A review of materials and their future development trends for lithium ion battery anodes

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Abstract. With the development of electric vehicles and clean energy, the demand for lithium batteries as an important energy storage system has increased significantly in the past decades. Anode, an indispensable part in lithium batteries system, is currently mainly selected from carbon-based materials, silicon-based, tin-based alloys, and metallic lithium materials. Lithium battery with traditional carbon-based material can basically meet the requirements of most current consumer electronics products. Silicon-based and metallic lithium materials have greater development potential in terms of high energy density anode. This article introduces the carbon-based materials, silicon-based, metallic lithium materials and their common modification methods that have been widely studied at the current stage and discusses the future development trends of various anode materials.

1. Introduction
Lithium batteries appeared in the last century, and due to their high energy density compared to zinc-manganese lead batteries, they have played an important role in daily consumer electronics, electric vehicles, and energy storage industries. However, with the in-depth development of sustainable energy and the high-speed revolution of electric vehicles, lithium battery system with high energy density have become an urgent research target and led to appearance of different lithium battery systems. Anode, as an important component of a lithium battery, its electrochemical properties could directly affect the performance of battery. Currently, anodes can be roughly divided into several categories by their composition, carbon-based anode, and metal alloy anode. Among them, carbon-based materials are well known by graphite which is most widely used in commerce, and metal alloy materials are prominently represented by silicon-based materials and metallic lithium materials.

2. Carbon-based material
Carbon-based materials are widely used in commercial batteries due to their low price, low electrochemical inertness, low charge-discharge platform, and low dendritic lithium formation. However, because of their low profit-capacity ratio, they have a theoretical limitation in high-energy battery applications.

Natural graphite has a good layered structure, in which carbon atoms form a carbon- carbon double bond connection by sp2 hybridization to form a hexagonal structure and extend in two dimensions and then form a plane. These layers are connected and stacked by van der Waals forces to form graphite crystals. Thus, Li ions can be stored in the interlayers, end faces and surface of graphite [1]. Therefore, the breadth, the surface area of edges, and the surface area of graphite are considered as the main
factors affecting lithium ion storage. Currently commercialized modified natural graphite capacity could reach 340 - 370 mAh/g, and the first Coulomb efficiency of 90 % - 93 %.

Natural graphite has the advantages of large reserves, low cost, low electric potential and stable charge curve, but it also has many disadvantages. First of all, graphite has a highly oriented layered structure. Its high crystallinity makes it poorly compatible with solvents, which means it is very sensitive to electrolytes [2]. Second, the graphite intercalation compound formed after the intercalation of lithium ions greatly changes the interlayer distance, which has an impact on the life of the graphite material [3]. In addition, the regular layered structure of natural graphite results in anisotropy, which makes the intercalation delay of lithium ions and the insufficient contact between graphite particles and the current collector. Besides, the uneven outer surface activity of natural graphite powder particles causes the surface structure to be damaged during charging and discharging, which is the reason for the low initial Coulomb efficiency and poor rate capability.

For the disadvantages of graphite, surface modification, coating, element doping, addition of alkali metals, improvement of preparation process and other methods are used to improve the electrochemical properties of carbon-based anodes. Surface modification is mainly based on surface oxidation and surface fluorination. Surface oxidation mainly refers to the use of a strong oxidant to convert the alkyl group on the surface of the anode into an acidic group, which is conducive to the formation of stable SEI and can effectively avoid the embedding of solvent molecules, thereby improving the cycle performance. Surface fluorination [4] refers to the chemical halogenation of the graphite surface, which reduces the internal resistance to a certain extent, which significantly improves the capacity and the charge-discharge performance. The surface of graphite coated by the soft carbon or hard carbon, polymeric is a common means of modification, which can not only maintain the advantages of graphite itself, but also further significantly improve its reversible specific capacity and enhance the cycle stability. For example, isaokunbayashi [5] covered graphite with amorphous carbon to form a core-shell structure, and used amorphous carbon to reduce the cracking and collapse of graphite, thereby improving cycle performance and charging and discharging rate. Pan Qinmin [6] covered graphite with an ionic polymer film to suppress and reduce the irreversible loss caused by the co-intercalation of the passivation film and solvated ions, which effectively improving the first Coulomb efficiency. In recent years, the element doping, and the addition of an alkali metal are more favored by researchers, Dong scholars [7] used vapor deposition method to prepare a novel multi-branched tubes nitrogen-doped graphite foam, and maintained a reversible specific capacity of 1049 mAh/g after 60 cycles (Fig. 1).

