electrode to be fabricated with graphene, there have been experiments and studies reporting the use of graphene in the positive electrode in a hybrid setting [18], [29].

A. Problems at the Cathode

The commonly used cathode materials of $LiCoO_2$ and $LiMn_2O_4$ have the electrical conductivities of 10_4 S/cm and 10_6 S/cm [30]. These values are fairly low when high charging and discharging rate is required, and therefore, opens scope for experimenting new materials as cathode. Atabaki and Kovacevic (2013) state that pure graphene cannot substitute cathode materials because of its very high charge-discharge rate and instability in charging cycles when used with other materials in the device. For this reason, graphene composites

hold greater potential to be used as cathode material than pure graphene sheets [31].

Some of the major reasons of using $LiMn_2O_4$ as cathode material is the low-cost production and easy handling of the compound in the fabrication process [32]. However, the low-cost comes with disadvantage of low electrical conductivity and charge-rate capacity [32]. The study by Zhao, Hayner, and Kung (2011) demonstrates that a composite of $LiMn_2O_4$ and graphene sheets can provide solution to the low rate capacity problem. The study found charge-rate capacity of 101 mAh/g at 100 C, which is fairly higher compared to the individual capacity output of $LiMn_2O_4$ [20].

A recent study by Jiang et. al. (2012) found that graphene can help reduce the deterioration rate of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, which has been nominated as another potential candidate to be used as LIB cathode [33]. Its high energy density and high rate capacity makes it a suitable choice to be used as a cathode compound; however, the occurrence of 'cation disorder' during the discharging phase of the battery [33]. Cation disorder mostly affects spinel structures, when they are exposed to high radiation dose or high external temperature [34].

As mentioned earlier that experiments on the use of lithium iron phosphate ($LiFePO_4$) as cathode material has received little success because of its low electrical conductivity (10-9 S/cm^2) and poor lithium ion diffusion (10-14 to 10-16 cm^2/S) [13]. Scientists still believe it to be a potential material as it offers very high charge capacity (170 mAh/g)and is cheap to produce. Amin and Maier (2008) have provided the following premises for graphene to be added with $LiFePO_4$ for making a more suitable cathode compound. First, graphene encompasses high electrical conductivity and this can compensate for low conductivity of $LiFePO_4$ [35]. Second, the low cyclic diffusion of $LiFePO_4$ can be overcome with the very high cyclic diffusion of graphene. This will provide a balanced composite when specific proportions of both the materials are maintained [35].

Ding et. al. (2010) prepared a $LiFePO_4$-graphene composite with only 1.5% weight of graphene [36]. The experiment showed a discharge capacity of 160 $mAhg^{-1}$ at 0.2 C and the rate capacity was maintained at 110 $mAhg^{-1}$ (at 10 C). The experiment was successful in achieving stable charging and discharging at different C-rates [36].

B. Problems at the Anode

The commonly used anode materials for LIBs are graphite-based, tin-based and silicon-based materials [37], [38]. These materials have high charge storing capacity, and therefore, can store large quantity of Li ions during the charging process [37]. However, the major problem with these anode materials is their surface volume change with the battery operations [29]. Zhu et. al. (2014) explain that when silicon goes through expansion and compulsion phenomenon during charging and discharging [19]. This continuous expansion and compulsion alters the surface volume of the electrode, which alters the voltage diffusion process through electrolyte, and thus, affects battery performance and life [9].

Zhu et. al. proposed that coating silicon with carbon can help reduce the volumetric expansion of silicon. In the charging process, silicon interacting with lithium-ions forms Li_4Si_4; however, during the discharging process, silicon and lithium form Li_3Si_{275}, resulting in a 270% volume expansion of Si [19]. Another study by Chan et. al. (2008) noted that coating silicon with graphene cannot only limit the volume expansion during the discharging process, but will also enhance electron and lithium ions transport capability during the charging process [39]. In this way, graphene coating with silicon would allow faster charging time and also improved battery life.

Another problem reported at the anode is the loss of interconnection between the cathode and anode due to chemical instability between the anode material and the electrolyte [40]. Partially reduced partially titanium oxides (e.g., Ti_2O_3, Ti_3O_5, and T_5O_{12}) have shown improved chemical stability when they are made to contact with the electrolyte for a longer duration [40]. Moreover, it also exhibits improved pathway between the cathode and the anode for the diffusion of lithium ions [1]. However, there still remains the issue of discharge capacity drop when using titanium-based anode [8]. Due to the oxidation phenomenon in Ti_2O_3, it does not send all charges back to the cathode during the discharge process [40]. Some ions are retained at the anode or are dissolved in the electrolyte, thus, decreasing the discharge capacity of the battery and causing charge loss.

