Present Development Of Anode Materials In Lithium-Ion Batteries: A Review

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Abstract- Recently the world is suffering from insufficiency of natural energy resources in comparison to higher energy consumption, lack of environmental health (Climate change, Air-pollution, plastic waste and so on) and the sudden enhanced usage of- portable electronics, electric vehicles, HEV on daily bases- motivates scientist to invent new, efficient, clean and low-cost alternative energy resources such as- Lithium Ion Battery. On account of high capacity, fast charge-discharge rates, light weight, long lifetime, high stability Lithium-ion batteries are very promising energy storage devices. Their great electrochemical performance makes them commercially viable. These rechargeable batteries have proved themselves as a rising star and contain a lot more potential to fulfil the future energy requirements. This paper will highlight a review on Li-ion Batteries from their birth till now, the growth and increments on their fabrication techniques. It also gives us an idea about why carbon nanostructures (CNS) as- graphene, CNTs, CQDs, and GQDs are the best additives for any anode materials for Li-ion Batteries. We hope to present a brief knowledge about different anodes with comprehensive study which were already available in the literature.

Keywords- Lithium-ion batteries, Cabon nano structures, Carbon nano tubes, Carbon quantum dots, Graphene quantum dots, Graphene nanosheets, porous carbons.

1. INTRODUCTION-

Li-ion battery; since its commercialization in 1991 till now, is one of the most dominating fields of energy storage researches. On account of high capacity, fast charging, light weight, long lifetime & high stability, Li-ion batteries are very promising energy storage device; their great electrochemical performance makes them commercially viable. Their advanced features have affected many electronic/power sectors directly. As these batteries are main power source for wide range applications in electric vehicle, HEVs and dominate the market of portable electronics of laptops and mobile phones as well.

A basic Li-ion battery consists of Cathode (positive electrode), Anode (negative electrode) and Electrolyte with Li-ions. The recursive storage and transportation of Li-ions between the anode and cathode terminals by electrolyte solution, is the basic chemistry behind these rechargeable Li-ion batteries [1]. The performance and lower cost of any battery mainly depends on the development of the electrode material [2]. The searching of best compatible combination of anode-electrolyte-cathode is the most interesting field of all time, but in this particular paper we will review several commonly studied anode materials. Commercially; Graphite is used as an anode material. However, Graphite is easily available having low cost and shows very good control over structural stability but it suffers from limited Theoretical capacity (372mAh/g) and poor rate performance [3], which may instigate researchers to find out new materials as anode having highly porous structure, large active surface area, good electric conductivity for the betterment of battery.

In these perspective unique properties of carbonic nano materials (nano diamonds, fullerenes, carbon nano tubes, graphene sheet, fluorescent carbon nano particles and carbon quantum dots) makes them an ideal choice of anode. This paper will highlight a review on Li-ion Batteries from their birth, commercialization till now the overall growth in fabrication techniques, followed by increments on their electrochemical performance. This paper will elucidate some commonly studied carbon-based nano-structured anode materials. It also gives us an idea about why carbon-based nanostructures and their composites are the best choice of anode materials for Li-Ion Batteries with comprehensive study of different anodic materials which were already available in the literature.

2. HISTORICAL DEVELOPMENT OF LI-ION BATTERY- How first Li-ion Battery was invented?

The invention of battery technology was the golden era having fantastic history of research over times. The idea of rechargeable battery was first adopted by British Chemist M. Stanley Whittingham in 1970, while studying the intercalation behaviour of Li and TiS_2. These reactions occurred rapidly and reversibly. It was the basis of rechargeable battery technology. Whittingham then took the idea and used titanium-

disulphide (TiS_2) as cathode and lithium metal as anode [4]; however, these batteries could never be made in practical, because of expensive fabrication and induced toxic materials. After that research were diverted to develop new electrodes, which contain lithium compounds instead of metallic lithium. The search of alternative cathode took scientists towards Lithium cobalt oxide. In 1979, John B. Goodenough and Koichi Mizushima [5] discovered Lithium cobalt oxide as a new cathode material and lithium metal as anode material. $LiCo_2$ is stable, can be paired with various combinations of anodes-electrolytes and proved as a most significant donor of Li-ions. Nevertheless, search for a new cathode material has been a very interesting field of research since a very long time. Since this paper purely focuses on different substitutions of anode material which consequently follows. The search of new anode was started with the inherent concept of intercalation and de-intercalation of Li-ions in graphite materials. In 1978, Samar Basu et al successfully demonstrated Lithium-Graphite intercalation compound [6] consequently in 1982- Yazami and Touzain reported the electrochemical intercalation and de-intercalation of lithium in graphite [7]. These experiments provided the scientific basis for the use of graphite as anode material- as commercially used in LIBs today. Getting inspiration from John Goodenough's work, Akira Yoshino was ready to set a new path in battery technology. In 1985, Yoshino et al used lithium cobalt oxide ($LiCo_2$) as cathode and carbonaceous materials as anode for the first time [8]. He patented it as a first Li-ion battery and becomes the commonly accepted inventor of Li-ion batteries. However, the safety concerns regarding to these rechargeable batteries were the next hurdle before its commercialization. Yoshino performed a Standard Safety Validation Test on his battery. In which, an Iron Lump was impacted on battery- where many battery technologies have failed, Yoshino's LIB was the only one which succeeds. Yoshino quoted this moment as - "The moment when Li-ion battery was born [9]".