![Figure 1](image_url)

Figure 1. Electrochemical performance of a 3D-BNG sample. a) Cyclic performance at a current density of 0.5 A/g. b) Galvanostatic charge/discharge profiles at 0.5 A/g over 60 cycles

Although the research on carbon anode materials is approaching perfection, there is space for development of high current and high magnification research on graphite materials. On the basis of safety and low price, the dynamic performance of carbon anode materials will be the one of the future research directions.
3. Silicon-based materials

Silicon has huge reserves in the earth’s crust (mass content of 26.4%) [8], and it has a highest theoretical capacity in anode materials. Besides silicon is inexpensive, environmentally friendly, nontoxic, and easy to industrialize. Therefore, silicon-based anodes have been widely studied as anodes for high-energy-density lithium batteries [9].

The Silicon material does not have a layered structure like graphite, and its lithium storage mechanism is mainly alloyed with lithium. During the first discharge, lithium ions diffuse to the silicon surface to form a LiSi alloy while accompanied by surface volume expansion. With lithium ion embedded process continuing, more lithium ions diffuse into the interior, the interior crystalline silicon then transfer to amorphous Li$_x$Si$_y$ alloy. This process continues to expand until all Si particles complete the reaction. Among various LiSi chemical phases, Li$_{22}$Si$_5$[10] has the highest theoretical battery capacity (4200mAH/g) and highest volume expansion (about 420%) [11].

In the process of lithium intercalation and removal, a huge volume effect is a major constraint on the commercialization of silicon-based material. During the charging and discharging process, the expansion and contraction causes the internal stress to increase, which in turn causes the Si-based material powdering and cracking, resulting in a rapid decline in battery capacity and low cycle life [12]. In addition, during the embedding process, the SEI film[13] on the surface ruptured due to the inability to withstand the stress caused by the expansion, which caused the internal silicon to be exposed and directly contact the electrolyte, resulting in more electrolyte consumption and new SEI film formed. The excessively thick SEI film will reduce the electron transmission rate and cause further attenuation of the silicon reversible capacity. In addition, the electric conductivity of Si is relatively low, and the diffusion coefficient of lithium in Silicon is relatively low, these disadvantages seriously affect the terrible rate performance of silicon-based anode.

In order to solve the shortcomings above mentioned, a large number of related researches and various effective improving methods have been developed, among which nanostructure, silicon-carbon composite, surface coating and other modification methods have been favored. Nanostructures not only have strong tolerance in volume effect but also reduce mechanical strain force and strain, and their large active surface area is beneficial for contact between the active material and the electrolytic solution. LI et al[14] used Si nanoparticle with 80nm as anode material of a battery, obtaining the initial discharge capacity of 2770mAh/g, and the charge capacity of 2090mAh/g. After 10 cycles, the battery capacity can be maintained at about 1700 mAh/g. Among the modification strategies, silicon-carbon composites are considered one of the most effective methods. For one thing, the carbon can provide space for the volume expansion. For another, the introduction of carbon helps to improve the conductivity of the composite material, allowing direct and effective transport of Lithium ions and electrons between the active material and the electrolyte. Chen et al [15] used microemulsion to compound conventional carbon material (carbon black) with silicon, and then used as anode for testing. At rate of 0.1C, the battery capacity was about 1350mAh/g after 50 cycles. New carbon material, graphene has a stable structure, high electrical conductivity, high specific surface area and other advantages. Based on this, Chou et al [16] simply composited graphene with nano-silicon to obtain a graphene/silicon composite material. After 30 cycles, its specific capacity reached 1170mAh/g, which significantly improved the stability of the material. KO et al [17] prepared Si/graphite alkenyl composites by freeze-drying nanotechnology, which can maintain capacity of 1103 mAh/g after 1000 cycle. As shown in Fig. 2, the cycling performance of a-SBG at a charge current density of 14 A/g and a discharge density of 2.8 A/g over 1000 cycles. This is because it creates a coated, three-dimensionally cross-linked porous network for silicon/graphite composite material, and it has a significant effect on improving silicon conductivity, alleviating the volume expansion of silicon, and stabilizing the SEI film.
With the requirements for high energy density of batteries, silicon-based anodes have increasingly become the focus of research and experience a rapid development. In current applications, silicon-based anodes still face two bottlenecks, huge volume effects and low electrical conductivity. Therefore, both higher capacity and good cycle stability of the silicon-based material will be the future direction of development.