Li et. al. (2012) found that a hybrid of T_5O_{12} and graphene exhibit similar charge and discharge properties, when the composite react with lithium ions. At lower rates (1C and 30C), the composite was found to discharge 100%, but at higher rates, the discharge capacity reduces to some extent. A 200C, the graphene coating T_5O_{12} anode exhibited a specific capacity of about 170 mAh/g during charging and nearly 13 mAh/g during discharging, with 80% capacity retention. Tominaka et. al. (2011) further adds that titanium-based anode is still in its infancy stages; however, the addition of graphene can provide great progress to the application of titanium-oxide as a stable charge storing material [41].

V. RESULTS AND DISCUSSION

This section will present the experimental results obtained as secondary data to present how graphene can be mixed with the presently used electrode materials, the benefits it offers, and the challenges it encompasses that need further attention and experimental research.

A. For Cathode

1) Graphene and $LiFePO_4$: Hu et. al. (2013) mixed 0.8 weight% of graphene with $LiFePO_4$ (LFP) and find that the capacity of the cathode material is enhanced significantly (figure 4). The black circles representing LFP drops sharply after 100 charging-discharging cycles, while on the other hand, the blue circles representing graphene-LFP composite remain stable even till 200 cycles [42]. The capacity of the composite is also significantly higher, which is because of the faster conductivity rate of graphene as compared to phosphorous.
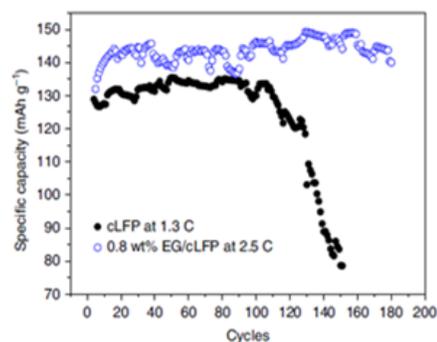

Fig. 4: Life cycle test for the Li+ ion battery cells based on the carbon-coated $LiFePO_4$ cathodes with 0 and 0.8 wt% of graphene

One of the problems reported in this cathode material was during the discharging process in which the voltage is observed, which results in reduced capacity at higher rates (2.5 28 C). To overcome this problem, more pure and high quality of graphene needs to be used with LFP, so that it does not stack-up to form graphite, which results in voltage polarization at the cathode [42]. However, even with this persisting challenge, the results show promising battery performance when a composite of graphene and LFP is used as cathode material.

2) Graphene and MnO_2: Yu et. al. (2011) find that the problem of low conductivity of MnO_2 can be significantly controlled by using solution processed graphene. The composite is created by adding 2 weight% of graphene with $Li - MnO_2$. It was found that the specific capacitance of the graphene composite is nearly three times higher than that of MnO_2, but it drops continuously as the charging rate increases [43]. However, the reduced capacitance at 100 mV/S is still higher than that offered by MnO_2 at the same rate (figure 5).
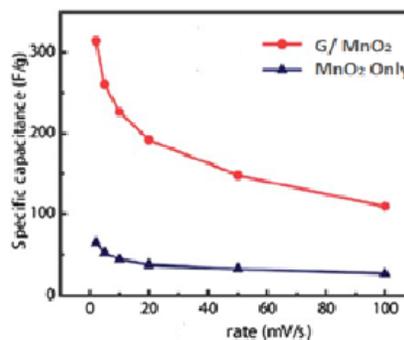

Fig. 5: Comparison of specific capacitance of MnO_2 only and hybrid of graphene and MnO_2

Moreover, the graphene/ MnO2 composite was found to maintain 95% of its capacitance for over 5000 cycles, while that of MnO_2 drops sharply after 1000 cycles (figure 6).
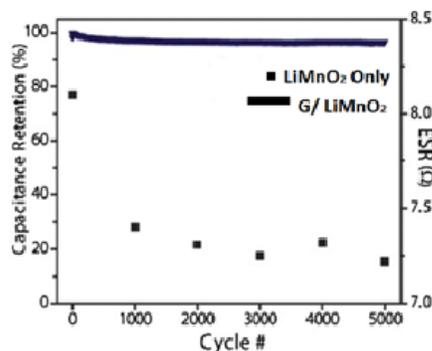
Fig. 6: Life cycle test for Li+ ion battery cells based on the $LiMnO_2$ cathode 2wt% of graphene

Xu et. al. (2013) found that the large surface area of graphene allows wide conductive paths for the diffusion of MnO_2, which results in fast electron transport, thus, greater battery conductivity [9]. The large surface area also reduces ion diffusion on the electrolyte (when graphene is also used in the anode), which sustains battery life and performance. The one problem that was noticed during the procedure was the increase in peak current value due to the high combined capacitance value of the composite [43]. This would demand an increase in capacitor value to sustain the high peak current and electrolyte material for maintaining constant ion transfer at peak current values and not overburdening the anode with ions bombardment at peak values.

