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Fabrication of Composite as an Anode Material for Li-ion Rechargeable Batteries: A Review

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ABSTRACT: Lithium-ion batteries are a result of the increasing research and development in this technology. In recent years research has led to lithium-ion battery (LIB) being the best device to store electrical energy for use in electric cars and mobile appliances. The very appealing properties of LIBs are to blame. These include their lightweight nature, high energy density and small size. They also have few memory effects. This review will discuss recent developments in anode material development for LIBs, as well as their benefits and drawbacks. The article will also highlight new approaches to alleviate the disadvantages of LIB anode material.Li-based alloys with other substances (e.g. Si, Sn P and Sb) can also be substituted. Si-based materials for anodes are popular candidates for the next-generation Li-ion battery due to their extremely high specific capacities, which is over 10 times greater than commercial graphite. However, Si anodes undergo large volume fluctuations and can form an instabile solid-electron interface (SEI), during electrochemical processing. Recent composites of Si/C (carbon and silicon) have been designed based on different carbon materials. This has helped to solve the volume expansion issue and SEI continuous formation. It has been discovered that carbon coatings and controlled porosity can prevent the pulverization Si particles. Carbon coatings can ensure stability in the solid electrolyte phase, preventing consumption of inner Si particles by continuously formed SEI. A carefully designed Si/C structure can provide a strong bond between electrode material and current collector. The unique design of Si-based materials and their excellent properties have been responsible for the overall improved performance. Literature reviews from various perspectives have examined the development of Si/C anode composite materials for Li-ion battery. In particular, Dou et al analyzed Si/C composites with various dimensions, Zhang et al presented nanostructured Si/C material and its related electrolytes, and Shen et al summarized progress by highlighting the different materials structures. A comprehensive review of Si/C anode composite materials, their preparation techniques and advanced characterization methods has yet to be published. The review is focused on how carbon materials can be used to improve the performance of Si. It includes a description of the one-dimensional (CNF) carbon nanofibers and nanotubes, two-dimensional (G) graphene sheets and the transition metal carbides (referred to by MXenes) as well as three-dimensional (3D), graphene-shell or amorphous-carbon-shell-coated Si particle and Si/graphite Composites. This review focuses on the use and preparation of carbon materials to enhance Si material performance. It gives a detailed description of one-dimensional (1D) graphene (G) sheets, two-dimensional (2D), transition metal carbides and carbonitrides (referred to as MXenes), three-dimensional (3D), graphene shell or amorphous carbon shell coated Si particles, and Si/graphite composites. We only consider carbon black as zero-dimensional carbon material.

I. INTRODUCTION

The Li-ion batteries revolutionized portable electronics, electric vehicles and other industries with their high energy density. They also have a long life cycle. Composite materials are promising alternatives to traditional anode material. They have the potential to improve battery performance. This review examines fabrication methods, properties and performance of composite materials used as anodes for Li-ion Batteries. The paper provides insight into different composite designs including metal oxide composites and silicon-based materials, while highlighting the advantages and disadvantages of each. The review also discusses how nanotechnology can enhance the electrochemical properties of these materials.

It emphasizes advances in synthesis and morphological controls. It is assessed in detail the impact that composite anodes have on battery performance, cycle stability and rate capabilities. This sheds light on their potential to be used as energy storage devices. The paper concludes by addressing critical challenges in developing composite anode material, focusing on cost effectiveness, environmental sustainability, and scalability. The review is a useful resource for scientists, engineers and policymakers who are working to advance Li-ion batteries.(Rangarajan, 2020)Due to their low self-discharge rate, high energy density and long life cycle, Li-ion batteries are the most popular energy storage solutions for electronic devices, electric cars and renewable energy sources. The choice of materials for the anode is

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crucial to Li-ion battery performance. The anode market has traditionally been dominated by graphite, but the demand for greater energy density and quicker charging has led to research on alternative materials. Composite anodes are one of these. This paper provides a thorough analysis of the properties and performance of composite materials used as anodes for Li-ion battery.(Lennon, 2019)

Composite Anode Materials: Types and Fabrication:
This paper divides composite materials for anodes into three groups, namely, carbon-based composites (CBM), metal oxide composites (MOCs), and silicon-based Composites. The paper discusses the advantages and disadvantages of various fabrication methods such as chemical vapour deposition, ball milling and sol-gel. The review highlights that nanotechnology is important in customizing the morphology of composite materials and their structure to enhance electrochemical properties.(Bitew, 2021)

