

Driving the Performance Enhancement of Lithium-Ion Battery: Anode Material Perspective

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Abstract. Electrical energy is one of the key sources supporting civilization, while the power structure dominated by thermal electricity leads to serious environmental problems in the 21st century. To meet the growing device performance demand and climate goals, exploitations exemplified by lithium-ion batteries (LIBs) are being sought. By fully understanding the electrochemical mechanisms and analysing, designing, and testing various electrode materials, LIB becomes one of the accessible power supplies in electric vehicles (EVs), aerospace, and information sciences. Herein, this paper aims at offering a critical overview of the LIB improvement from the anode material perspective. By focusing on three advanced types of anode materials and going over their mechanism, microstructure, and testing results, current challenges, and future potentials of the development of LIB are highlighted, along with scale-up issues. Note that the focus of future study ought to be recognized as detailed mechanism understanding, material selecting and synthesis, and "jumping out of the lab".

Keywords: Lithium-ion battery, anode material, mechanism, scale-up.

1. Introduction

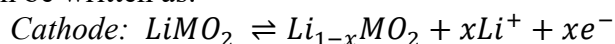
Lithium-ion battery (LIB) is a popular rechargeable battery consisting of multiple cells in which lithium ions (Li^+) are transferred between the positive and negative electrodes in the charge-discharge cycles. It has attracted extensive attention from academia and global in the last decade because of its enormous specific energy, good stability, low self-discharge, and maintenance cost. LIBs are the most popular battery in portable electronic devices like smartphones and laptops and, more importantly, tend to replace the traditional lead-acid battery promoting the development of electric vehicles (EVs). Anode, as an important of LIB, is one of the focuses now. In recent years, many works have been accomplished which focused on improving the stability and safety of anode materials (including Li dendrites), exploring smoother mechanisms of lithium-ion embedding and extraction to form stable SEIs and reducing the volume expansion of anode materials (especially in metallic and semi anode) to improve battery performance. However, as many types of anode materials are available, their respective Li^+ charging and discharging mechanisms, material structures and morphology are relatively fragmented, and the interactions between the different classes of materials still need to be studied and summarized. Aware of this and based on previous studies, this paper intends to deepen the understanding of anode materials by introducing a variety of advanced LIB anodes belonging to different classifications, supporting the future development of LIB through a comparison of their characteristics and performance enhancement. In detail, the working mechanism of LIB will be first introduced, and then the details of three types of anode material will be given, including microstructure, preparing method, working mechanism and beyond.

Nomenclature

LIB	lithium-ion battery
EV	electric vehicle
IC	internal combustion vehicle
SEI	solid electrolyte interphase
CNT	carbon nanotube
SWCNT	single-wall carbon nanotube
MWCNT	multi-wall carbon nanotube
ECNT	entangled carbon nanotube
CNTA	carbon nanotube array
GNS	graphene nanosheet
HCNS	hollow carbon nanosphere
SiNW	silicon nanowire
SiNT	silicon nanotube

2. The working mechanism of LIB

A full LIB contains five main components: an anode, a cathode, Li^+ conducting electrolyte, a separator, and two current collectors. These components are stacked together to form a sandwich structure (Figure 1) [1]. One of the most widely applied cathode active material types is lithiated transition metal oxides like LiCoO_2 , LiFeO_4 , and LiMn_2O_4 . The electrolyte is usually an inorganic salt solution of Li^+ , which is cut into halves by the separator. The separator is a selectively permeable membrane that works for three functions: (1) It acts as a wall that prevents the electrical interactions of the two electrodes and avoids the battery short-circuit [2]. Compared to traditional batteries, LIB has lower thermal stability. The LIB separator is one of the essential methods ensuring the fire safety performance of the system, and it is also one of the key topics of EV development (2) The porous structure leads to full absorption of Li^+ , strengthening the Li^+ conductivity. (3) The separator prevents the chemical waste from moving from one side of the battery to the other. The current collector is the bridge between the external circuit and the electrodes. The active material particles of the two electrodes have adhered to the current collectors with the binder, as shown in Figure 2. Carbon is also an additive for its high conductivity and large relative surface area, giving the electrons a "conductive path" to the collector [3]. Copper and aluminum are the current anode and cathode collectors in most commercial LIBs. The charging and discharging cycle of LIB is achieved by the cyclic intercalation (embed) and extraction (dis-embed) of Li^+ between two electrodes. In discharging mode, Li^+ carries the current inside the battery from the anode to the cathode through the separator diaphragm. In charging mode, the emf of the power supply acts as the driving force forcing the directional movement of electrons in the external circuit from positive to negative; hence the Li^+ migrate in the same direction in the interior of the battery, where they become embedded in the porous or layered anode in a process known as intercalation. In general, the half-reaction of LIB (assume the anode is graphite) can be written as:



Anode:



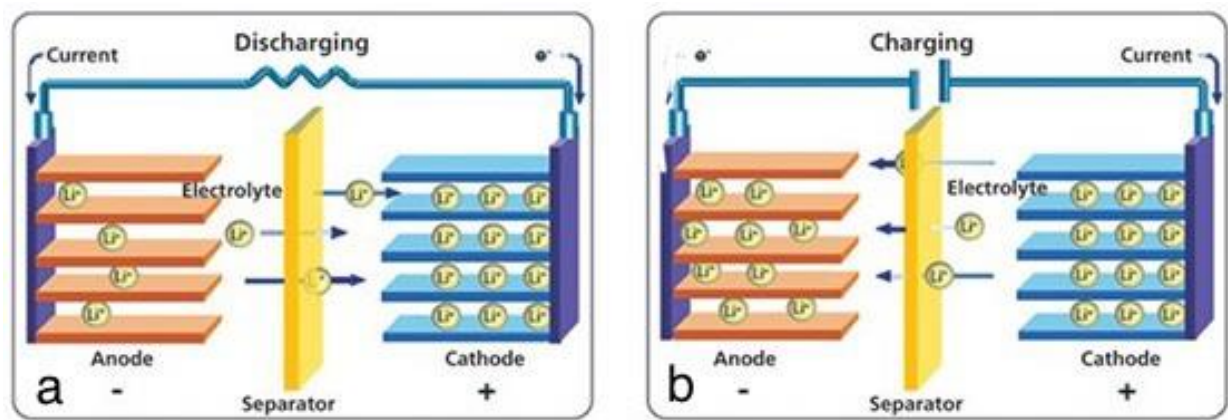


Figure 1. (a) The discharging of LIB; (b) The charging of LIB [1].

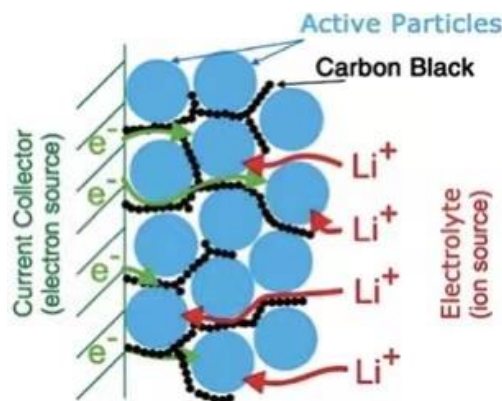


Figure 2. The connection of the current collector and the active material [1].

3. Advanced design of anode material

As mentioned before, the anode is a crucial component of the battery system. The battery depends not only on the qualities of the anode material, such as its lithium capacity, but also on its morphologies, such as its shape, layered, crystalline, or amorphous structure [4]. Down below are the advantages and setbacks of four varieties of anode material. Based on this, three main types of anode material will be discussed in detail: carbonaceous anode, lithium alloy, and silicon-based nanomaterials.

Table 1. The advantages and setbacks of three main varieties of anode materials.

Materials	Advantages	Drawbacks
Carbon	(1) High conductivity	Low capacity, energy density, and rate capability
	(2) Layered structure for intercalation	
	(3) Availability and low cost	
Lithium alloys	High theoretical conductivity	expansion and pulverization
Silicon (normal)	(1) Highest theoretical capacity	safety risks (pulverization and dendrites)
	(2) Abundance and low cost	

3.1. Graphitic carbon anode

3.1.1. Carbon nanotube in anode

The nanotube is a classical one-dimensional nanomaterial. The number of walls can classify the carbon nanotube (CNT) into single-wall CNT (SWCNT) and multi-wall CNT (MWCNT), as shown in Figure 3. The geometric shape of single-walled carbon nanotubes resembles a coiled monolayer of graphene with exceptional electrical and mechanical capabilities. MWCNT is composed of separated levels of SWCNT nested within each other like concentric rings [5]. As stated above, the lithiation

and de-lithiation of the anode are fundamental to LIB; hence the mechanism of lithium intercalation is of great importance. For SWCNT, it is demonstrated that lithium intercalation can happen both on the inside and outside of the nanotube [4]. At the same time, the interior surface is more energetically favorable as it has a -0.98-eV lithium absorption energy lower than the exterior surface (-0.86 eV) [6]. When it comes to MWCNT, lithium can be stored not only in the carbon layers but also in the middle between separate sheets or in the hollow core of the nanotube.