3) Graphene with Co_3O_4: Tao et. al. (2012) prepared graphene-Co_3O_4 nano rods composites using the micro-mechanical ex-foliation method [44]. The problem Tao and workers were working after was the poor discharge capacity of $LiCoO_2$ cathode. The prepared composite exhibited a significantly large reversible capacity of 935 $mAhg^{-1}$ after 30 cycles, maintaining capacity efficiency of nearly 98%. Graphene nano composites (GNS) exhibited a low discharge capacity of just over 300 $mAhg^{-1}$ from the 8th cycle onwards, while Co_3O_4 alone exhibited even lower capacity of 85 $mAhg^{-1}$ from the 10th cycle onwards [44]. This shows how quickly the discharge capacity of the conventional batteries is degraded using the conventional materials only. Comparatively, Co_3O_4 nano rods/GNS nano composites maintained a capacity of 1310 $mAhg^{-1}$ at the 40th cycle, at a point where the capacity of Co_3O_4 was dying out (figure 7).
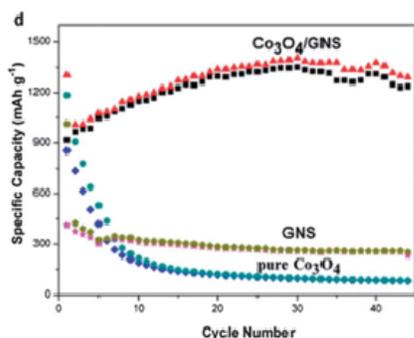

Fig. 7: Cyclic performance test of pure Co_3O_4, pure graphene, and composite or Co_3O_4 nano rods and graphene

The finding by Tao et. al. supports the assertion by He et. al. (2010) that graphene can fuse-in with cobalt oxide to decrease the ohmic losses, which will result in improved electronic conductivity at the cathode [45]. One of the drawbacks of this composite formation was the formation of Co_3O_4 particles on the graphene nano composite, after 12 hours of the battery operation. This would mean that the battery would require more frequent maintenance in order to remove extra Co_3O_4 particles from graphene nano composite as this would imbalance the proportion of graphene in the cathode material [44]. Also, changing the method of graphene extraction and modifying the weight% of graphene in the composite can also control the formation of supplementary Co_3O_4 particles [45].

B. For Anode

1) Graphene and $Li_4Ti_5O_{12}$: Li et. al. (2012) combined graphene with $Li_4Ti_5O_{12}$ (LTO) in order to combine the benefits of high capacity of LTO and high cycle stability of graphene at anode [31]. At 1C rate, the capacity of both LTO-only and graphene-LTO composite was found to be nearly 140 mAh/g, but LTO compound was found incapable of maintaining its capacity at higher rate, and becomes nearly zero at the rate of 200 C (figure 7). On the other hand, the composite was able to maintain its capacity at higher rates, with 80 mAh/g reported as the lowest capacity at 200 C (it is the lowest observed capacity, and would decrease further at rates ¿200 C) [31].
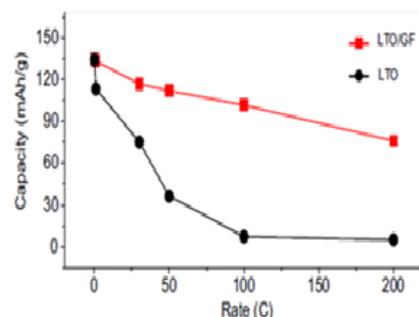

Fig. 8: Comparison of specific capacities of LTO/GF and reference LTO at various Li+ ion battery charge/ discharge rates

The cyclic stability of graphene-LTO composite at 30 C and 100 C is presented in figure 8. It can be seen that the capacity of the composite decreases negligibly after 500 cycles at 30 C and decreases less than 4% after 500 cycles at 100 C. This demonstrates the significant electrochemical stability of this composite when used as the negative electrode for LIBs [31]. Moreover, the problem of unavoidable surface reactions with LTO anodes is also suppressed by graphene coating as it offers low reactance with the conventional electrolyte material [46].
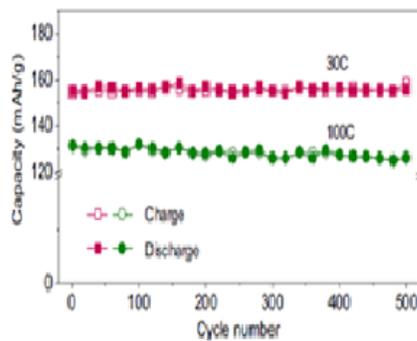
Fig. 9: Test of specific capacities and life cycles at various charge/discharge rates for LTO/Graphene composite