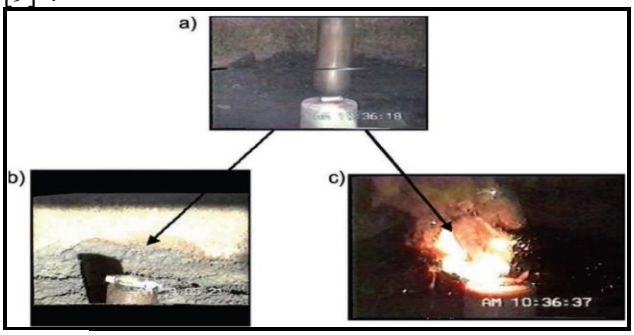

Figure 1: Photos of the safety validation tests performed for Yoshino: (a) image after the cells was impacted with the iron lump, (b) Yoshino's LIB after impact, and (c) the flaming aftermath of the LMB cell. **(Reproduced with permission from [9])**

Shortly, in 1991-Sony Corporation and in 1992- A & T Corporation (Asahi Kasei Corporation, Tesla Corporation in a partnership) commercialized the Li-ion battery [10]. Finally, a battery was invented which was small in size, light weighted, extremely durable at the same time reasonable priced for electronic systems, firstly used in cell phones/ Mobile phones. Till now, it has a wide range of applications in- electric vehicles (Nissan and Tesla cars), mobiles, laptops, digital cameras and heavy electric vehicles as well. In 2012- J. Goodenough, R. Yazami and A. Yoshino were awarded the 2012-IEEE Medal for environmental and safety technologies, to acknowledge their tremendous contribution to the development of LIB Technology [11]. In 2019- The Nobel Prize of Chemistry was given to J. B. Goodenough, M.S. Whittingham and A. Yoshino for the development of Li-ion batteries [12]. Till now there are many other opportunities for the improvement of Lithium-ion battery performance by developing new efficient carbonaceous electrode materials

3. THE BASIC PRINCIPLE EVOLVED IN LI-ION BATTERIES & ITS SUPERIORITY AGAINST OTHER BATTERY TECHNOLOGY:

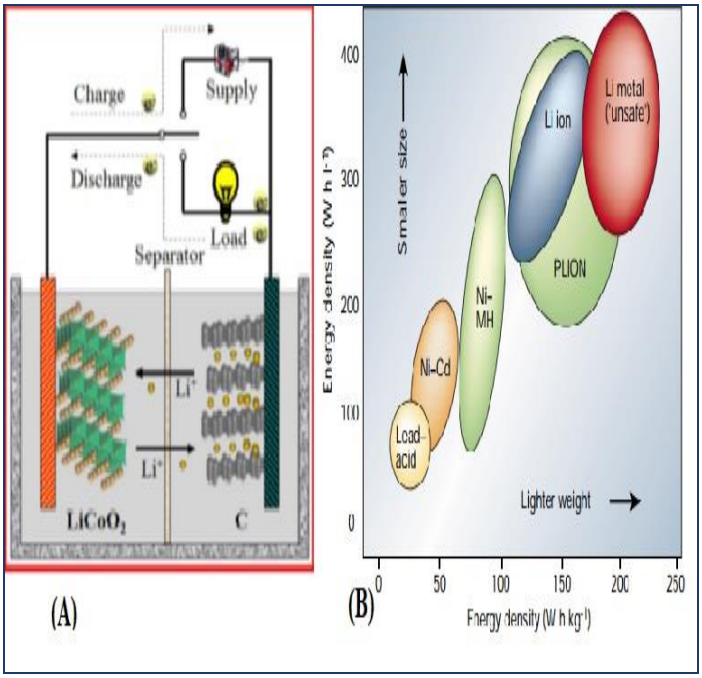

Figure 2 (A) Illustrates the basic principle and operation of a Li-ion battery **(Reproduced with permission from [13]),** (B) Illustrates Energy density of different batteries, **(Reproduced with permission from[14].**

Basic chemistry of batteries is "the consecutive intercalation and de-intercalation of positively charged ions between the electrodes" Figure 2 (A). Li-ion battery consists of two electrodes (cathode "positively charged" & anode "negatively charged") and an electrolyte solution (medium that allows ions to transfer between both the electrodes consequently). The electrodes are separated by a separator which is usually made of micro-porous polymer. This micro-porous structure of separator allows the exchange of Li-ion between the two electrodes by crossing the electrolyte but not allow electrons to transfer from it. While charging the battery- Li-ions deteriorate and extracted from cathode transport through the electrolyte medium and finally inserted into anode this reaction is called charging process. While using these batteries as energy source- Li-ions are extracted back from the anode during discharging transport through the electrolyte and inserted back to the cathode, this reaction is called discharging process, a whole charging and discharging process is known as one cycle [1]. The continuous charging and discharging cycles may result as formation of solid electrolyte interface (SEI) layer. SEI layer blocks and prevents any direct contact between the ions and electrolyte. Sometimes save electrodes and electrolyte form permanent damage which implies as the improved performance of the battery [2]**.**

The performance of any battery is mainly evaluated by some parameters – specific energy density (Wh/kg), specific capacity (Ah/kg), cyclic life (stability of battery during charge /discharge cycles), charge and discharge rates/C-rates, safety and low-cost fabrications are some basic parameters of an ideal battery.

Since the development of Li-ion batteries many other technologies were also investigated in parallel manner. Such as- Sodium-Ion Battery, Magnesium-Ion Battery, Potassium-Ion Battery, and so on but the applicability of Lithium-ion batteries is much higher than any other techniques, as Lithium is the lightest metal (atomic size 3) and containing only one electron in its outer shell, it has highest tendency to lose that electron, which implies the smoother transportation of ions and electrons. If we discuss about Na-ion or K-ion batteries- they are said to be the most significant alternative because of using cheap, abundant raw materials and shows slightly similar electro-chemical properties. But their lower energy density, higher atomic size and toxic electrolyte combination bounded their commercialization [15, 16]. Another alternative is Mg-ion Battery – these can say to be the real competition for Li-ion battery regarding to their high theoretical capacity, safe and inexpensive raw material. But the only demerit is to find out suitable combination of cathode-electrolyte-anode materials, which makes them unviable [17]. At present Li-ion batteries are the superior option for energy storage devices and electric vehicles. A comparative kind of illustration of different battery technology is presented in Figure 2: (B).

4. PRESENT DEVELOPMENTS ON LIBs ANODE:

The research for anode that was safe and more stable had already gone under great progress. Various significant efforts have been made in the last decade to develop efficient anode. Some of them are- Carbon nano-tubes, Graphene / Carbon quantum dots, Porous Carbon structures, Silicon and their composites, transition metal oxides, transition metal sulphides. In this section we are going to discuss about some of them.