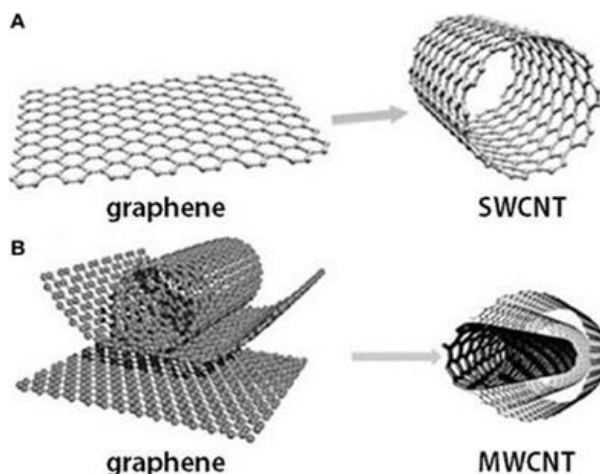


Figure 3. SWCNT and MWSNT sketch [7].

When the CNT is applied in an anode, it forms two kinds of structure: entangled CNT (ECNT) and CNT array (CNTA), as shown in Figure 4. More contact points in an ECNT anode build connections between separate tubes to form a clearer conductive path that improves the conductivity [4]. The traditional route of preparing ECNT anode is mixing the CNT powder with polyvinylidene fluoride binder and then scattering it on the current collector [4]. In contrast, CNT can play the roles of active anode material, binder, and current collectors of its well-performing mechanical and electrical properties. This provides an opportunity to lower the LIB weight and improve the battery energy density and thermal stability because most traditional binders become unstable when the temperature rises [8]. The CNTA anode can be obtained by two methods: (1). transferring already-made CNTA from the substrate (e.g., silica) and (2). direct growing on current collectors, while the latter is more favorable because of the homogeneous final structure [9]. There is a prominent reduction of charges (ions, electrons) transferring path distance due to the nanotubes grown directly on the current collector.

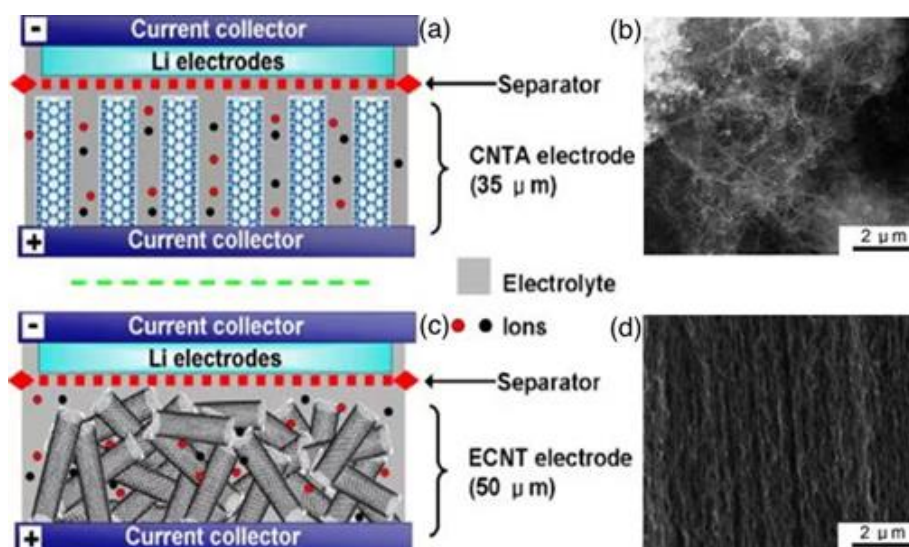


Figure 4. (a) and (c) Sketches of the basic structure of ECNT anode and CNTA anode in a LIB [10]; (b) and (d) SEM image of ECNT and CNTA anode [9].

A previous study shows that the LIB capacity with a purified SWCNT anode has a capacity of around 430 mAh/g, while this Figure can be increased to approximately 1000 mAh/g due to the introduction of CNT lattice defects [8]. The SWCNT can be categorized into the armchair, zigzag, and chiral chirality according to different basis lattice vectors and chiral angles. A previous study demonstrated that improving the degree of homochirality of CNTs can significantly increase the conductivity of the electrode [6]. A "single-surfactant multicolumn gel chromatography method" has already been proposed by Liu et al. (2011). This method utilizes the different interaction strengths between the allyl dextran-based gel and chiral SWCNTs. In brief, when the gel columns combine with the CNT, the first gel column will bond the CNT with the highest interaction strength. In this way, chiral CNTs have separate columns [11]. Hence one of the future focuses of SWCNT anode could be designing a method of effective and low-cost mass-separation of homochiral SWCNT.

The multiple layers of graphene in MWCNT may belong to different categories but allow lithium intercalation similarly to graphite. As discussed above, there are three ways to store lithium in an MWSNT, meaning that it has a larger capacity than graphite.