4. Metallic lithium

In recent years, metallic lithium anodes have once again attracted researchers' interest because of their potential in high-energy batteries. Lithium possesses the smallest atomic mass and density in alkali metal, and it is possible to achieve a high theoretical capacity (3860 mAh/g)[18]. In addition, lithium is active alkali metal with the lowest electrochemical potential of -3.04V[19-20] with strong reducibility and thermodynamic instability. In the case where the battery is charged, the lithium is reduced and deposited on the anode, as for discharging, the lithium dissolved due to oxidation[21-22].

In battery applications, metallic lithium anodes are not widely used in commercial application because of their low safety and reduced Coulomb efficiency after large cycles. Lithium, with low melting point and strong reducibility, can react with almost all organic solutions, electrolyte salts, and additives to form electronically insulated but ionically conductive solid electrolyte interfaces, namely SEI films[23]. Further, the metallic lithium undergo a large volume expansion during the charge-discharge process, which causes the original SEI film to crack and regrowth and dead lithium[24]. This phenomenon leads to irreversible loss of the lithium source and shows that the Coulomb efficiency continues to decrease. As the charge-discharge process continue with the non-uniform deposition of the lithium after each cycle [25], lithium dendrites will generate and accumulate in the lithium anode. Lithium dendrites may pierce the separator and cause internal short circuit, resulting in the dangerous conditions such as battery swelling and explosion.

In order to improve the cycling stability of lithium anodes and ensure the safety of commercial applications of lithium anodes, artificial SEI films, interface protection, and three-dimensional skeletons are considered as the most conventional and effective solutions. Guo et al [26] used situ reaction between metallic lithium and a polyacrylic acid (PAA) to prepare the artificial SEI film having high denseness, small thickness, high lithium-ion conductivity and excellent mechanical properties, which successfully stabilize the lithium stripping and plating. By using a highly elastic LiPAA polymer SEI film to alleviate the volume change of lithium and thereby stabilize the lithium anode, the purpose of inhibiting lithium dendrite growth could be achieved. Yang [27] uses a special method to prepare a three-dimensional copper current collector with sub-micron-sized pores. It is safe to suppress the formation of dendrites by reducing the current density and the uneven distribution of current density. In the experimental results, the three-dimensional copper current collector can maintain an electrode utilization of 98.5% after 600h at a current density of 0.5 mA/cm² (Fig. 1).
Figure 3. Voltage profiles of Li metal plating/stripping at 0.2mA/cm² in symmetric Li|Li@Cu cells with planar or 3D Cu foil as current collector.

Under the guidance of the market, metallic lithium is bound to be one of the best anode materials for high energy density. In the optimization of the metallic lithium anode, not only the growth of the lithium dendrite is required to be suppressed, but also the Coulomb efficiency must be greatly improved. In the current modification methods, there are several research hotspots, including reducing the current density on the electrode surface and homogenizing the mass transfer flow of lithium ions to the surface of anode.