Performance and Electrochemical Characteristics:
This review is centered on a comprehensive evaluation of electrochemical performance in composite anodes. The review discusses how the design of compositematerials affects parameters such as capacity, cycle stability and rate capabilities. Numerous studies have demonstrated the advantages of composites, including enhanced conductivity and structural stability as well as increased lithium storage. The real-world applications of composite materials in electric vehicles and portable electronic devices are also discussed, highlighting the potential for composite anodes as a solution to current battery technology limits.(Aghamohammadi, 2018)

Lithium-ion battery concept
As the name suggests, a lithium-ion is a rechargeable type of battery which stores and releases energy through the movement or motion of lithium ions from the cathode to the anode, between electrodes of opposite polarity. The lithium-ion batteries function is dependent on the continuous flow of lithium ions between the anode and the cathode. As shown below, the anode (also known as negatively charged electrode) discharges lithium into the electrolyte. The ions discharged are then conveyed by the anode to the cathode (also known as the positively-charged electrode) where they absorb. In a nutshell, this is how LIBs discharge energy. In the same way, the process of charging involves a gradual migration of the lithium ions via the electrode to the anode. It is evident from the above that the charge procedure is the opposite of discharge.(Nzereogu, As the name suggests, a lithium-ion is a rechargeable type of battery which stores and releases energy through the movement or motion of lithium ions from the cathode to the anode, between electrodes of opposite polarity. The lithium-ion batteries functio, 2020)

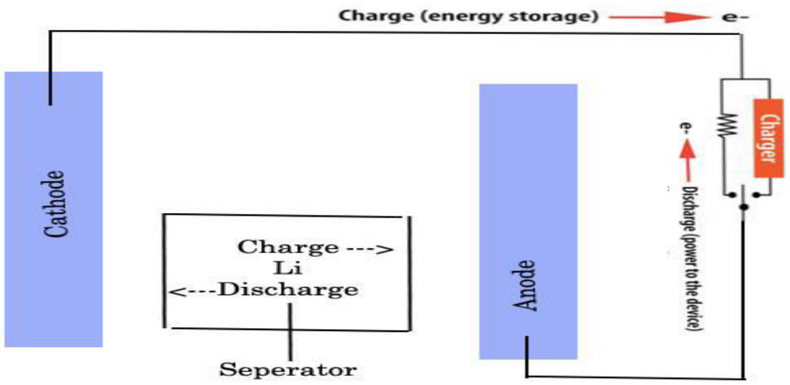

Figure: Schematic diagram

Lithium-ion (LIB) batteries have attracted a lot of attention in the research and technology development field in recent years. This is due to their high energy density, long-lasting durability, and environmentally friendly nature. In addition, they have been proven to be the best power source for portable, wearable and flexible electronic gadgets, appliances and devices such as mobile phones, digital cameras and laptops. This is due to their superior qualities when compared with alkaline and traditional Ni-MH and Ni-Cd battery types. LIBs have become the preferred power source for large-scale applications, including solar cells and electric vehicles. The quality of the electrodes has a significant impact on the performance and efficiency of LIBs. It follows that an improvement in the quality of electrodes will improve overall

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battery performance and quality, including its energy density, cycleability and lifetime. It is possible that LIBs will be used in all electric vehicles (EVs, HEVs), and in other applications for energy storage.(Mahmud, 2018)

Anodes are a vital part of rechargeable batteries. Their properties and morphology have a significant impact on their overall performance. Due to its hierarchical nature, graphite is the most common material for anodes. The large space between the two layers of carbon in graphite provides insertion sites to the lithium ions. This prevents the shape, size and structure of the anode from being altered during the charging-discharging process. Other novel mechanisms were also explored in addition to the conventional lithium-ion interaction. These mechanisms include the redox reaction of transition metal oxides and the displacement reactions of alloy anodes.(Ding, 2019)

In LIB tests, certain parameters are prioritised in order to evaluate and quantify the performance of batteries. These include the rate capacity, coulombic efficiency and reversible/irreversible capacity. In earlier studies, it was thought that the outstanding rechargeable characteristics of LIBs were due to the reversible recycling of lithium ions, but in effect, numerous losses take place inevitably in the actual intercalation/de-intercalation cycle. The formation of an SEI layer is responsible for one of the biggest losses. It occurs in the first phase of charge and discharge and results from the reaction between electrolyte material and electrode. SEI is not completely detrimental to LIBs because it helps ensure the free movement of lithium ions and restricts the embedding solvent in the electrode. SEI layer formation results in the removal of several lithium-ions, and SEI is irreversible in battery capacity.(Tornheim, 2022)