3.1.2. Graphene-Based anode

Graphene is a two-dimensional single nanosheet of graphite (GNS) with multiple advantages (Figure 5). Graphene has a substantially greater specific surface area than graphite and CNT, 2620 m²/g. Both surfaces of graphene can absorb lithium in a lithiated electrolyte environment. With more active electrochemical sites, it is expected to exhibit a higher theoretical capacity. The theoretical ratio is Li₂C₆ (LiC₃) instead of LiC₆, raising the theoretical capacity to 744 mAh/g, which keeps a potential to increase further [4]. The high surface-to-volume ratio of graphene leads to a high-rate capability. Compared with brittle graphite, graphene's flexibility offers an opportunity to modify flexible energy storage devices [12]. There are usually controlled functional groups attached to the surface of the graphene, which pave the way for forming a GNS-based nanocomposite.

GNS can be used as a LIB anode directly. Besides, metallic nanoparticles can be integrated with GNSs to form a nanocomposite anode (Figure 6) which is why the sub-title for this session is "Graphene-based". The GNS-based nanocomposite shows a comprehensive performance enhancement, including higher maximum capacity, stronger rate capability, and lower capacity fading [12]. The large capacity and low-capacity fading correspond to the high-rate capability, a harsh standard in devices requiring instantaneous discharging.

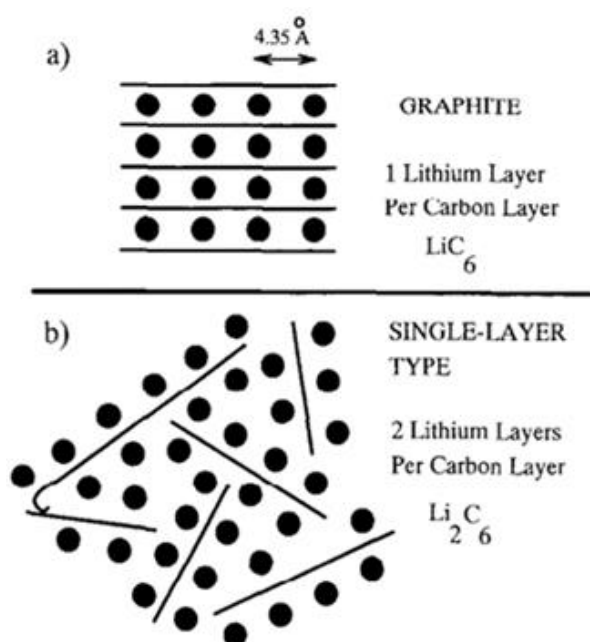


Figure 5. Diagram reflecting the Li:C ratio in graphite and graphene [13].

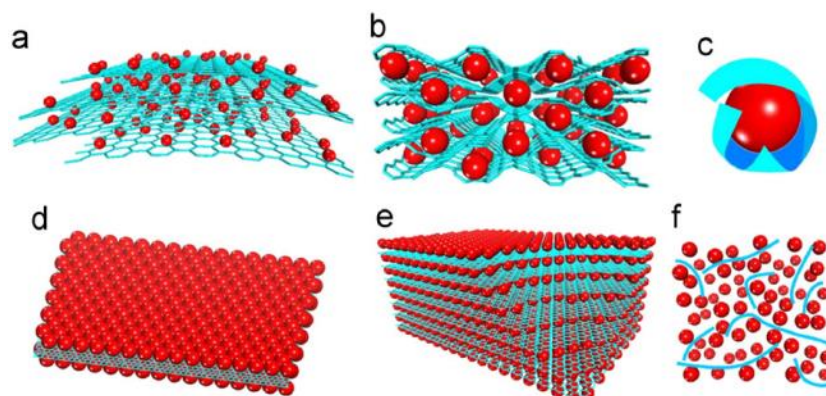


Figure 6. Six graphene-based nanocomposite models (The red represents the nanoparticles, the blue for the graphene substrate): (a) nano-oxides anchoring model (b) graphene-wrapped (c) graphene-encapsulated model (d) sandwich model (e) layered model (f) 3D mixing model [12].

By comparing (a), (b), and (c) in Figure 7, the GNS- Co_3O_4 shows not only a higher capacity but also an even more stable one in the first 20 cycles. It is demonstrated by Yoo et al. (1996) that the spacing between the GNS impacts lithium insertion [13]. This can be qualitatively understood as the extent of overlap in some regions of the GNS increases with the decrease in the average spacing of nanosheets, leading to a decrease in the effective specific surface area. As noted in previous paragraphs, the functional groups in the GNS structure play a part in the anode composite formation. The hydrophilic group, represented by hydroxyl, carboxyl, and other organic groups, is easily dispersed in aqueous or organic solutions. When the combination of GNS matrix and metallic oxide nanoparticles ends, the different layers of GNS tend to narrow the distance between each other and hence largely inhibit the anode or battery performance. A solution that involves the participation of supporting nanoparticles between separated layers has been proposed. However, this is expected to be incorporated with the build-up of a better GNS-nanoparticle interface and a deeper comprehension of the lithium absorption and release mechanisms of both the GNS and the nanoparticles. This is one of the current difficulties but a breakthrough point.

