Anode Material Innovations for Boosting Battery Energy Density

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Abstract. As global efforts intensify to combat climate change, reducing carbon emissions has become a priority, driving the adoption of electric vehicles (EVs) that rely on lithium-ion batteries. However, enhancing battery energy density is essential for extending EV driving ranges and further reducing greenhouse gas emissions. This review examines advancements in anode materials for lithium-ion batteries, focusing on their impact on energy density. Traditional anodes, such as graphite and lithium metal, are limited by low energy density and safety concerns. Recent innovations, including silicon, tin-based, transition metal oxides, and alloy-based anodes, offer higher theoretical capacities but face challenges like significant volume expansion, low thermal stability, and poor cycle performance. Strategies to mitigate these issues, such as nanosizing, structural design, and composite synthesis, are discussed. Despite progress, achieving the ultimate energy density remains elusive, with no single material meeting all the necessary criteria. Future research must focus on balancing energy density with durability, cost-effectiveness, and safety to realize the full potential of next-generation lithium-ion batteries.

Keywords: Anode materials; lithium-ion batteries; battery energy densities.

1. Introduction

As global warming becomes increasingly critical, reducing greenhouse gases, particularly carbon dioxide, has become a global priority. Electric vehicles (EVs) are gaining popularity as they produce no carbon emissions during operation, contributing to this goal. However, as the EV market grows, so do the demands for improved performance, particularly regarding battery energy density, which is crucial for achieving long driving ranges [1]. Energy density, defined as the amount of energy stored per unit volume [2], is significantly influenced by the anode materials in the battery. The capacity and overall performance of a battery largely depend on the intrinsic properties and morphology of these anode materials [3]. Therefore, advancing anode materials is essential for enhancing battery capacity, lifespan, and overall efficiency [4].

Lithium-ion batteries are currently the most widely used due to their lightweight, compact size, environmental benefits, and high energy density [3]. Despite these advantages, there remains significant room for improvement. Researchers are actively exploring various anode materials to maximize energy density. Traditional anode materials like graphite and lithium metal, while widely used, have limitations, including lower energy density and safety concerns. Consequently, new materials such as silicon and tin are under investigation. However, these novel materials also present challenges. This paper will review existing research on Li-ion battery anode materials, focusing on innovations aimed at enhancing energy density and the associated challenges. It will begin by discussing traditional materials, then explore recent advancements, and finally, outline future directions and challenges in anode material development for achieving ultimate energy density.

2. Traditional Anode Materials

1.1. Graphite Anodes

Graphite is a conventional anode material used in Lithium ion batteries. The relatively large spacing between adjacent graphite layers creates ample sites for the intercalation of Li-ion due to the weak intermolecular forces (London dispersion forces) between graphene layers, which facilitate ion

intercalation and deintercalation across the prismatic surface [5]. During lithiation, lithium ions intercalate into the graphite, forming LiC6, with a theoretical specific capacity of 372 $mAhg^{-1}$ and a theoretical volumetric capacity of 850 $mAhcm^{-3}$ [5]. However, compared to materials like silicon, graphite offers lower energy density. Additionally, graphite suffers from limited rate capacity, particularly during the lithiation process [6]. Studies have shown that the lithium-ion diffusion coefficient is approximately 10^{-7} cm^2s^{-1} for Stages 1 and 2 when many vacancies are present, but it decreases to around 5×10^{-9} cm^2s^{-1} in the fully lithiated state [7]. Furthermore, the risk of lithium metal plating on the surface of electrode can lead to safety issues such as short circuits, rapid aging, and accelerated battery degradation [6]. Another significant shortcoming of graphite anodes in Li-ion batteries is the irreversible capacity loss due to electrolyte decomposition, which consumes a substantial amount of lithium ions as charge carriers [8].

1.2. Lithium Metal Anodes

Lithium metal is also utilized as an anode material in Li-ion batteries due to its remarkable theoretical capacity. It offers a specific capacity of 3860 $mAhg^{-1}$ and a negative electrochemical potential of -3.040 V relative to the standard hydrogen electrode. Additionally, its low density (0.534 gcm^{-3}) makes it lightweight [9]. Despite these advantages, lithium metal anodes face significant challenges, particularly the growth of lithium dendrites [10]. When lithium ions migrate to the anode, they do not always distribute evenly across the surface of the lithium metal [11]. Instead, some lithium ions cluster on previously deposited ions, leading to the gradual formation of dendrites [11]. These dendrites, which are needle-like structures, can pierce the solid electrolyte interphase (SEI) layer intended for protection. If the dendrites reach the cathode, they can cause short circuits, resulting in serious safety hazards. These safety concerns limit the practical use and application of lithium metal anodes in batteries.

3. Innovative Anode Materials

1.3. Silicon-based Anodes

New anode materials have been developed to enhance energy density, with silicon being a prominent example due to its high theoretical capacity of approximately 4200 $mAhg^{-1}$. During lithiation, silicon forms the compound $Li_{15}Si_4$, allowing each silicon atom to accommodate 3.75 lithium ions [12]. Additionally, silicon has an average voltage platform of 0.4 V (vs. Li/Li^+), which is higher than that of graphite (0.125 V). This characteristic helps prevent lithium plating and dendrite formation during charging [12]. Owing to its high capacity, silicon anodes have the potential to significantly increase battery energy density.