In the design of LIBs, it is important to consider the coulombic efficacy. Coulombic efficacy is the ratio between lithium extraction and penetration in a cycle. It is the ratio between the lithium discharging and charging capacities for cathode materials, or vice versa. Coulombic efficiency may be affected by the decomposition of electrolytes and changes in active electrode materials. LIB capacitiy varies with current. As high capacity can beobtained with low currents, the rate capacity (also known as discharge capacity) at higher currents becomes an important consideration. Note that excessive charging and/or discharging of lithium-ion battery will cause irreversible damage to the anode and cathode. Power density, along with volumetric and specific capacities is considered an important consideration in practice. Reports claim that reducing electrode thickness to the bare minimum can be a powerful and effective way to increase the power density while decreasing current density and resistivity. Moreover, it is crucial to improve manufacturing technology, as well as the efficiency of production, in order to meet market demands for small, light, mobile electronic and electric products.

In general, it is believed that LIB breakthroughs would require new chemistry for the electrolyte and electrode components. It is the goal of this initiative to find, "doctor" and use materials with capacities and performance higher than the conventional anode/cathode. This review aims to present the latest innovations in the development of new anode material as a potential replacement for graphite used in LIBs. The review will discuss four categories of anode material used to develop high-performance LIBs: Alloy Materials (ii. Compounds of Transition-Metal type for conversion (iii.) Compounds based on silicon and (iv.). Carbon-based Compounds. The review also discusses the various bottlenecks that prevent the full integration and use of anode materials into commercial LIBs, as well as possible solutions.(Boaretto, In general, it is believed that LIB breakthroughs would require new chemistry for the electrolyte and electrode components. It is the goal of this initiative to find, "doctor" and use materials with capacities and performance higher than the conventional , 2018).

II. MATERIAL AND METHOD

Lithium-ion (LIB) batteries have attracted a lot of attention in the research and technology development field in recent years. This is due to their high energy density, long-lasting durability, and environmentally friendly nature. In addition, they have been proven to be the best power source for portable, wearable and flexible electronic gadgets, appliances and devices such as mobile phones, digital cameras and laptops. This is due to their superior qualities when compared with alkaline and traditional Ni-MH and Ni-Cd battery types. LIBs have become the preferred power source for large-scale applications, including solar cells and electric vehicles. The quality of the electrodes has a significant impact on the performance and efficiency of LIBs. It follows that an improvement in the quality of electrodes will improve overall battery performance and quality, including its energy density, cycleability and lifetime. It is possible that LIBs will be used in all electric vehicles (EVs, HEVs), and in other applications for energy storage.(Mahmud, Lithium-ion (LIB) batteries have attracted a lot of attention in the research and technology development field in recent years. This is due to their high energy density, long-lasting durability, and environmentally friendly nature. In addition, they have , 2019)Anodes are a vital part of rechargeable batteries. Their properties and morphology have a significant impact on

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Synthesis Methods:

Researchers have investigated various methods of synthesis to create composite materials.

Chemical Vapor Deposition: CVD is a process that has been used to deposit materials such as carbon nanotubes and enhance electrical conductivity. It also improves structural stability. Researchers have optimised CVD parameters in order to control the growth of CNTs and align them, which has resulted in an improved capacity for lithium-ion batteries.

Sol-Gel Processes - Sol-gel processes have allowed precise control of material composition and structural characteristics. Sol-gel techniques have been used by researchers to create metal oxide and carbon composites. This allows them to harness the synergistic effect of both materials for improved lithium storage.

The ball milling process has been successfully used in the production of nanoscale composites. The method increases the surface area and reduces particle sizes, while improving lithium-ion diffusion. Researchers have investigated various combinations of metal oxide and carbon materials in order to improve electrochemical performance.

Electrochemical Performance:

Recent studies have evaluated electrochemical performances of composite materials in great detail:

Composite anodes have higher storage capacity than traditional graphite. This enhancement is achieved by incorporating high-capacity material such as metal oxides or silicon.Better Rate Capability: Composite structures that are well-designed with porous morphologies, controlled interfaces, and controlled interfaces promote rapid diffusion of lithium-ion resulting in an improved rate capacity. It is especially important for applications that require fast charging and discharge. Many strategies have been developed to address the challenges of volume expansion during charging

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and discharging cycles. The use of nanostructured composites, as well as improvements in mechanical stability has improved the cycling stability. This is essential to extending battery life.