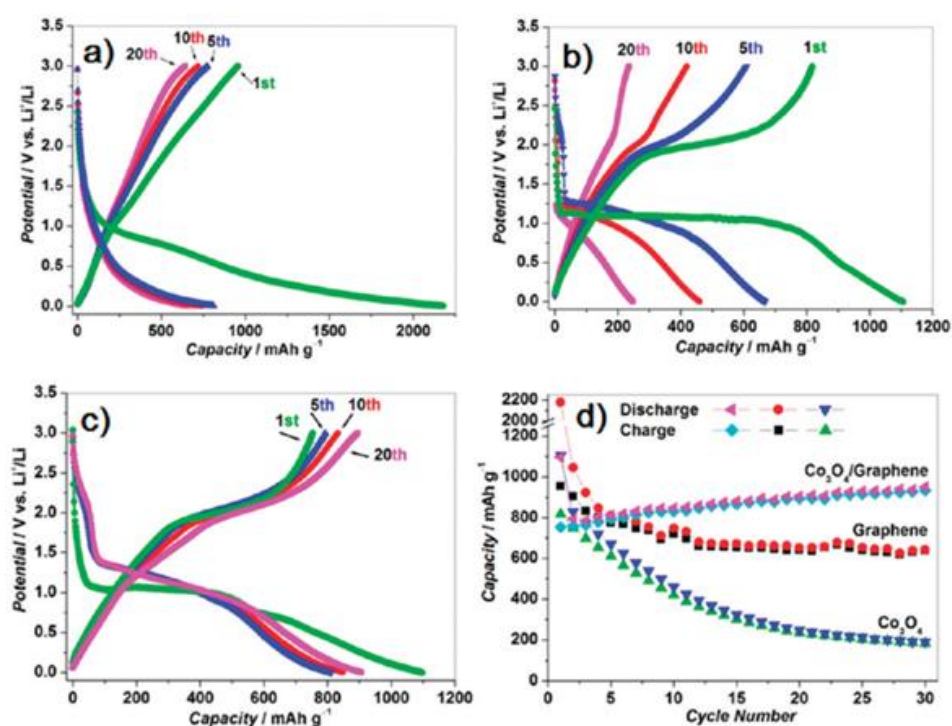


Figure 7. The charging-discharging experiment of GNS- Co_3O_4 LIB anode [14].

3.1.3. Carbon nanosphere in the anode material

Usually, a high-rate capability requires a short lithium diffusion length and a higher contact surface between the lithiated electrolyte and active anode material. Therefore, the carbon nanosphere (CNS) is also chosen for its three-dimensional structure and large specific surface area. The hollow carbon nanosphere (HCNS) is usually combined with other nanoparticles to compensate for their shortcomings. For instance, Fe_2O_3 and MnO_2 nanoparticle is combined with HCNS. Coated with HCNS, the anode's greater specific area and shorter lithium diffusion length result in a significantly increased electrical conductivity. In addition, a space is left between the HCNS coating and the nanoparticle to account for the volume expansion during lithiation. A similar mechanism also exists in silicon anode and will be discussed later. It is worth noting that the drawback of CNS anode is the relatively low Coulombic efficiency and the fading of active lithium. This is because the larger surface area in a unit volume contains a proportion of surfaces with no sites for lithiation and de-lithiation, resulting in SEI, which consumes active lithium. Not much research about this can be found except the pre-lithiated CNS anode proposed by Holtstiege et al., which prevents the loss of active lithium, maintain the rate capability, and increases the specific energy of the LIB [15]. There ought to be more studies on this topic hence paving the way for the application of CNS in full LIB.

3.2. Lithium alloy anode

Before the graphite anode was commercialized and popularized by SONY, people developed lithium metal as the anode of LIB, but problems continued to arise. In general, there are three problems: (1). The uncontrollable anode-electrolyte interphase reaction leads to thick SEI covering the anode, which highly degrades the battery performance like Coulombic efficiency and capacity. (2). Li's "hostless" plating and stripping on the anode causes cyclic volume expansion and shrink, leading to uncertainty. (3). The deposition of Li dendrites may permeate the separator, heightening safety issues and potentially leading to catastrophic battery failures. The detached Li dendrites, known as the so-called dead Li, also increase the volume expansion [16]. Dendrite generation is now attributed to the imbalance between the Li^+ transporting speed and the redox speed. However, no uniform explanation exists. Lithium reacts with most metals to form multiple kinds of alloy and intermetallic compounds, reducing the anode's reactivity [17].