5. Conclusion
Carbon-based materials have reached the stage of commercialization, and in terms of energy density, they are very close to their theoretical capacity, implying their development space is limited. Therefore, carbon composite materials are the main method to solve the energy density bottleneck. In the field of high energy density, silicon-based and metallic lithium materials have attracted much attention. Among them, silicon-based materials have the highest theoretical specific capacity, but the volume expansion effect brings the disadvantage of low cycle stability, therefore, the research aims to reduce the volume effect and suppress the SEI film thickening. Metallic lithium, as a high theoretical specific capacity anode that was abandoned due to safety at past, have become a hot topic again with the breakthrough development of SEI film and lithium dendrite theory. Throughout the development of the anode material, researches generally move in the direction of high energy density, high cycle stability, and high safety. In terms of specific material, researchers use methods such as modification, composite materials, and building new material systems to address the stability and security of lithium batteries to achieve the goal of commercialization.

References
[1] Woo, K. C., Mertwoy, H., Fischer, J. E., Kamitakahara, W. A., & Robinson, D. S. (1983). Experimental phase diagram of lithium-intercalated graphite. Physical Review B, 27(12), 7831-7834. doi:10.1103/PhysRevB.27.7831
[2] Wang, Q., Zhong, L., Sun, J., & Shen, J. (2005). A Facile Layer-by-Layer Adsorption and Reaction Method to the Preparation of Titanium Phosphate Ultrathin Films. Chemistry of Materials, 17(13), 3563-3569. doi:10.1021/cm050646w
[3] Balogun, M.-S., Luo, Y., Qiu, W., Liu, P., & Tong, Y. (2016). A review of carbon materials and their composites with alloy metals for sodium ion battery anodes. Carbon, 98, 162-178. doi:10.1016/j.carbon.2015.09.091
[4] Matsumoto, K., Li, J., Ohzawa, Y., Nakajima, T., Mazej, Z., & Žemva, B. (2006). Surface structure and electrochemical characteristics of natural graphite fluorinated by ClF3. Journal of Fluorine Chemistry, 127(10), 1383-1389. doi:10.1016/j.jfluchem.2006.06.012
Kuribayashi, I., Yokoyama, M., & Yamashita, M. (1995). Battery characteristics with various carbonaceous materials. Journal of Power Sources, 54(1), 1-5. doi: 10.1016/0378-7753(94)02030-7

Pang, Q., Guo, K., Wang, L., & Fang, S. (2002). Ionic conductive polymer encapsulated graphite as anode material for lithium ion batteries. Battery Bimonthly, 32(S1), 38-40. doi:10.3969/j.issn.1001-1579.2002.z1.014

Dong, J., Xue, Y., Zhang, C., Weng, Q., Dai, P., Yang, Y., . . . Wang, X. (2017). Improved Li+ Storage through Homogeneous N-Doping within Highly Branched Tubular Graphitic Foam. Advanced Materials, 29(6), 1603692. doi:10.1002/adma.201603692

Huggins, R. A. (1999). Lithium alloy negative electrodes. Journal of Power Sources, 81-82, 13-19. doi: 10.1016/S0378-7753(99)00124-X

Lee, K.-L., Jung, J.-Y., Lee, S.-W., Moon, H.-S., & Park, J.-W. (2004). Electrochemical characteristics of a-Si thin film anode for Li-ion rechargeable batteries. Journal of Power Sources, 129(2), 270-274. doi: 10.1016/j.jpowsour.2003.10.013

Huggins, R. A., & Boukamp, B. A. (1984). United States Patent No.

Goodenough, J. B., & Kim, Y. (2010). Challenges for Rechargeable Li Batteries. Chemistry of Materials, 22(3), 587-603. doi:10.1021/cm901452z

Wu, H., Zheng, G., Liu, N., Carney, T. J., Yang, Y., & Cui, Y. (2012). Engineering Empty Space between Si Nanoparticles for Lithium-Ion Battery Anodes. Nano Letters, 12(2), 904-909. doi:10.1021/nl203967r

Bates, J. B., Dudney, N. J., Neudecker, B., Ueda, A., & Evans, C. D. (2000). Thin-film lithium and lithium-ion batteries. Solid State Ionics, 135(1), 33-45. doi:10.1016/S0167-2738(00)00327-1