Future prospects and Applications:

There are several applications of composite anode material that have been highlighted in the literature.Portable Electronics: Composite anodes with high energy densities can increase the battery life of smart phones, laptops and wearable's.Composite anode material is a promising option for electric vehicles (EV). Its improved rate ability and capacity retention make it a good choice. The properties of composite anode materials reduce the charging time and improve driving range.Grid-scale Energy Storage Systems: The enhanced cycling stability of composite materials and their high capacities will benefit grid-scale energy storage system, which in turn can facilitate the integration of renewable sources of energy into the grid.The use of various coatings, do pants, and cathode materials, such as LiMnsub>2/sub>Osub>4sub>, such as $LiCoO_2$, $LiCoO_2$, and SiO_2 and SnO_2 and MgO and Ag, and Al as well as carbon nanotubes (CNT), have been shown to reduce Mn dissolution LBO was first used as a coating on $LiMn_2O_4$. It has excellent ionic properties and is resistant to oxidation even at higher potentials (4 V). LBO surface treatment increases storage capacity, but reduces cycling life due to the reduction in average Mn valence on the surface caused by solid boron species.Al doping $LiMn_2O_4$ showed improved cycling performance when heated to high temperatures. The initial capacity of the manganese spinel compound prepared using polyvinylpyrrolidone as a precursor improved. LiMn2O4/CNT Composites with high rates and improved capacity retention are reported for flexible electronic applications. The LiCoO2 coated 5nm LiMn2O4 improved cycle life, reduced self-discharge and increased capacity. However, the LiCoO2 layer was unable to store Li, resulting in a slight reduction in capacity for pristine LiMn2O4. The cycle life was improved by synthesis of submicron or nano-sized LiMn2O4 and the doping of LiMn2O4 (i.e. partially replacing the Mn sites in LiMn2O4) with nontransition and transition metals. The one-pot method of molten-salt preparation resulted into nano-sized (50nm), hollow, spherical $LiMn_2O_4$ particles that showed better capacity retention (i.e. 96% retention for 5C-rate). The nano-sized $LiMn_2O_4$ particles also showed good performance at 50 degrees Celsius, which is associated with the high crystallinity of these particles and their spherical shape. In another study, Ru doped LiMn2-xRuxO4 (x = 0.1 and 0.25) was shown to reduce the capacity fading as compared to undoped sample by mitigating the spinel-to-double-hexagonal transition at 4.5 V, and due to the presence of Ru4+ - Ru5+ redox couple and better electronic conductivity of the Ru doped samples. Other dopants for $LiMn_2O_4$ studied were Co, Cr, Al, Ni and Fe. Sakunthala et al. The Co-doped LiMn2O4 was able to retain 94% of its capacity after 1000 cycles, at a 5C rate. In practice, the coatings and the dopants mentioned above are inactive and reduce the capacity of spinel $LiMn_2O_4$. They also increase the costs of preparation. A more alternative approach is to combine the $LiMn_2O_4$ material with NMC, a cathode that has a higher stability.

Graphitic Carbon is the most common anode material in Li-ion battery technology. Its advantages include its low cost and mechanical and chemical stability, as well as low operating voltage (0.25V vs. Li/Li^+). Graphite is a material with a capacity of 372 mAh/g, based on the stoichiometry LiC_6. Hard carbons, which are non-graphitic, have a higher capacity, cycle life and good rate capability. They also cost less to produce. However, their disadvantages include low density, a larger irreversible capacitance and hysteresis of the voltage. Metal-carbon composites were extensively investigated to improve performance of anode material. Composite anodes in general showed better performance than mixing metals and anode materials mechanically. Chemically depositing Ag onto graphite increased the cycle life. This was due to enhanced electron conductionwithin graphite because of the lowelectrical resistance in Ag. The capacity of an Ag-graphite composite was also superior to a graphite alone cathode, since Ag is capable of forming LiAg alloy when it interacts with Li. The graphite deposited with Ag was also shown to have a higher resistance to moisture (>1000ppm), which makes it easier to manufacture Li-ion battery. Microencapsulation with Ni nanoparticles improved initial charge-discharge, Coulombic efficacy and cycle life. It was proposed that the Ni-deposition of graphite edges reduced the irreversible capacitance by decreasing the surface area exposed to electrolyte. This in turn made the edge surfaces more permeable for solvated Liions. The same effects were observed with Cu-deposited graphite. In addition to suppressing electrolyte degradation and co-intercalating solvated Liions, an improvement in the high-rate capability of natural graphite was also reported. Al-deposited natural graphite increased cycle life and rate capabilities due to a decrease in charge transfer resistance. Au, Bi and In were also studied as metal-graphite alloys. All of these metals coated using vacuum evaporation improved rate capability. Rate capability is dependent on film thickness. Too thick coatings reduce the Li mobility and therefore decrease the rate ability. Another way to enhance the electrochemical properties of graphite is by coating it with carbon. Propylene Carbonate (PC, melting temperature = -49 degrees Celsius) based solutions are one way to improve the performance of Li-ion Batteries at low temperatures. It is known, however, that PC can decompose on graphite surfaces, and therefore cannot form a solid electrolyte layer (SEI), which results in shortened cycle lives. Studies on graphite coated with carbon using thermal or chemical vaporization