3.2.1. Li-Al anode

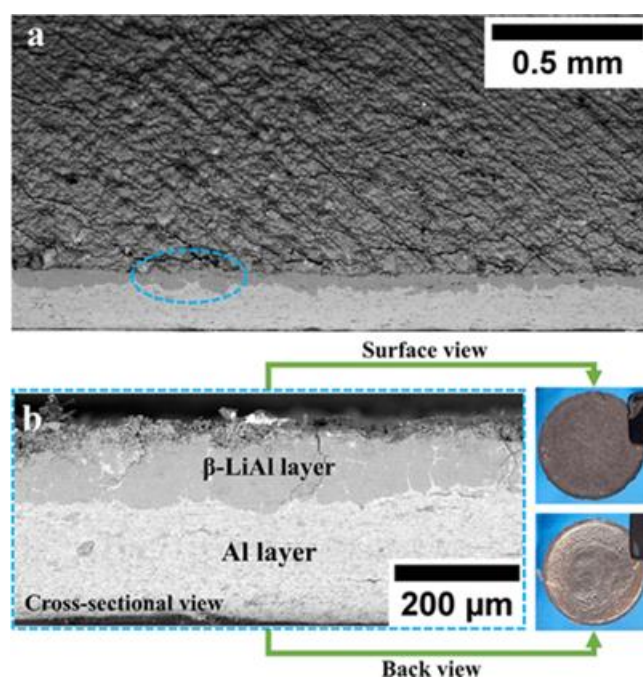


Figure 8. The cross-sectional SEM view of Al-LiAl interphase. The darker part represents the LiAl. (b) is 200x magnitude of (a) [18].

Al is a common metal with a stable structure, and more importantly, Al has a low energy barrier for Li to deposit, so the Li-Al anode is our concern. Zheng et al. (2022) proposed a Li-Al alloy anode based on the α -Al and β -LiAl phase transformation (Figure 8). In this case, the AL film is partially pre-lithiated before application. The remaining pure Al is used as the current collector. To keep the stability of the Al and LiAl phases, the battery (anode) is only cycled within the Li solubility range of the LiAl phase. Zheng et al. tested the performance of this LiAl anode in a full battery experiment that uses LiFePO_4 as the cathode. The LIB shows 95.8%, 90.9% and 81.5% discharge capacity retention after 500 cycles at 0.10, 0.50 and 1.00 mA/m^2 discharging rate which is an excellent performance [18]. A similar LiAl anode is also tested by Zaghbi et al. (2003) while in this case. The anode is formed by extrusion, where a thin Li foil is compressed together with an expanding Al sheet with 50% extra void spaces inside and covered with a carbon nanocomposite. Compared to the bare Li anode, the 3D LiAl structure provides more sites for a redox reaction, which is beneficial to the equilibrium between Li transferring and redox reaction on the electrodes to prevent the accumulation of Li^+ hence the Li dendrite formation. Besides, the 3D LiAl anode also provides extra space for volume expansion [19].

3.2.2. Li-ZnO anode

According to previous reports, all transition metal oxides obey a similar Li-storing mechanism. In comparison to SnO_2 (600 mAh/g) and CuO (674 mAh/g), the high theoretical capacity of ZnO (987 mAh/g) garners greater attention. [20]. However, it has been discovered that a substantial volume expansion of up to 228% may occur in a standard ZnO anode, causing the failure of LIB (Figure 9). For a small part of a micro- ZnO combination, this volume expansion leads to a large local stress field under the interaction of incoming Li^+ and the stress field results in micro-cracks on the surface of micro-silicon clumps in duty cycles leading to initial fracture until the final pulverization and fragmentation of the anode [21]. Given that the macroscopic anode is comprised of many micro-clumps, a collapse will sever the connection between the current collector and the anode, lowering battery stability, energy density, and cycle life. Building up advanced nano- ZnO anode (one to three dimensions) or nanocomposite with carbon-based material like graphene or CNT has proved an effective way of solving pulverization leading to the increasing capability and capacity rate. It is easy to find that most of the advanced anodes addressed in this paper are all related to nanomaterial, which has entirely different behaviors with the microscale or larger in some respects. This trend is also in line with today's development direction in LIB.

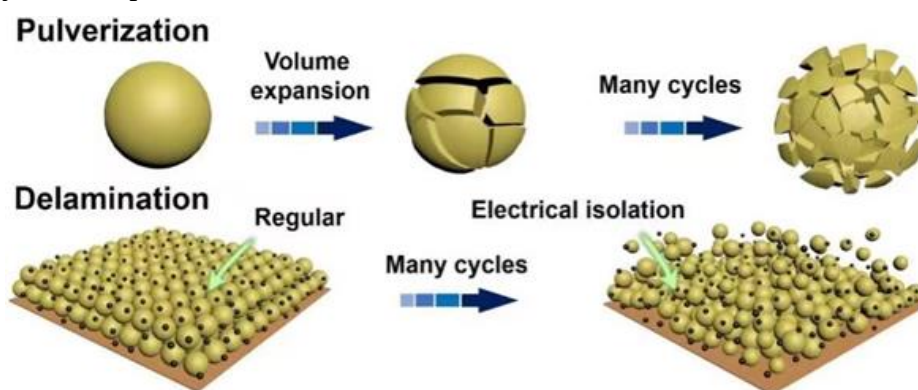


Figure 9. Pulverization and failure of the anode material [22].

