Characteristics and properties of anode materials for lithium-ion batteries

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Abstract. Lithium-ion secondary batteries (LIBs) are battery systems with high energy densities. They are essential components of today's information-rich, mobile society's portable, entertainment, computing, and telecommunications technology. After 1981, most of the research on anode materials mainly focused on the anode containing Li, such as LiAl alloy, LiC alloy, etc. These materials have high prices, unstable cycling performance, and are difficult to be commercialized. The successful commercialization of LIBs began in 1991 with SONY's manufacturing of petroleum coke-based anode materials. Among them, anode plays a crucial role in LIBs. Anode materials that have been commercialized include carbon, alloys, and lithium titanate. Lithium-ion batteries using carbon anode materials and lithium titanate anode materials can meet the needs of electric vehicles (EVs) and large-scale energy storage applications to a certain extent, and alloy anode materials can promote the energy density of LIBs. The properties of the commercialized anode materials are covered in this paper. Next generation anode materials such as silicon anode materials are also introduced.

Keywords: lithium-ion batteries, anode materials, graphite anode, $Li_4Ti_5O_{12}$, Si anodes

1. Introduction

If a chemical reaction occurs on two spatially separated electrodes, an electric current is generated in the external circuit connecting the two electrodes. In general, if the change in the free energy of the basic chemical reaction is ΔG, then $\Delta G<0$; Only in a reversible reaction is $\Delta G=-nFE0$ satisfied, where E0 is the open circuit voltage [1]. The battery is therefore a tool for converting chemical energy into electric energy. Waterless lithium-ion battery systems with extremely high power densities have been developed. Lithium metal has a very negative electrode potential and a very low relative atomic mass, which gives it a high theoretical specific capacity. According to the electrode potential of lithium, it can be found that as long as it is combined with a suitable cathode material, it is possible to form a voltage of more than 4 V of battery.

The concept of LIBs appeared in 1972 with the rocking chair battery proposed by Armand et al. [2], cathode and anode materials using intercalation compounds, and Li^+ shuttles back and forth between the cathode and anode. SONY researchers such as Yoshio Nishi found the right combination of anode and cathode materials and electrolyte materials in 1989, finally promoting $LiCoO_2$ as the Li source cathode, petroleum coke as the anode, LiPF6 dissolved in propylene carbonate (PC) and ethylene carbonate (EC) as the electrolyte can be rechargeable and discharged secondary lithium batteries, and began to be commercialized in 1991, marking the arrival of the LIB era. In addition, there are lithium metal batteries with lithium alloy as a negative electrode. The research of Li-containing alloys appeared in the early days of LIBs. To discover novel anode materials to replace metal Li, lithium alloys of various systems were mainly studied when lithium was used as anode. Compared with metal Li, the lithium alloy anode can avoid the growth of dendrites to a certain extent, which improves safety. In addition to SnCoC and SiO small batch applications, most of the high specific capacity alloy anode materials have not been industrialized, because the huge volume change of the electrode material during Li intercalation results in cracks, stripping, and the pulverization of active substances from the collector, resulting in rapid electrode performance failure. At the same time, the continuously exposed the surface in contact with the electrolyte will continue to produce unstable SEI, which is a common phenomenon in alloy anode materials. A typical structure of a 18650 LIB is depicted in Figure 1. Anode collector adopts copper foil, cathode collector adopts aluminum foil [3], and the Li polymer batteries, in which polymer gel is used as an electrolyte (Figure 2).

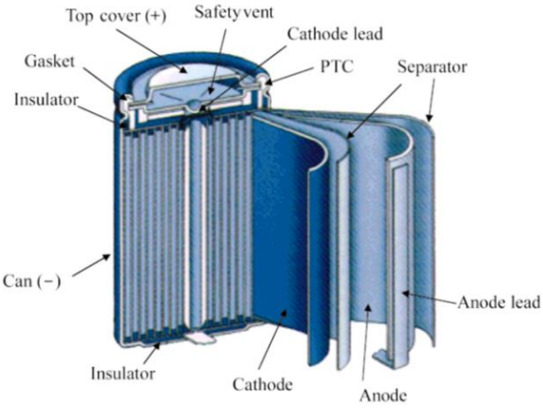


Figure 1. Structure of a lithium-ion battery [3]

Figure 2. Lithium polymer battery [3]

According to the application of the cathode and anode, the research and development of LIBs can be broadly divided into three generations (table 1) [4]. At present, the proportion of third-generation batteries in the total market of lithium-ion batteries is still low, and all use liquid organic solvent electrolytes.