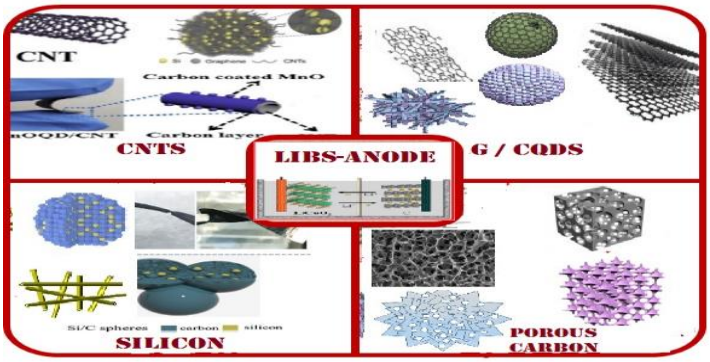

Figure 3: Schematic of the four main types of anode material for lithium-ion batteries (LIBs) as- CNTS, G/CQDS, SILICON and Porous Carbon.

a) Carbon nano-tubes (CNT) and Composites-

These are the strongest material which can be prepared in laboratory have achieved considerable attention as anode; because of their high aspect ratio, excellent electrical conductivity, superior mechanical strength, accessible surface area, and porous cylindrical structure. CNTs have been recognized as a solution for improving the performance of LIBs. It is said that the incorporation of CNT network can enhance the conductivity, decrease the agglomeration problems and increase the electrochemical properties of electrodes [18]. The maximum reported reversible capacity of Single Walled CNTs (SWNT's) is 1000mAh/g; which is far better in comparison to graphite (372mAh/g) and ball milled graphite (708mAh/g) [19].

It is very essential that thermal treatment over sample can result into better performance; consequently, in 2001 T. Prem Kumar et al presented a comprehensive study on electrochemical performance of CNT and Heat-treated CNT (Thermal Oxidation) [20]. The results revealed that

thermally treated samples have increased porous sites and demonstrated superior electrochemical performance compared to CNT. But it was not sufficient according to increasing demands, that's why there is a need of improved technologies. Recently scientists are interested in CNT-based composites instead of pristine CNTs. Literature has many evidences that CNT Composites with nitrogen, Lithium alloying metal (Li-CNT, Ni-CNT-Li) [21], transition metals and their oxide such (tin, manganese, titanium etc.) [22], conductive alloys (FeF_3, BiF_3, MoS_2 etc.) [23] could results into a better candidate. Such sample of CNT@CNF was prepared in 2008 by J.Y. Zhang et al, via Chemical Vapor Deposition technique [24]. Such sample illustrated reversible capacity of 400mAh/g and were stable over 120 cycles.

TMOs are also studied as efficient anode such as SnO_2, which showcased higher initial capacity but poor rate performance and volume variation restricts their applications. To overcome such demerits- Tin Dioxide incorporative Multi Walled CNTs (SnO_2-MWNT) sample was prepared in 2009 by Guodong du et al using simple Solvo-thermal Method. It demonstrated reversible capacity of 709.9mAh/g at first cycle. Although it seemed to be lower than bare SnO_2 but it illustrated more stable rate performance till 100 cycles and CNT content provided better control over volume variation and prevents tin agglomerates [25]. Further improvement in the rate performance was appeared by introducing copper oxide with SnO_2/CNTs such composite of copper oxide, tin oxide and CNTs was reported in 2014 via simple in situ chemical treatment, Cu_xO/SnO_x@CNT and Cu_xO/SnO_x@SnO_2/CNT- anodes provided a dramatic improvement in the initial capacities of - 1710 and 1426mAh/g. and capacity retention after 70 cycles was 580 and 800mAh/g respectively which was far better than the ordinary SnO_x@CNT (rev. capacity of 106mAh/g after 70 cycles) composites[26].

In 2016- a very unique structure of Mn_3O_4 embedded 3D N-doped graphene- CNT network was introduced. It demonstrated brilliant electrochemical performance and high lithium storage capacity [27]. Similarly in 2019 S. Huang et al, prepared a composite of MnO quantum dots- N-doped carbon layer anchored on CNT as a freestanding anode. The schematic is represented in figure 4(A). Studies revealed that well dispersed carbon layer over MnO can reduce the volume expansion risk and enhanced electrochemical performance. It demonstrated highly stable capacity of 883mAh/g even after 1000 cycles see in figure 4(B). This was obviously higher than theoretical capacity of MnO, Mn3O4 and graphene as well [28]. In this list, Titanium Dioxide comes next and their CNT composite was introduced in 2017 TiO_2-CNT structure had shortened the ion diffusion length and ensured the excellent electronic conductivity [29]. "**Recently NEO Battery Materials Signs a Collaboration Agreement with Applied Carbon Nano Technology Ltd. in South Korea in June 15, 2022"**. The collaboration agreement establishes strategic cooperation to further advance related to carbon nanotube ("**CNT**") coating technology for silicon anode materials. CNT can act as an effective damper for the volumetric expansion problem of silicon anodes during cycling. Additionally, the superior electrical conductivity of the material allows the performance of the anode to be maximized [30].