Li, H., Huang, X., Chen, L., Wu, Z., & Liang, Y. (1999). A High Capacity Nano-Si Composite Anode Material for Lithium Rechargeable Batteries. 2(11), 547-549. doi:10.1149/1.1390899

Chen, Y., Nie, M., Lucht, B. L., Saha, A., Guduru, P. R., & Bose, A. (2014). High Capacity, Stable Silicon/Carbon Anodes for Lithium-Ion Batteries Prepared Using Emulsion-Templated Directed Assembly. ACS Applied Materials & Interfaces, 6(7), 4678-4683. doi:10.1021/am404947z

Chou, S.-L., Wang, J.-Z., Choucair, M., Liu, H.-K., Stride, J. A., & Dou, S.-X. (2010). Enhanced reversible lithium storage in a nanosize silicon/graphene composite. Electrochemistry Communications, 12(2), 303-306. doi: 10.1016/j.elecom.2009.12.024

Ko, M., Chae, S., Jeong, S., Oh, P., & Cho, J. (2014). Elastic a-Silicon Nanoparticle Backboned Graphene Hybrid as a Self-Compacting Anode for High-Rate Lithium Ion Batteries. ACS Nano, 8(8), 8591-8599. doi:10.1021/nn503294z

Goodenough, J. B., & Park, K.-S. (2013). The Li-Ion Rechargeable Battery: A Perspective. Journal of the American Chemical Society, 135(4), 1167-1176. doi:10.1021/ja3091438

Lin, D., Liu, Y., Chen, W., Zhou, G., Liu, K., Dunn, B., & Cui, Y. (2017). Conformal Lithium Fluoride Protection Layer on Three-Dimensional Lithium by Nonhazardous Gaseous Reagent Freon. Nano Letters, 17(6), 3731-3737. doi:10.1021/acs.nanolett.7b01020

Palacin, M. R., & de Guibert, A. (2016). Why do batteries fail? Science, 351(6273), 1253292. doi:10.1126/science.1253292

Rosso, M., Brissot, C., Teyssot, A., Dollé, M., Sannier, L., Tarascon, J.-M., . . . Lascaud, S. (2006). Dendrite short-circuit and fuse effect on Li/polymer/Li cells. Electrochimica Acta, 51(25), 5334-5340. doi: 10.1016/j.electacta.2006.02.004

Brissot, C., Rosso, M., Chazalviel, J. N., & Lascaud, S. (1999). Dendritic growth mechanisms in lithium/polymer cells. Journal of Power Sources, 81-82, 925-929. doi: 10.1016/S0378-7753(98)00242-0

Ota, H., Shima, K., Ue, M., & Yamaki, J.-i. (2004). Effect of vinylene carbonate as additive to electrolyte for lithium metal anode. Electrochimica Acta, 49(4), 565-572. doi:10.1016/j.electacta.2003.09.010
[24] Xu, W., Wang, J., Ding, F., Chen, X., Nasybulin, E., Zhang, Y., & Zhang, J.-G. (2014). Lithium metal anodes for rechargeable batteries. Energy & Environmental Science, 7(2), 513-537. doi:10.1039/C3EE40795K

[25] Li, Z., Huang, J., Yann Liaw, B., Metzler, V., & Zhang, J. (2014). A review of lithium deposition in lithium-ion and lithium metal secondary batteries. Journal of Power Sources, 254, 168-182. doi:10.1016/j.jpowsour.2013.12.099

[26] Li, N.-W., Shi, Y., Yin, Y.-X., Zeng, X.-X., Li, J.-Y., Li, C.-J., . . . Guo, Y.-G. (2018). A Flexible Solid Electrolyte Interphase Layer for Long-Life Lithium Metal Anodes. Angewandte Chemie International Edition, 57(6), 1505-1509. doi:10.1002/anie.201710806

[27] Yang, C.-P., Yin, Y.-X., Zhang, S.-F., Li, N.-W., & Guo, Y.-G. (2015). Accommodating lithium into 3D current collectors with a submicron skeleton towards long-life lithium metal anodes. Nature Communications, 6(1), 8058. doi:10.1038/ncomms9058