However, silicon anodes face significant challenges, primarily due to their substantial volume expansion, which can reach up to 280% of their initial volume [12]. This continuous expansion and contraction lead to a sharp decrease in capacity and rapid deterioration of cycle performance. The stability of the solid electrolyte interphase (SEI) layer is also compromised, causing it to reform continuously and expose fresh silicon to the electrolyte, leading to electrolyte degradation. To address these issues, nano-sized silicon anode materials have been developed. The smaller particles help mitigate the physical stresses caused by the large volume changes, while grain boundaries provide faster diffusion paths for lithium ions [13].

Despite these advantages, nano-sized silicon anodes have their own drawbacks. One major issue is the high irreversible capacity due to reactions between lithium ions and silicon oxide, which consume lithium ions and lower capacity, resulting in low coulombic efficiency. Another challenge is the low mass loading of nano-sized silicon. Mass loading is an important factor in determining the specific energy density of a battery. Most nano-sized silicon anodes demonstrate excellent capacity and cycle life at mass loadings of less than 1 $mgcm^{-2}$, which is only one-tenth of that for graphite anodes [14]. Wei et al. studied the relationship between silicon mass loading and specific energy density and found that there is a plateau in specific energy density at around 5 $mgcm^{-2}$ [14]. Therefore,

increasing the mass loading of silicon to 5 mgcm^{-2} is essential for optimizing battery performance (Figure 1).

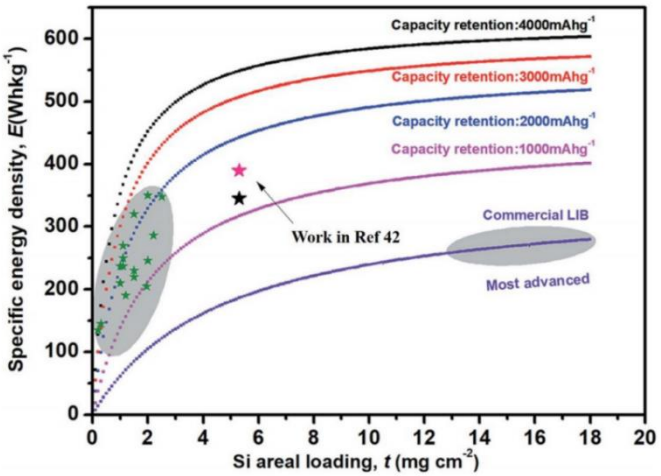


Fig. 1 Estimating the specific energy of a Si/Li (NixCoMnz)O_2 (x + y + z = 1) full cell at various stable capacity retentions after cycles [14]

Thirdly, nano-sized silicon anodes exhibit poor thermal stability. The electrolyte on the anode surface is more likely to react with silicon nanoparticles due to their high surface area, which can lead to thermal instability [12]. Park et al. conducted a study on the thermal stability of lithiated silicon powders with particle sizes of 15 μm (S1), 5 μm (S2), and 30–50 nm (S3) [15]. Their results, presented in Figure 2, illustrate the varying degrees of thermal stability across these different particle sizes, highlighting the challenges associated with nano-sized silicon anodes.

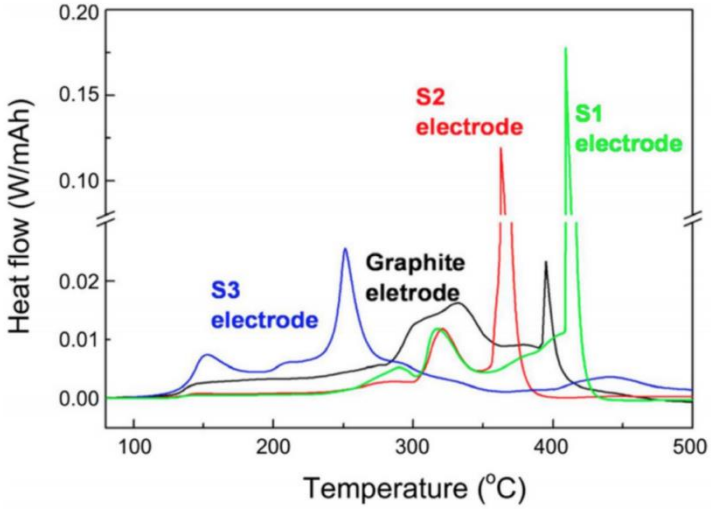


Fig. 2 Capacity normalized heat flow from DSC measurements conducted on various active materials lithiated to 5 mV. S1: 15 μm Si, S2: 5 μm Si, S3: 30–50 nm Si, graphite: carbon-coated natural graphite [15].