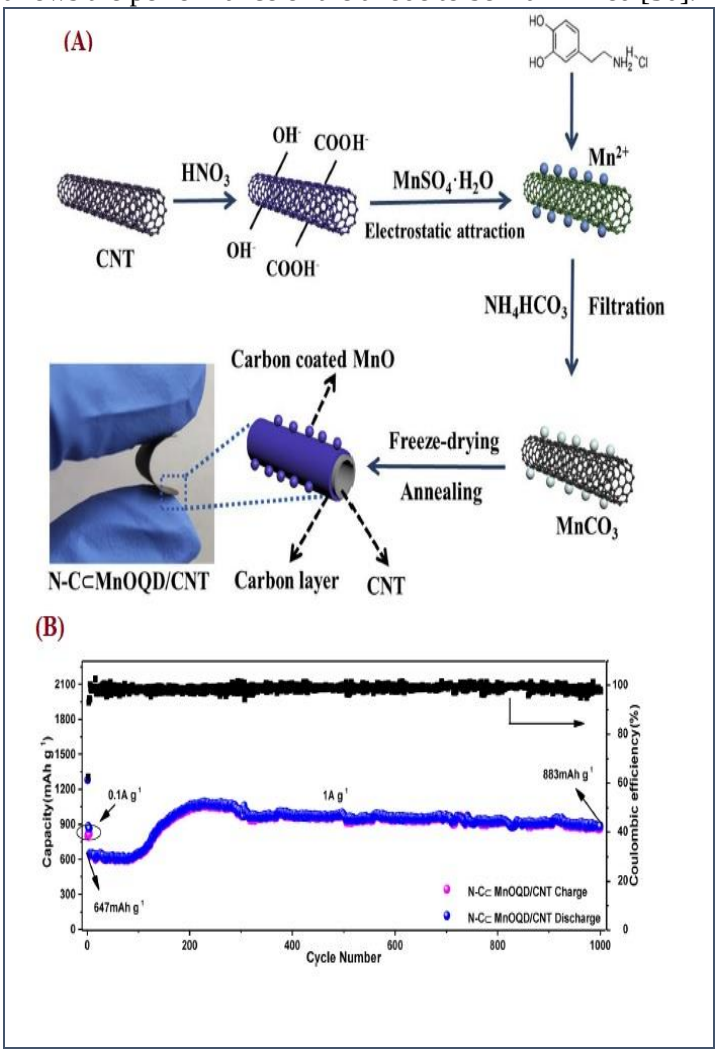

Figure 4: (A) Schematic illustration of fabrication process of the flexible free-standing N-C< MnO QD/CNT film with pathways for Li-ion battery. (B) Long cycling performances of the flexible free-standing N-C<MnO QD/CNT electrode at a current density of 1 A/g **(Reproduced with permission from [28]).**

Most recently in 2022 Novel anode materials were synthesized by in situ growth of spheres of graphene and carbon nanotubes (CNTs) around silicon particles, see in figure 5(a, b and c). Due to their high mechanical resilience

and electrical conductivity, these composite materials can withstand the high pressure and induced stress that are created during the charging and discharging of the electrodes. The resulting electrodes have adequate volumetric capacity (1006 mAh/cm^3), excellent cycling durability (90% capacity retention at 2 A/g after 700 cycles or a capacity fading rate of 0.014 percent per cycle), and superior cycling performance, see in figure 5(d). whereases, figure 5(e) demonstrated SEM analysis report of G-Si-CNTs sphere [31].

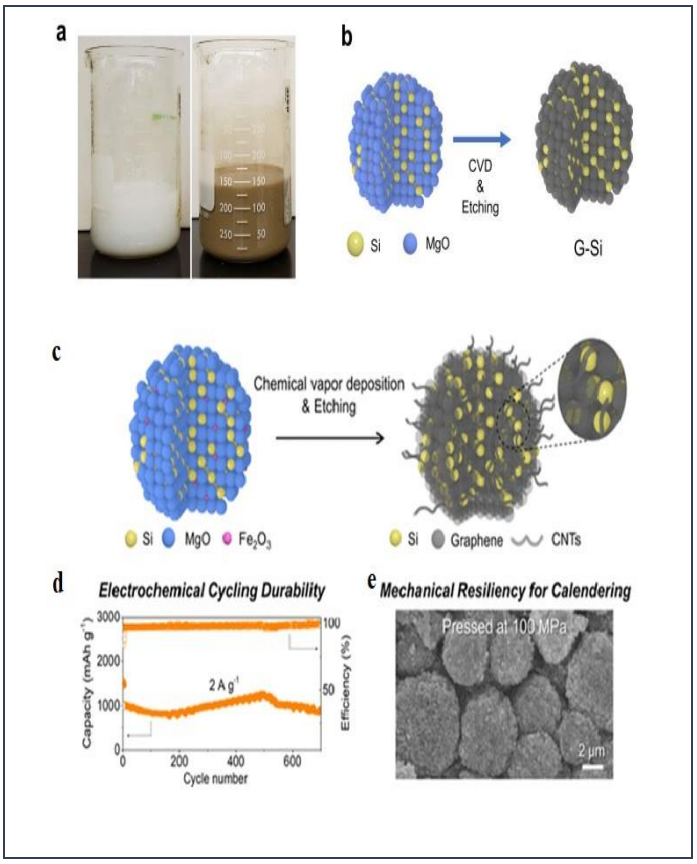

Figure 5: (a) Photographs of aqueous precursors. Left: MgCO3. Right: MgCO3, Si, and Fe (NO3)3. (b) A synthetic schematic of G-Si. (c) A synthetic schematic of in situ growth of spheres of graphene and carbon nanotubes (CNTs) around silicon particles. (d) Cycling performance of sample at 2A/g current density. (e) SEM image of an individual G-Si-CNTs sphere**. (Reproduced with permission from [31]).**

b) **CQD/GQD and Composites**:

Carbon quantum dots (CQDs) are nanoscale carbon particles having a diameter of less than 10 nano-meters. X.U. et al. was the first who found these 0-dimensional CQDs accidentally in 2004 while purifying single walled carbon Nanotubes [1]. Similarly, Andre Geim and Konstantin Novoselov developed graphene, one of the most widely utilized allotropes of carbon, and were awarded the "Nobel Prize in Physics in 2010" for "Ground breaking experiments regarding the 2-dimensional material Graphene"[32]. Graphene is a two-dimensional planar sheet of carbon atoms that is one atom thick. It has many structural and fundamental properties similar to carbon nanotubes [33]. The features of these nano-sized carbonic dots are incredible, including - strong and tunable fluorescence emission, structural and chemical stability, huge active surface area and electrical conductivity, low toxicity and good conductivity, strong intercalation ability, low density, and outstanding mechanical and electrochemical capabilities are just a few of the many characteristics of these CQDs/GQDs.