Fig. 11: Test for areal capacity and life cycles of the c comparison of pure Si, 2wt% AC-Si composite, 1 wt% Gr-Si composite, and 5 wt% Gr-Si composite

2) Graphene and Si: Maronia et. al. (2014) found that volumetric changes occurring at the anode due the creation of Li-Si alloy can be controlled through graphene coating [29]. To test this, Son et. al. (2015) conducted a study to directly grow graphene on Si via chemical vapour deposition process with the inclusion of CO2 [47]. The study tested the specific capacity and cyclic stability of pristine/pure silicon with its composites with 2 wt% amorphous carbon (AC), 1 wt% graphene, and 5 wt% of graphene (figure 10). The sample was taken different capacity rates and temperatures.
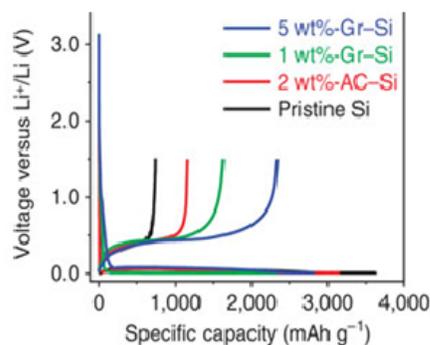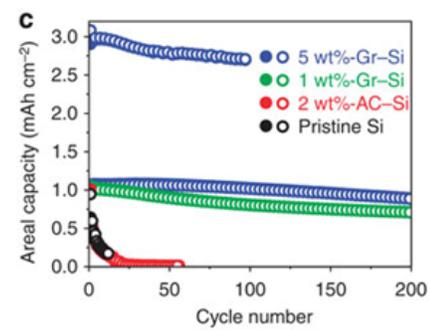

Fig. 10: Comparison of specific capacities of pure Si, 2wt% AC-Si composite, 1 wt% Gr-Si composite, and 5 wt% Gr-Si composite at different voltage ratings

All observations shows graphene coating on Si can greatly improve its conductivity during the discharging process and also enhance its areal capacity. This means that Si goes through smaller volumetric changes when Li ions are diffused into it, and this allows Si to absorb more charges without going through volumetric changes. The 5 wt% graphene-Si composite was able to maintain areal capacity of more than $1 mAhcm^{-2}$ for 200 cycles with nearly 96% capacity retention rate. Also, the 1 wt% graphene-Si composite exhibited a capacity of 0.8 $mAhcm^{-2}$ for 200 cycles with 91% retention rate (figure 11). On the other hand, both pure silicon and AC-Si composite failed to maintain their areal capacities and also exhibited very low voltage diffusion and specific capacities [47].

VI. CONCLUSION

Graphene applications as a stand-alone material for supporting electrons conductivity and high rate mobility is still limited by its high cost extraction and the scarce research done on it. However, this study confirms the hybridized application of graphene when used as a supplementary electrode material for the lithium ion batteries. Using very small proportions of graphene as electrode material can help achieve significantly high conductivity rate, high specific capacity, and longer battery life. It has been found that graphene can be used as a supplementary or coating material with both the cathode and anode materials to support the overall battery performance. The current applications already use carbon family elements like graphite, silicon, and other high reactive elements as the negative electrode, thus, graphene addition at the anode has been observed to be less challenging. Graphene is the smallest derivative of graphite, and therefore, encompasses a number of chemical and electrical properties of graphite. In addition, graphene's 2D honey-comb structure with a bond length of 0.142 nanometres provides it added flexibility and resistivity against high thermal activities and peak current loads. Thus, graphene serves as one of ideal elements to be used as a supplementary element with the currently used anode materials of silicon, silicon oxide (silica), and titanium oxide.

Graphene composite at the cathode also showed improved results, but was confronted with greater challenges than at the anode. One of the common problems found with all graphene composites at the cathode was the reduced performance at higher rate when the battery is being discharged. This means that graphene has comparatively less potential to be used as cathode material than as anode material in applications requiring higher charge discharge. Another problem observed when graphene was hybridized with MnO_2 was of the high peak current value during the charging process, which can cause damage to the anode. However, setting appropriate capacitance value at the anode or making graphene alloy with the existing anode material can enable resolving this issue. Regardless the drawbacks, graphene still exhibits higher charge capacity and cyclic stability at both cathodes and anodes. Working on the existing challenges and limitations can broaden the scope of graphene to be used as electrode material for the lithium ion batteries. An area of research that remain untouched in this

study was the comparison of capacitance, cyclic stability, and the overall battery performance when graphene is used at a single electrode and when it is used at both electrodes i.e. at both cathodes and anodes simultaneously. Future researchers can investigate if adding more graphene at either electrode can yield added benefits or the pertinent drawbacks would outweigh the benefits.

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