Table 1. Lithium-ion battery generation division based on cathode and anode materials

	cathode	anode	time
1st generation	$LiCoO_2$	needle coke	1991-
2nd generation	$LiMn_2O_4$	graphite	1994-
	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	artificial graphite	

Table 1. (continued).

3rd generation	$LiFePO_4$	lithium titanate	2005-
	high voltage $LiCoO_2$	soft carbon	
	$LiNi_{x-0.5}Co_yMn_zO_2$	hard carbon	
	$LiNi_{0.8}Co_{0.15}Al_{0.5}O_2$	SnCoC	
	$LiFe_{1-x}Mn_xPO_4$	SiO_x	
	xLi_2MnO_3-$Li(NiCoMn)O_2$	Nano-Si/C	
	$LiNi_{0.5}Mn_{1.5}O_4$	Si-M alloy	

LIBs have the advantages of high energy density, high energy efficiency, outstanding cycle performance, no memory effect, fast discharge, low self-discharge rate, wide operating temperature range, safety, and reliability. It has become an important orientation for scientists all over the world to study. For example, to improve the endurance mileage of pure electric vehicles, New Energy and Industrial Technology Development Organization set a goal in 2008: By 2030, it aims to raise battery energy density to 500 Wh/kg, and by then, it expects to reach 700 Wh/kg [5].

Higher energy density, better cycle performance, and enhanced safety are critical requirements for LIB research in the context of EVs and large-scale energy storage device development. The LIB industry has been growing rapidly since SONY brought LIBs to the attention of consumers. Currently, LIBs are evolving into two significant emerging fields: large-scale industrial energy storage systems and electric vehicle technology. Among these, anode materials are essential to the development of LIBs.

2. Anode in LIBs

Anode materials, an essential component of LIBs, have been widely concerned nowadays to develop LIBs with high energy density, power density, superior cycling performance, and rate performance. The selection of anode materials should meet the following conditions [6]: 1. The intercalation reaction of Li should have a low redox potential to meet the high output voltage of LIBs. 2. During the intercalation reaction, the electrode potential changes little, which is conducive to the battery obtaining a stable operating voltage. 3. The capacity is large to meet the high energy density of LIBs. 4. The LIB has strong structural stability so the battery has a long cycle life. 5. The surface of the anode should be able to form a stable solid electrolyte interface (SEI), thereby preventing continuous consumption of the electrolyte on the anode surface and consumption of Li from the cathode. 6. The battery has a low transport impedance to electrons and lithium ions to obtain a high charge-discharge ratio. 7. The electrode material has strong chemical stability after charge and discharge, which improves the battery’s safety and cyclicity and lowers the self-discharge rate. 8. The manufacturing and disposal of batteries do not negatively impact the environment considerably. 9. Its inexpensive manufacture and use costs and straightforward preparation method make it simple to scale up. 10. There is an abundance of resources available for mining.

There are multiple kinds of anode materials, which are mainly classified as carbon and non-carbon materials (figure 3).