As GNS have stacked multilayered structure, it has a potential to capture ions on both sides of every graphene sheets. Such type of report was firstly presented by Peng Guo et al in 2009. Graphene nano-sheets (GNS) were synthesized from artificial graphite by oxidation and ultrasonic treatment. Such prepared GNS presents Variety of voids and cavity which provides an excellent initial charge and discharge capacity, good cycle performance and high-rate charge/discharge properties. But a huge loss of capacity was induced during the upcoming cycles [34]. It is suggested that large irreversible capacity of GNSs can be decreased by the surface modification through various methods. This kind of modification was performed over GNS through chemical treatment in 2011. As a result, these GNS structure demonstrated superior reversible capacity of approximately 600mAh/g in 2nd cycle which was maintained till 80th cycle [35]. To achieve enhancement in rate performance, a coal based porous graphene structure (CPG) was developed in 2018 by Baolin Xing et al. They used an inexpensive graphitization, liquid oxidation and thermal reduction synthesis routes. Such prepared samples have high specific surface area and large pore volume, which provides sufficient active sites for Li-storage. CPG demonstrated very high initial capacities and tremendous reversible capacity of 601mAh/g which maintained till 110 cycles [36]. In 2020 another network of 3D-carbon honeycomb material (bco-C20; from graphene network) was introduced by S. Wang et al, which provides high theoretical capacity of 893mAh/g [37].

Even with lots of advantages, graphene anodes also faced some demerits such as incorporation of agglomerates during fabrication, which restricts its large-scale development. This can be solved by using composites of graphene instead of pure graphene. We will be discussing some of them below. In 2015- Jiantie Xu et al introduced nitrogen doping on holey graphene. We have already witnessed that introduction of heteroatoms into carbonic structures could results better electrochemical performance. These results indicate that N-hG contains high packing densities and excellent ion insertion and extraction tendency which makes it an ideal anode. And even after 6000 cycles its discharge

capacity was still maintained to 553.5mAh/g at very high current rate of 5A/g; whereas pristine graphene possesses only 198.1mAh/g [38]. These results implied that N-hG exhibited significantly better initial capacities and stabilities compared to pristine graphene.

It is well known from the literature that transition metal oxides and graphene both have been individually proved themselves as milestone in energy storage applications. And their carbon embedded composites can provide better performance. However, their composite illuminate's high reversible capacity but induced agglomerates, volume variation and weak electrical conductivity demands some modifications in fabrication and structure of samples. Many other anodes such as- **(**(Co, $Mn)_3O_4$ / rGO**)** composite in 2016 [39] and SnO_2/ rGO composite in 2019 [40] are present in the literature.

In response to this, Z. Deng and T. Liu demonstrated another nanostructure of Bi_2O_3-rGO in late 2017. Bismuth oxide nanoparticles of single crystal type were evenly distributed throughout the surface of reduced graphene oxide sheets. This generated samples demonstrated superior reversible capacity of 347mAh/g at 1C rate after 100 cycles with 79% CR, which was unquestionably superior than bare -Bi_2O_3 (169mAh/g with 43%-CR) [41,42]. Another study found that Bi_2O_3 and CQD composites provided excellent stability and prevented electrode cracking. A. Prasath et al created a CQD-Bi_2O_3 composite using a hydrothermal technique in 2019. Its unique construction guaranteed improved ion transport and a very high discharge capacity of 300mAh/g after 30 cycles at 100% CR [43].

In 2015 by M. Jing et al used manganese oxides (Mn_3O_4) and CQDs composite instead of individual CQDs for battery applications. Since manganese oxides have already demonstrated their application as anode [44], very soon it became the most convincing choice of electrode material. But lower conductivity and induced pulverization restricted their commercial acceptance. These deficiencies could be overcome by making their composites with carbon matrix. A CQD coated Mn_3O_4 sample via Electro-chemical process was fabricated. CQD coating can control the volume variation and provide better ion transportation, which results as great enhancement in the cycling stability and rate performance and capacity was maintained to 791mAh/g even after 100 cycles [45] which was better than bare Mn_3O_4 (114mAh/g after 100cycles). After two years in 2018, S. Wang et al prepared nitrogen doped CQD from egg yolk via hydrothermal reaction. Nitrogen is a well-known dopant, and proper content of nitrogen can surely enhance Electro-chemical properties of any carbon matrix. Its layered structure, high surface area and small diffusion path provided high rate and cycling performance and porous structure provided sufficient interstitials for ionic transportation [46]. Such prepared N-CQDs demonstrated high rate and cyclic stability as even after 100cycles it delivered high reversible capacity of 711mAh/g with almost 100% CE. In 2020- D.Y. Shin et al etched F-CQD (hydrothermal & post calcinations) directly over Cu foil through electrochemical and spray coating techniques. F-CQD @ etched-Cu foil: exhibited specific capacity of 297.3mAh/g with 94.3% capacity retention after 100 cycles at 100mA/g current density, which was evidently very better than bare Cu (specific capacity-251.4mAh/g with capacity retention-80.9%) and etched Cu (specific capacity-279mAh/g with capacity retention-89.2%). These samples provide very good area coverage over Cu foil resulted as improved ionic/ electrical conductivity and easy transportation channel for ions as well [47]. In 2018 M. Javed and fellows find out an unique CQD fabrication technique from D-(+) glucose via chemical oxidation technique. Such prepared samples exhibited reversible capacity of 864.9mAh/g after 500 cycles at 0.5C rate with 91.6% CR [48].

We are presenting variety of CQD based metallic composites. In the same year Z. Xu and his group studied Molybdenum trioxide and CQD composite. Individually MoO_3 provides specific capacity of 1117mAh/g which was good enough, but its poor electrical conductivity and large volume change restricted its viability. To avoid these difficulties, MoO3/CQD composite was fabricated via hydrothermal technique. These composites provided better control over volume variation of sample and great rate performance with 71.2% CE. And capacity sustained up to 890mAh/g at 0.1A/g even after 100 cycles, see in figure 6(A, B) [49]. Transition metal carbonates ($MnCO_3$, $CoCO_3$, $ZnCO_3$ and so on) have also proved themselves as potential electrode materials. This kind of research was reported in 2020. B. Jiang et al developed $FeCO_3$ and N-doped CQDs anode ($FeCO_3$/N-CQD) via one step hydrothermal synthesis technique. CQD content provided stability and control the volume expansion. Their unique hierarchical porous structure and large surface area represented better electrochemical reactions. Its reversible capacity reached to 872mAh/g at 200mA/g current rates after 460 cycles, see in figure 6(C, D) [50].