3.3. Si-Based anode

Si is one of the rising anode materials because of the approximately tenfold greater maximum capacity than graphite. However, a substantial volume expansion of up to 400% may occur during lithiation, causing the collapse of the anode, known as pulverization, as discussed in 3.2.2. Previous studies have demonstrated that developing a nanoscale anode can be a solution; hence, the silicon nanowire (SiNW) anode arises. Based on the microstructure of SiNW, as shown in Figure 10 (a), a comparison is conducted between conventional silicon and nano one.

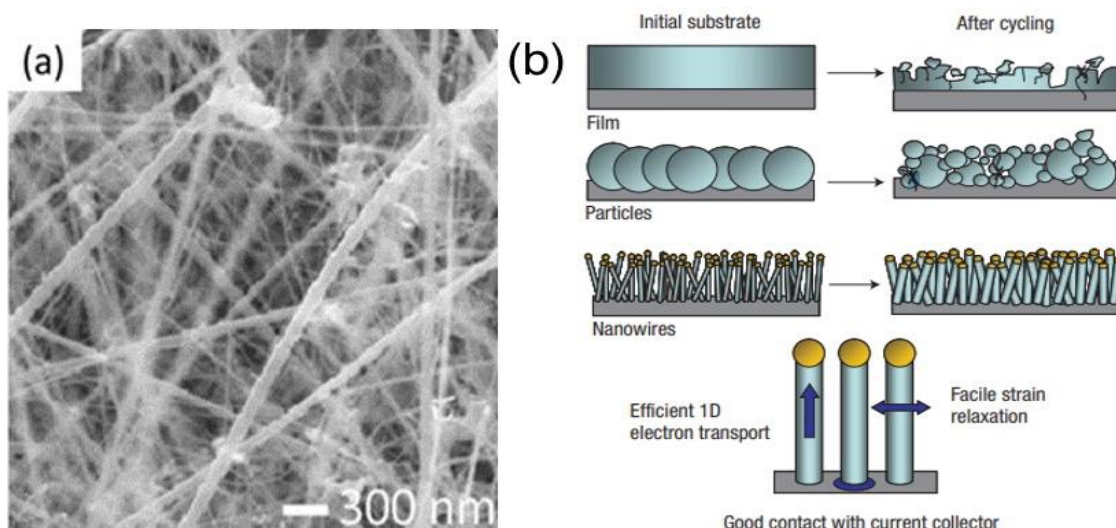


Figure 10. (a) The TEM image of SiNW [23]. (b) Comparison between conventional Si anode (film and microparticle types) and the nanowire [24].

In this configuration, the SiNWs have grown directly current collector (often Cu) or alloy substrate. For instance, Chan et al. (2007) used the vapor-liquid-solid technique with gold as the catalyst on a steel substrate to accelerate crystal nucleation and development, resulting in vertically-standing SiNW ultimately. This geometry with a much smaller fiber diameter leads to a far "better accommodation known as strain relaxation for volume expansion", which happens in duty cycles and balances the local stress field, improving the battery stability and cycle life [24]. Besides, each nanowire rests directly on the current collector, which minimizes the battery's weight and increases the charge transfer efficiency. It is necessary to highlight that since a nanowire is a one-dimensional nanomaterial with long fiber carrying more sites for a redox reaction, which contributes to a higher possibility of fulfilling the theoretical maximum capacity [21].

The electrochemical performance of the SiNW anode is shown below in Figure 11 [24]. According to Figure 11(b), a prominent capacity enhancement is shown in the SiNW anode, which aligns with expectations. Specifically, the SiNW anode gives a 4277 mAh/g battery capacity which is close to the theoretical value according to (a) corresponding to the first two cycles of the square and circle sets in (b). The Coulombic efficiency of the first cycle is 73%, while this Figure grows to ~90% in the second cycle and keeps stable in the followings.