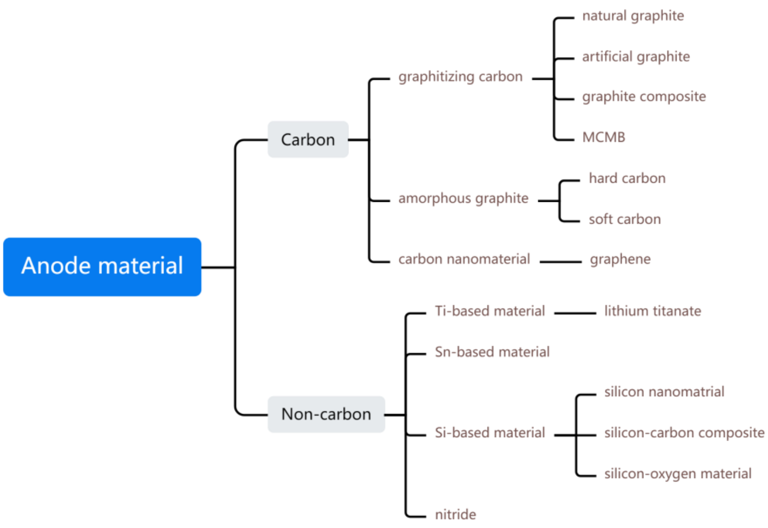
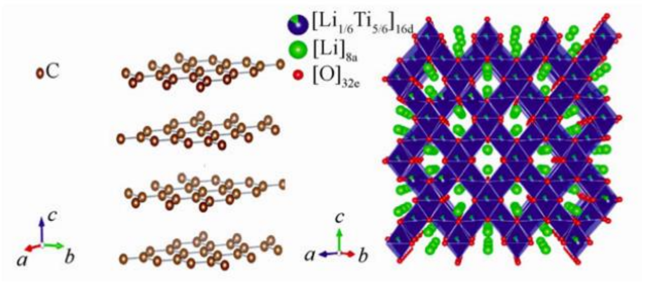


Figure 3. Classification of multiple anode materials

Graphite materials are the most widely used anode materials with the best comprehensive properties. The biggest challenge in developing new anode materials is the need to find materials with one or more outstanding advantages according to the application requirements, while also taking into account other properties. Although more than thousands of anode materials have been studied, the number of anode materials that can eventually be used commercially is actually very small. Electrode materials need to be considered in the development process of many factors, while considering the performance of the battery (including voltage, coulomb efficiency, cycle life, rate characteristics, energy efficiency, self-discharge, safety, cost, environmental adaptability, environmental hazards, etc.), but also need to consider the physical and chemical properties of the electrode material (chemical composition, microstructure, surface composition, surface composition, etc.). Particle size and shape, impurity content, true density, mechanical properties, porosity, conductivity, diffusion coefficient, etc.)

3. Typical anode materials

At present, the commercial and widely used lithium-ion battery anode materials are mainly divided into the following two categories: 1. hexagonal or rhomboid layered structure of artificial graphite and natural modified graphite; 2. Cubic spinel structure of $Li_4Ti_5O_{12}$ (LTO)(Figure 4) [7].



(a) (b)

Figure 4. Structure scheme of two commercialized anode materials, a) graphite; b) $Li_4Ti_5O_{12}$ [7]

3.1. *Layered graphite anode material*

Graphite has two crystal structures including hexagonal graphite and rhomboid graphite. The carbon atoms in graphite are sp^2 hybridized. The layers are combined by van der Waals forces, the atoms in the layers are combined by covalent bonds, and the intercalated Li between the graphite layers can form different "stage" structures. "Stage" is defined as the number of graphite layers separated between the two adjacent Li layers, such as "1st-stage", which means that there is only one graphite layer between the two adjacent Li layers. The schematic diagram of the graphite "stage" is shown in Figure 5. Li and graphite can be combined chemically to synthesize a variety of intercalation compounds, such as LiC_{24}, LiC_{18}, LiC_9, LiC_6 and so on [8], which are graphite intercalated compounds.

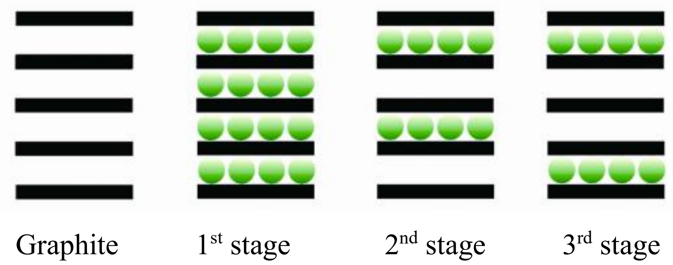


Figure 5. "Stage" structure of graphite intercalation [8]

Mesophase carbon microbeads (MCMB) are a significant kind of artificial graphite. It was first used in the 1960s. The microbeads were spherical (larger ones) or lemon-shaped (smaller ones). From the results of pyrolytic gas chromatography and I.R. (infra-red), it is considered that components of the microbeads depend on the composition of the raw pitch [9]. The main factors contributing to MCMB's superior electrochemical performance are its easy formation of a stable SEI and homogeneous reaction activity. However, the manufacturing cost of MCMB is comparatively high. Consequently, researchers have attempted to alter natural graphite materials in an effort to lower the cost of anode materials.