Our former studies indicate that most of the materials genuinely faced volume variation, which introduced Sevier or permanent damage on conductive network of battery. To avoid such circumstances, self-healing materials and CQD composites have been grabbing the attention of scientists. In 2020 J. Gua and collogues prepared a hollow Ga_2O_3@N-CQD composite as self-healing anode via simple microwave and chemical treatment. Gallium content provided it the self-healing ability (Due to its lower toxicity and lower

melting point (29.8°C)). Hollow structure decreased the diffusion path between electrode and electrolyte. N doped CQD layer provided structural stability and electrical conductivity. It delivered high discharge and charge capacity, good control over sample. Excellent reversible capacity 410mAh/g was achieved at 2A/g rate after 1000 cycles with CR of100%, see in figure 6(E, F) [51], which was undoubtedly far better than any other gallium-based nanostructures. Another approach is assembling the anode directly over the collector (Cu foil) to provide better stability and cycling capacity.

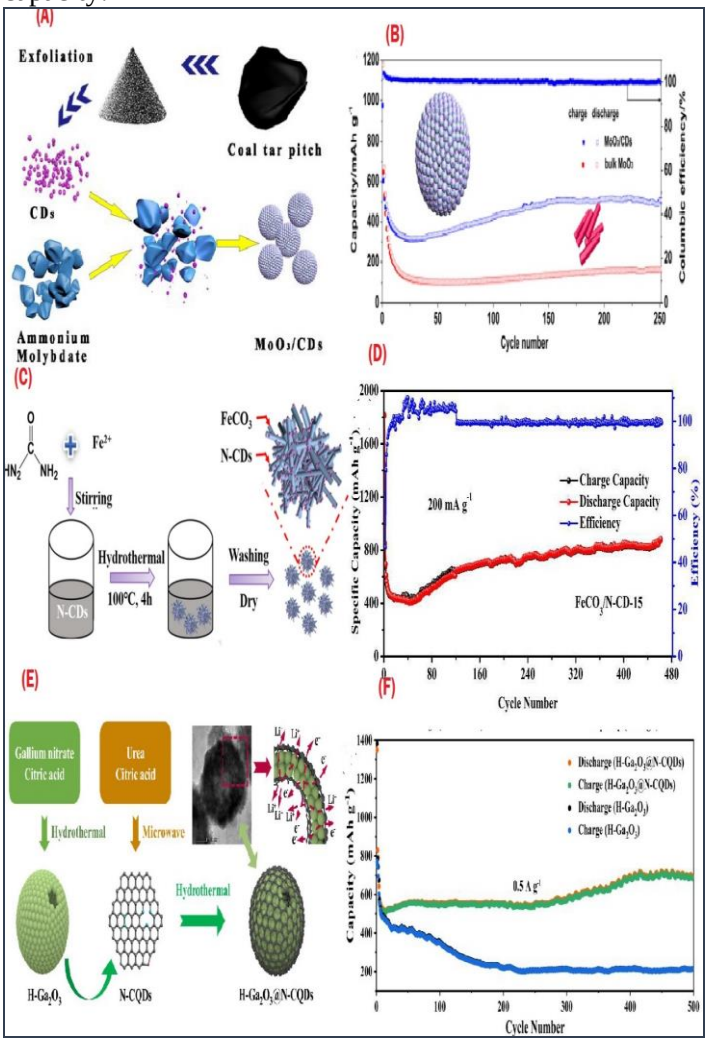

Figure 6: (A) Diagram of the synthesis process for the MoO3/CDs, (B) The cyclic performances of the MoO3/CDs and MoO3 at a current density of 0.5 A/g **(Reproduced with permission from [49])** (c) Schematic illustration of the formation process for FeCO3/N-CD Composites, (D) cycling performances of FeCO3/N-CD-15 at 200mA/g rate **(Reproduced with permission from [50]).** (E) The synthesis schematic illustration of the H-Ga2O3@N-CQDs nanospheres, (F) cycling performances of the H-Ga2O3 and the HGa2O3@N-CQDs electrodes at 0.5 A/ g, the first three cycles are under 0.1 A/ g **(Reproduced with permission from [51]).**

c) **Porous carbon and Composites**:

The research for anode that was safe and more stable had already gone under great progress. Various significant efforts have been made in the last decade to develop efficient anode. The porous carbon was deemed as one of the most promising candidates amongst them because of their high stability, brilliant porous morphology, excellent electronic conductivity, and easy transportation of ions [3,9]. The literature has various reports like -Nitrogen doped porous carbon nano fibre webs (CNFWs) in 2012. The presence of heteroatom on carbon surface can give rise to reactivity and electrical conductivity of sample [52]. Porous graphite carbon nano-sheets (PGCs) in 2013. via consecutive chemical treatments. The unique 2D highly porous structure of sample provided it a better stability, mechanical flexibility, and electronic conductivity. It demonstrated higher electrochemical performance [53]. Candle soot fractal like CNPs in 2015 was fabricated by collecting candle soot over current collector directly. Their unique amorphous nature and parallel stacked graphene layers can enhance their transportation capacity and electrochemical performance. [54]. Floral variant mesoporous carbon (FMCs) in 2016 via direct pyrolysis. Their floral morphology, mesoporous structure and large inter layer void rooms provided it such enhanced performance as anode for LIBs [55]. Another structure of carbon is –Cheese like bulk carbon with nano-holes was investigated in same year by X. D. Liu et al via simple annealing method. Their exceptional enhanced performance attributes to its cheese like highly porous structure which provides high surface area and better contact area between electrodes and electrolyte [56]. Doping of heteroatoms is a technique which is used since very long time to enhance materials electrical conductivity. In this regards a lot of reports are available as – in 2016 SnO_2 QDs, anchored on 3D Nitrogen & Sulfur dual doped porous carbon (NSGC@SnO_2). Its specific 3D porous architecture, high concentration of individual SnO_2 QDs and synergetic properties of N and S co-doping provided it tremendous electro-chemical performance, which was far better than individual SnO_2 and porous carbon anodes [57]. In a Similar manner N-doped porous carbon scaffold (NPCSs) was synthesized in 2017 [58]. Multi-doped carbon architectures were trending in terms of energy storage device fabrications. Nitrogen Oxygen Sulfur doped carbon architecture (NOSDA) was synthesized via Carbonization and activation procedure by M. Lu and W. Yu. Its performance attributed to its large surface area, pore volume and N-O-S coupled doping [59]. Fe_3O_4 nano-particles embedded in N-doped porous Carbon (NPC-Fe_3O_4) was introduced in 2020. It delivered phenomenal reversible capacity and cy-