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techniques revealed that Coulombic efficiency could be significantly improved. The carbon layer acts as a barrier between the graphite surface and PC-based electrolyte. This leads to a compact, thinner SEI film. High rolling or calendaring pressures are not recommended when using carbon-coated graphite as anode in Li-ion batteries. These pressures could destroy the coating. Carbon coatings also store Li, so they do not affect graphite's specific capacity.Li anode, due to its dendrites and safety issues is currently not considered a good candidate. Si and Sn alloys have received the most interest due to their high volumetric and gravimetric capacity. These alloy anodes undergo a large volume change of >300% upon Li intercalation, which results in particle cracking or pulverization during cycling. This leads to a poor cycle life. This large volume change prevents a stable SEI coating from forming on alloy anodes. The SEI layer continuously consumes Liions and leads to low Coulombic efficacy. To suppress rapid degradation of the cycle life for Si anodes, a composite anode containing low Si content (i.e. Si 33% wt%), and high binder content (i.e. 33-56.6% wt%) is a simple, but effective, strategy. The high amount of inactivematerial in the composite cathode limits its specific capacity to 250mAh/g (after 400 cycles).A second approach would be to replace some graphite by Si. Carbon-coated composite graphite/Si anodes showed improved performance over Si alone. However, the rapid degradation of cycle lifetime is still of concern for these materials. Carbon and metal coatings were used to increase the Coulombicefficiency and cycle life of Si anodes. Thecoatings create a buffer between the Si and the electrolyte, which reduces the decomposition of the electrolyte on Si anodes. However, due to the significant volume changes in the Si anode the coatings lose their structural integrity and new Si surfaces become exposed to the electrolyte. Another study showed that nanocrystalline Si particle of 20-80nm encapsulated within a carbon aerogel had a stable and reversible capacitance of 1450mAh/g after 50 cycles. The carbon aerogel works as a cushion during the expansion-contraction of the nanocrystalline Si particles, and maintains the three dimensional electrical network; this way, Si particles stay in physical contact with the carbon matrix at all times. Recent studies of Si anodes focused on minimising the Si surface exposed to electrolyte. This was achieved by encapsulating a single Si nanoparticle within a carbon shell, i.e. a yolk-shell structure. The carbon shell has sufficient void space for volume changes to occur during Si de-/lithiation. The carbon shell is less likely to deform during cycling. This helps achieve a SEI layer that remains stable over the shell. After the first formation cycles, this Si-carbon composite had a reversible capacitance of 1500mAh/g. It also retained 74% its original capacity after 1,000 cycles. A similar method, inspired by the pomegranate, encapsulates carbon-coated Si nanoparticles in a secondary carbon layer. The SEI layer forms mainly on the secondary carbon layer, which has a lower surface area, rather than the nanoparticles themselves (which have a higher surface area). After 1000 cycles, this composite Si-carbon anode inspired by pomegranates retained 97% of its capacity (i.e. 1160mAh/g).

III. CONCLUSION

This comprehensive review concludes with a detailed insight into fabrication, properties and performance of composite materials used as anodes for Li-ion batteries. The review highlights the importance of nanotechnology and composite design in improving the electrochemical properties of anodes. The review also highlights composite materials' potential to meet the urgent demands of high performance energy storage systems. The development of composite materials for anodes is a key area for research and innovation within the Li-ion batteries field as the world strives to find cleaner, more efficient solutions. The literature review highlights the potential for composite anodes in Li-ion batteries. The studies show that composite materials can overcome limitations in traditional materials and unlock higher performance. Composite anode materials will play a key role in the development of future battery technologies as the need for sustainable and advanced energy storage solutions grows.

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