Won Chang Choi et al. prepared metal-graphite composite materials by the gas suspension coating method. They demonstrated that altering the active electrode materials for LIBs with gas suspension spray coating is an effective method. (Table 2) [10]. After modification, the electrochemical performance of natural graphite has been greatly improved, and the first efficiency can reach 90%, which can basically meet the requirements of consumer electronic products for battery performance.

Table 2. Initial efficiency and first charge-discharge cycle capacity of metal-coated and graphite for 1 M $LiPF_6$ in EC

	Discharge capacity (mAh/g)	Charge capacity (mAh/g)	Efficiency (%)
raw MCMB	284.45	309.58	91.8
2.67 wt.% Ag-coated	319.71	350.94	91.1
5.22 wt.% of silver-coated graphite	334.32	337.68	90.9
2.46 wt.% Ni-coated	311.34	337.68	92.2
1.18 wt.% Ag–1.1 Ni-coated	317.28	349.04	90.9

Higher standards are at present being set for the energy density, power density, and cycle life of the future generation of LIBs in the field of EVs, and people have further carried out research on nanopore, micron pore graphite, and polyhedral graphite, to solve the high power needs of LIBs [11]. The main application field of LIBs using graphite materials is portable electronic products, and modified graphite has begun to be applied in power batteries and energy storage batteries.

3.2. *Cubic spinel structure of $Li_4Ti_5O_{12}$*

In the research of anode materials for LIBs, another anode material that has entered the market is the $Li_4Ti_5O_{12}$ anode material with a spinel structure proposed by Jonker in 1956 [12]. Although the operating voltage of LTO is high, due to the excellent cycle performance and rate performance, it has higher safety compared with carbon materials, so there is an irreplaceable application demand for this material in the energy storage LIBs. However, one of the problems faced in the application is that the chemical reaction of $Li_4Ti_5O_{12}$ with the electrolyte during use leads to bloating, especially at higher temperatures. Flatulence can cause lithium-ion battery capacity attenuation, shortened life, and reduced safety. In order to solve the flatulence problem of $Li_4Ti_5O_{12}$ and improve the electrochemical properties of $Li_4Ti_5O_{12}$, researchers have proposed a variety of methods to modify it: 1. Control the water content in the battery. 2. Control the impurity content in $Li_4Ti_5O_{12}$. 3. Optimize the battery formation process.

3.3. Hard carbon and soft carbon anode material

In addition to graphite, hard carbon and soft carbon are two significant anode materials (Figure 6). The difference is that their crystallinity is lower, and the lamellar structure is not as orderly as graphite, as shown in Figure 6. Among them, hard carbon is difficult to graphitize carbon, which is an amorphous structure of pyrolytic carbon of polymer, and cannot be completely graphitized even at 2500 °C.

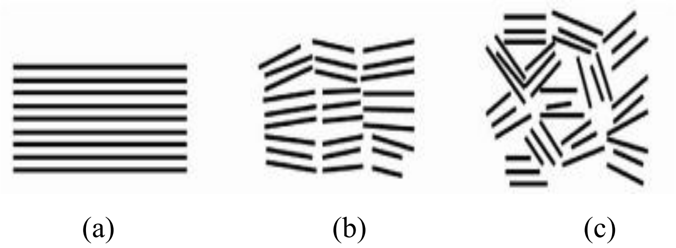


Figure 6. Structure models of graphite (a), soft carbon (b) and hard Carbon (c) materials [12]

Hard carbon has a relatively high capacity of 1.5~0 V vs. Li^+/Li (200~600 mA·h/g). The voltage curve consists of two parts: the first part is a slope with a voltage range of 1.0~0.1 V and a capacity of about 150~250 mA·h/g; The other part is the platform, which performs a capacity of 100 to 400 mA·h/g.