clic performance. Its hierarchical porous structure, nitrogen doping reduced the diffusion path which may play the key role in its enhanced performance [60].

In 2022 An efficient, in figure 7(A) one-step porous activated carbons structure with a large surface area was fabricated. in figure 7(B) The SEM analysis report has been shown where all samples have porous 3-D structure, which improvise the access of the electrolyte to the active material and enhance the migration of electrodes and ions. The initial discharge capacity reached 931mAh/g and a reversible capacity of 320mAh/g was maintained over 100 cycles at 0.1 C. High-rate performance and stable cycling performance of the AC from agar [61]. In 2020, Biomass reed flowers are used to create hierarchically porous carbon (HPC), figure 7(C) demonstrated the preparation of hierarchical porous carbon (HPC) In figure 7(D) shows a SEM and TEM image of the HPC. It is clearly shown that the HPC exhibits a typically porous structure with rich macropores (a few hundred nano-meters in diameter). The material exhibits good cycling stability, providing an excellent reversible capacity of 581.2mAh/g after cycling for 100 cycles at a current density of 100 mA/g. The high specific surface area of the HPC network, which offers abundant and quick pathways for electron and ion transfer as well as large contact areas and reciprocal interactions between the electrolyte and active materials. [62].

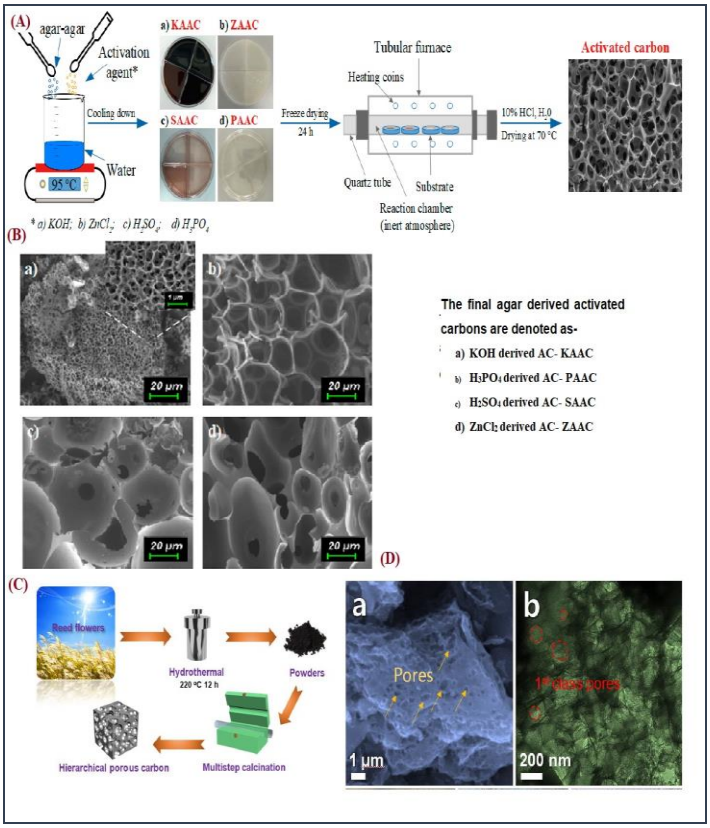

Figure 7: (A) Preparation method of AC with four different activating agents: (**a**) KOH; (**b**) $ZnCl_2$; (**c**) H_2SO_4; (**d**) H_3PO_4. (B). SEM images of ACs with four different activating agents: (**a**) KAAC; (**b**) ZAAC; (**c**) SAAC;(**d**) PAAC. **(Reproduced with permission from [61])** (C) Schematic illustration of the synthesis procedure for the preparation of hierarchical porous carbon (HPC), (D) (**a**) Scanning electron microscopy (of HPC) and (**b**) transmission electron microscopy (TEM) images of HPC. Red marked shows first class pores. **(Reproduced with permission from [62].**

d) **Silicon/Carbon and Composites** -

Silicon is another extremely promising anode material as each Si atom is able to capture around 4 Li atoms through a conversion reaction in the lithiation process. This results in its highest gravimetric and volumetric capacity among all the elements known and also is of low cost. The working potential of Si-based anodes is also low which can avoid risks compared with graphite electrodes. However, the high lithium storage capacity of Si anodes leads to a large volume expansion, [63-66] causing huge volume variation which is a significant disadvantage associated with the application of Si.

Low conductivity and the solid-state phase transition, which results in massive irreversible capacity loss, are the other roadblocks. This is also a subject of investigation in this study. To address these issues, nano structuring Si for use as an anode material has been proposed. Another approach is that, Carbon nanomaterials are appropriate as additive materials for Si-based composite electrodes because they are tunable, have excellent electrical and mechanical properties, and are lightweight. [67] Si/C composite anodes have been extensively researched in a variety of frame architectures. Silicon has a high specific and volumetric capacity but suffers from significant volume expansion and contraction, whereas the carbon matrix could accommodate the volumetric fluctuations, preserve electrical stability, and structural integrity while reducing battery capacity. As a result, the silicon content of the Si/C composite has a significant impact on the attributes of rechargeable batteries [68-72].