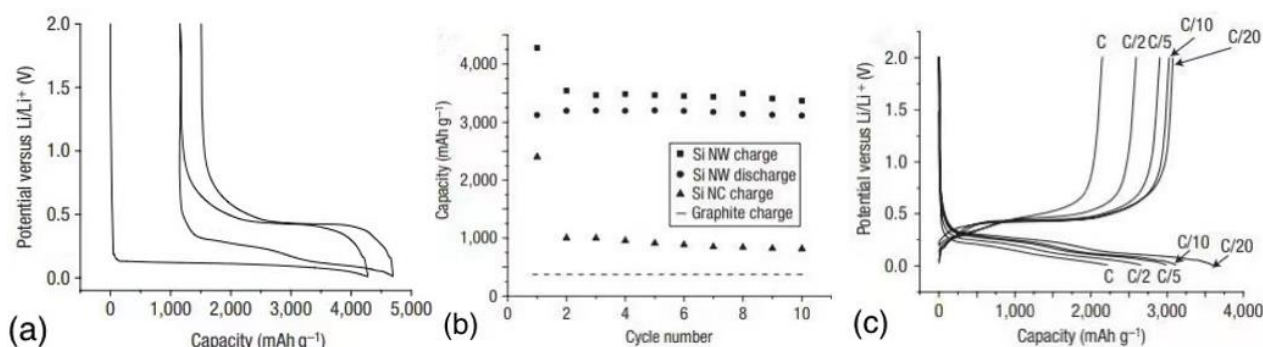


Figure 11. The SiNW anode performance. (a) The voltage curve of SiNW in the first two duty cycles at the C/20 rate (b) The capacity after multiple cycles (c) The voltage curves of SiNW at different rates [24].

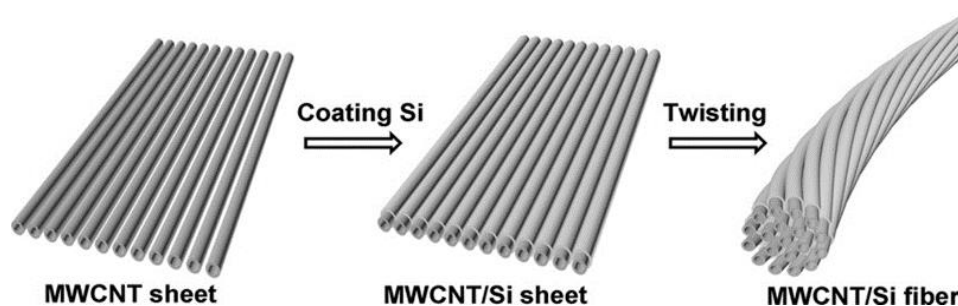


Figure 12. The exterior wall of the carbon nanotube is coated with Si using the atomic layer decomposition technique, followed by a twisting process that yields a nanotube bundle [25].

Based on the SiNW anode, Si nanotube (SiNT) is then blended with SiNW in some cases, forming a hybrid nanostructure as a solution to the two problems in the SiNW anode: (1). During operation, the Si maintains amorphous which possesses a not that good electrical conductivity in the duty cycle. (2). SiNW exhibits increasing polarization at high current rates, which may lead to capacity fading in multiple duty cycles [26]. Hollow silicon nanospheres, for instance, demonstrated an initial discharge capacity of 3052 mAh/g at a rate of 2000 mA/g, but the remaining capacity after 50 cycles was less than 25% (around 1000 mAh/g) [25]. By filling the empty cores of a SiNT with conductive materials or coating the walls of the tube with conductive material, the conduction of charges will be smoother.

Experiments completed by Lin et al. (2013) show the great capacity reserving ability of nanotube anode structure, a nanocomposite with MWCNT substrate and Si coating, as shown in Figure 12. A thin film of Si is coated on the exterior surface of the aligned MWCNTs to generate a structure that can completely use Si's high lithium capacity and continuously utilize the carbon nanotube structure. The SiNT anode shows a good battery performance according to the half-cell experiment set by Lin et al. [25].

4. Conclusion

By focusing on the working mechanism, morphology and microstructure of three varieties of anode material with the support of multiple examples, this article provides a more comprehensive understanding of sophisticated technologies and design ideas. It can be summarized that the carbon-based anode material increases the energy density and LIB capacity with the help of nanotechnology. The intermetallic compound and the interaction of multiple Al phases exhibit extraordinary capacity retention, as the Zn-based anode achieves this by applying nanoparticles to prevent pulverization. On the other hand, Si anode is a semiconductor itself; hence, a comprehensive battery performance enhancement is gained with nano-Si in different morphologies built. Generally speaking, it can be concluded that the performance of LIB is highly related to the structure of the anode and also the interaction and fitment of selected materials. One of the far-reaching research directions is to gain a deeper knowledge of the Li storage mechanism, as there is still a lack of knowledge of interactions between electrode materials and Li^+ . Besides, it is of great importance to seek a method of designing an anode (material and structure) that makes full use of the advantages of different classifications, i.e., the combination of the major classifications of anode material today (carbon-based, metallic and semi) With the help of innovated theories and practical uses, there is a promising future of developing LIB with far better performances than we imagine, a possibility to apply the ideas in LIB widely in other kinds of batteries and hence promoting the EV industry, aerospace and even pushing forward the onset of real energy structure transition.

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