The hard carbon material has good cycling performance and high specific capacity. However, low efficiency in the first cycle, potential lag, low potential lithium storage, poor rate performance, etc. All affect the application of hard carbon. The electrochemical properties of hard carbon can be improved by coating doping.

From the current practical application point of view, hard carbon materials are more

suitable for high-power lithium batteries and hybrid vehicles. Honda introduced HEV (Hybrid Electric Vehicle) using hard carbon as an anode material. Nissan’s HEV with hard carbon materials has an output density of 3550-4000 W/kg, which is three times higher than the 1200 W/kg of NIMH (Nickel-Metal Hybrid) batteries.

In contrast to hard carbon, which is difficult to graphitize, soft carbon is an amorphous carbon that can be graphitized at high temperatures up to 2500 °C. Common soft carbon mainly includes petroleum coke, carbon fiber, needle coke, etc. It has strong adaptability to electrolytes, good resistance to overcharge and over-discharge, high capacity and good cycling performance. Due to the avoidance of graphitization treatment, the cost of soft carbon anode materials is low, and the cycle performance is improved to 1500~3000 times, which is expected to be applied to energy storage batteries, HEVs, electric vehicles (EVs), etc.

3.4. Silicon anode material

Anode materials make up around 10% of the total cost of materials used in the development and manufacturing of batteries. Low-cost and high-capacity anode materials are currently the focus of research on lithium-ion batteries.

Silicon is considered an anode material for the forthcoming era of high energy density LIBs due to its high theoretical capacity (4200 mAh/g), environmental friendliness, and high energy density. The capacity values of typical anodes are shown in Table 3 [13].

Table 3. Capacity values of typical anodes

Formula	Capacity (mAh/g)	Charge Transfer (max)	Voltage (V) (vs. Li^+/Li)
Si	4200	4.4	0.04000
BN	3240	3.0	-0.3448
AlN	1962	3.0	-0.5472
$P4O_{10}$	1888	20.0	1.497
SiO_2	1784	4.0	0.6895
Al_2O_3	1577	6.0	0.1750
V_2O_5	1474	10.0	1.437
B_2S_3	1365	6.0	1.847
TiO_2-R	1342	1.0	0.6046

The massive volume expansion and contraction leads to the pulverization of silicon anodes, and the active substances fall off from the conductive network and cause cracks in the Si particles, which affects the mechanical stability of the silicon particles and the electrode, the electrical contact between the active particles and the stability of the SEI, and ultimately leads to the low cycle life of the silicon anode. A silicon anode made without binders or current collectors has been used in certain previous research. The advantage over conventional electrode preparation techniques is the prevention of active substances falling off the collector during the process of shrinkage and expansion, which lowers the electrode load.

The unstable SEI film is an additional impediment to the commercial application of Si anode materials. Because of its low discharge and its huge volume expansion during the cycle, which leads to cracks, the fresh Si surface exposed to the electrolyte will continue to produce SEI. It is noteworthy that the volume change and the unstable SEI of Si anode material are intrinsic problems. Therefore, to further improve the cycle performance and coulomb efficiency of Si anode materials, it is necessary to solve the problems caused by Si anode materials in the process of volume change, such as separation from the conductive network, cracks, and failure to form a stable SEI with the existing electrolytic liquid system and SEI continuous growth.

The researchers found that reducing the Si particle size plays an important role in the electrode, and can effectively improve circulation compared to nano-Si particles. To produce a nano-Si composite material, carbon black, and nano-Si powder were combined at various weight ratios using manual grinding in the air (NSCM).

No obvious improvement in the reversibility of normal Si anodes in the same voltage range (curve 1 in Figure 7) [14]. This indicates that the particle size of Si powder is a key factor that influences the reversibility of Si-based anodes.

Besides acting as a conductive additive, carbon black’s function is to give nano-Si particles an elastic and distributed habitat. It can lessen Li-Si alloys’ volume variation during discharge-charge cycles (curve 6).