In 2018 by Fu J. et al a paper like flexible Silicon/CNT composites via low-cost Electro-deposition technique, in which silicon layer was uniformly electrodeposited over the CNT substrate see in figure 8(A). This anode was very flexible and feasible for the development of flexible electronic devices such as thin and light weight Li-Ion Batteries [73]. This anode demonstrated very high initial volumetric discharge and charge capacity of 4434 and 2084mAh/g see in figure 8(B). This superior performance attributed to its higher tensile strength and high volumetric capacity. This paper like flexible Si/CNT composite was one of the most promising combinational candidates for LIB applications.

Relatively in 2019 spherical onion like silicon and carbon (Si/C) composite was developed by D. Wang et al via

one step simple direct injection pyrolysis technique [Figure 8(C). This composite demonstrated exceptional Li-storage performance, with capacity as high as 1391mAh/g after 400 cycles at a current density of 0.2 A/g and rate capacity retention of 63.9% at 2 A/g to 200 mA/g [Figure 8(D)]. Its superior electrochemical performance may be attributed to its unique onion-like structure, as well as its excellent control over ion and electron stability and transport [74]. The battery capacity would be increased by maximizing the amount of carbon used to relax strain produced during the lithiation/de-lithiation process, though stable cycles could be guaranteed through careful surface coating material selection and heat treatment with high security through appropriate research.

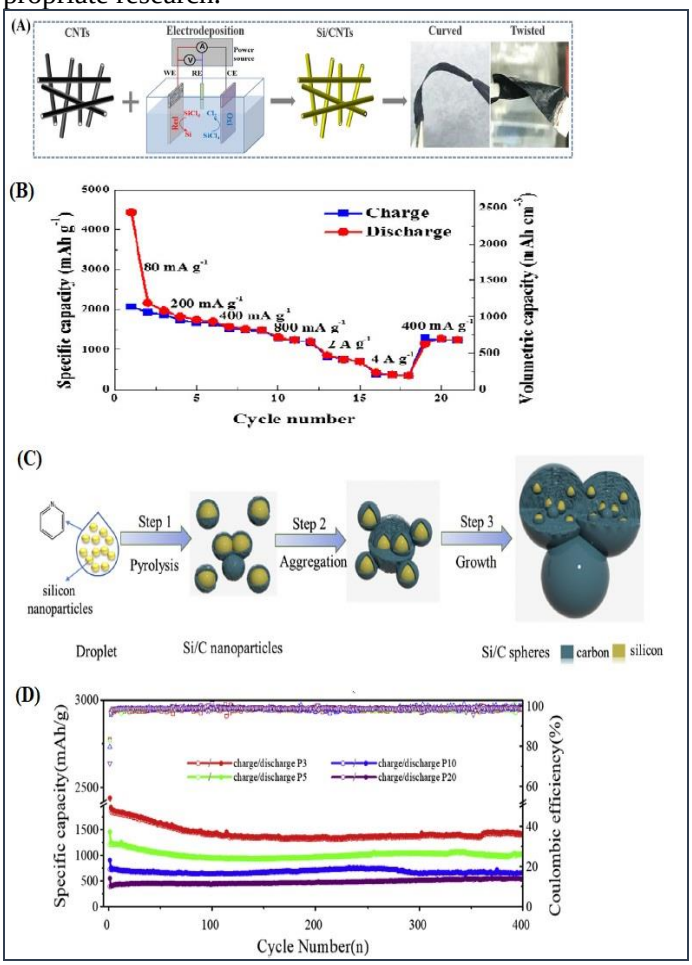

Figure 8: (A) Schematic of the synthesis of the Si/CNTs and the photographs of this composite at curved and twisted states. (B) The discharge/charge capacities of this electrode at different rates. **(Reproduced with permission from [73]).** (C) Schematic illustration of the formation of onion-like Si/C spheres. (D) Cycle performance of four samples (P3, P5, P10 and P20, respectively). **(Reproduced with permission from [74]).**

CVD, sol–gel, pyrolysis, mechanical milling, hydrothermal, and electro spinning processes are the most often used synthesis methods for silicon/carbon composite anode materials. Unfortunately, most standard synthesis techniques are low-yielding and unfriendly to the environment; as a result, it is necessary to develop scalable processes that will allow us to attain high productivity for the practical application of Si-based composite anodes [75,76].

5. CONCLUSION AND FUTURE ASPECTS:

The recent condition of world states that there is an urgent need of advanced rechargeable battery technology. It is very evident that a revolutionary era has started since the birth of Li-ion Batteries in 1990s. Li-ion batteries have undoubtedly fulfilled all the energy requirements brilliantly. However, we cannot ignore the fact that a basic Li-ion battery is not sufficient to fulfill the increasing demands of energy because of its low theoretical capacity. In this regard it is necessary to find out better electrode materials. The last couple of decades have been an exciting time for research in this field. Many materials and fabrication strategies have been found but lithium storage on the anode side has been still dominated by carbon based nano-materials since carbon embedded structures provides highly porous and layered structure, very large active surface area, provides better control over structural morphology as they can solve the instability and inhibits volume expansion completely. Research on carbon structures still offers many surprises and scopes for more systematic experiments in this field.

There is an urgent requirement to pay more attention in this field for more progress- some improvements are genuinely required as- more knowledge about carbonaceous materials and their composites is required, aiming to design more reliable and durable anode architecture with excellent capacity and stability. There is a need of more customized, cost effective, environment friendly and safe synthesis mechanism for the wide range production of highly efficient electrodes for commercially viable batteries. To find out convenient set of electrodes that can compliments each other properties, right electrolyte combination is required to avoid damaging reactions associated with electrolyte and electrode interface. In this paper we have tried to summarize the basics of Li-ion battery, its fundamental working, background and commercialization. We have studied many alternative materials of anode from the available literature, many carbon-based anodes from synthesis to structural morphology and electro-chemical performance were investigated. It also provided us knowledge about the advantages of using carbonaceous anodes over other materials; Exploring new material and fabrication strategies of anodes for Li-ion batteries will undoubtedly have a greater impact on our near future.

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