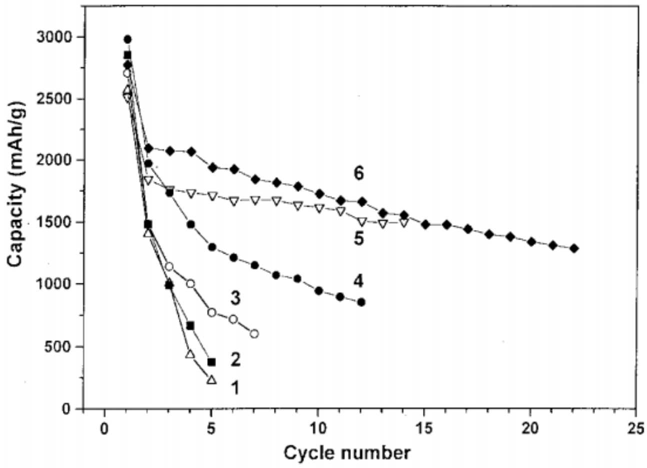


Figure 7. The cyclability of Si-based anodes under different circumstances. The cell is Si/ 1 M $LiPF_6$, in EC-DEC (EC- diethyl carbonate). (1) normal Si/CN (carbon nanotube) [0.0-0.8 V]; (2) normal Si/CB (carbon black), [0.0-2.0 V]; (3) nano-Si/CB [0.0-2.0 V]; (4) nano-Si/CB [0.0-0.8 V]; (5) nano-Si/CB [0.0-0.8 V]; (6) nano-Si/CB [0.0-0.8 V] [14]

The production of nanostructured Si electrodes, such as nanotubes, nanowires, 3D silicon membranes, hollow spheres, and so on, has been widely explored to limit mechanical damage and improve high rate capability. Unfortunately, the nanostructured silicon accelerates the degradation of the liquid electrolyte, leading to premature electrode failure. Additionally, the application for LIBs is restricted because solvents are typically required for the synthesis of nanostructured silicon.

Physical vapor deposition (PVD) of silicon thin films is a technique suitable for foundational research and miniaturization equipment. This method does not require solvents, additives, or adhesives to provide low resistance and high-purity films. However, there are restrictions on the thickness of PVD generated Si films (≈100 nm). At this point, Marta Haro et al. [15] describe a novel method of producing nanostructured electrodes that takes advantage of scaffolds positioned between amorphous Si layers. This allows for the utilization of the benefits of both continuous and nanoparticulated Si films while avoiding the drawbacks of both. Metal Ta’s outstanding aptitude for NP (nanoparticle) synthesis in conjunction with size selection, chemical stability, and post-growth behaviors including sintering and oxidation make it the ideal material for the NP scaffold.

The Si/Ta multilayered anode shows fast cycleability due to the fast diffusion of Lithium that causes low polarization of the electrode. The prototype is adaptable to any type of 3D structure for practical applications and offers considerable potential as a foundational study for optimizing nanostructured Si anodes.

4. Conclusion

The characteristics and properties of the anode materials utilized by LIBs are presented in this article. When compared to conventional secondary batteries, LIBs have a wide range of traits including a higher operating voltage, higher energy density, a lower self-discharge rate, no memory effect, and operation at a variety of temperatures.

Currently, the main objectives for anode material research are high energy density, high cycle performance, low cost, and high energy density (such as porous graphite and lithium titanate). Numerous studies are being conducted on new batteries, including lithium sulfur, lithium air, and lithium all-solid batteries. The forthcoming generations of lithium-ion batteries will gradually utilize high-capacity alloy anodes, including silicon anode materials.

However, the problem faced by alloy anode materials is the volume change associated with their high capacity. Even if the problems such as circulation and rate characteristics are solved, because the practical application of the battery cell volume is not allowed to change greatly (generally less than

5%, the maximum allowed 30%), and the capacity of alloy materials is proportional to the volume change, the alloy anode materials are limited in the LIB. Although its application can improve the energy density of existing LIBs to a certain extent, it cannot meet theoretical expectations.

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