According to Figure 2, nano-sized silicon exhibits lower thermal stability compared to graphite. Therefore, enhancing the thermal stability of nano-sized silicon anodes is a critical focus for future research. Another innovative material is silicon nanowires, which offer several advantages: (1) their structure increases the surface area, thereby enhancing the surface area-to-volume ratio,damage [creates more active surfaces for electrode-electrolyte interactions; (2) they provide efficient electron transport channels along the nanowire direction, as well as effective ion transport pathways; and (3) their small diameter helps accommodate volume changes and mitigates structural damage [16].

Despite these advantages, silicon nanowires also face challenges. For example, during repeated charging and discharging cycles, nanowires tend to aggregate, leading to capacity decay and increased internal impedance. Additionally, the large surface area induces side reactions with the electrolyte,

resulting in low coulombic efficiency and reduced cycle life. Furthermore, silicon nanowires have lower electrical conductivity due to a shortened electron mean free path caused by surface scattering [16].

1.4. Tin and Tin Oxide Anodes

Tin (Sn) and tin oxide (SnO_2) anodes are the innovated anode materials. When Li ions flow through, the compound $Li_{22}Sn_5$ is formed. This anode material has a theoretical capacity of 994 $mAhg^{-1}$[17]. Due to its high theoretical capacities, SnO2 has attracted a lot of attention. The real-world application of SnO2 anodes is still a significant challenge because they suffer from large volume expansion, just like silicon [18]. Large volume changes of SnO_2 during lithiation and delithiation process limit its stability and cycle performance [19]. Due to the significant volume change and the repeated recycling of bulk tin dioxide, anode pulverization takes place, and the electrical contact is reduced. Thus, this leads to a rapid drop in capacity over several life cycles. Other disadvantages of pure tin dioxide are its low electronic and ionic conductivity [19]. Tin dioxide has a very low conductivity at room temperature. This property greatly limits its storage and rate capability as an anode material. The measured apparent lithium-ion diffusion coefficients are also very low; reported values range from 10-16 to 10-14 $cm2s^{-1}$ for sputtered metallic tin films (3 μm thick) to 10-15 to 10-13 $cm2s^{-1}$ for amorphous tin dioxide-tin oxide films (≈1.5 μm thick) [19]. The ways to solve these problems are nanosizing the particles and therefore improving the structural stability of the material and helping to have fast reaction kinetics [18]. Tin dioxide nanoparticles with various nanomorphologies can achieve volume expansion through built-in porosity and reduce the aggregation of tin clusters through homogeneous dispersion in the Li_2O matrix. In addition, it reduces the required Li ions diffusion pathway by significantly increasing the electrode-electrolyte interface, resulting in higher ionic flux and the fabrication of high-rate anodes [19]. A better performance of nanosized Sn materials can be seen in Figure 3. However, it can also be concluded from the figure that its cycling stability is still insufficient.

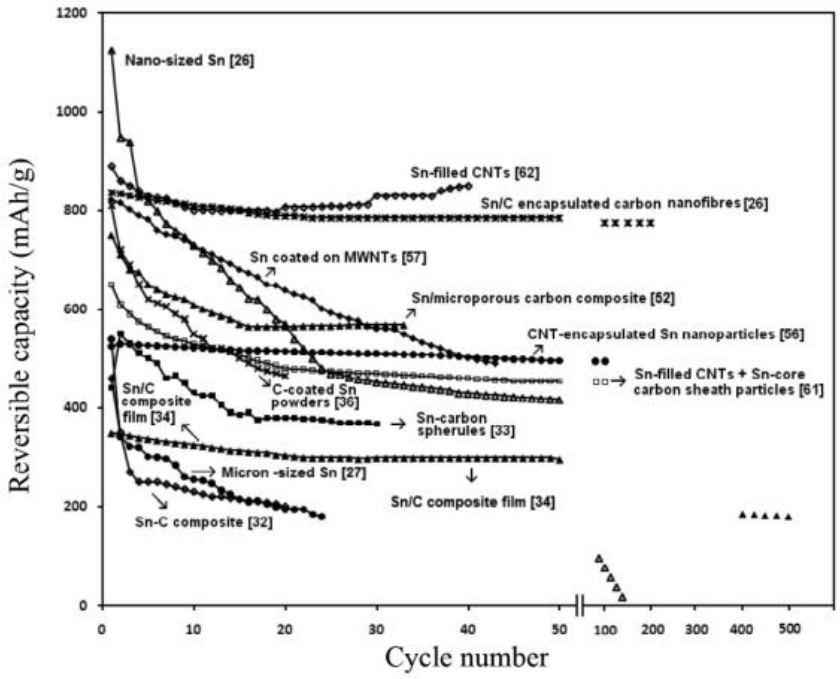


Fig. 3 Reversible capacity of different Sn-containing materials versus the cycle number [17].

Another approach to addressing the issue of volume expansion in anodes is the use of appropriate metal composites, such as SnSb/Sb. These new materials offer relatively high reversible capacity compared to graphite. For instance, the SnSb composite forms two lithiated phases, Li_3Sb and $Li_{22}Sn_5$, when reacting with lithium ions. During the formation of Li_3Sb, the ductile Sn phase acts as a buffer

to accommodate the expansion. The capacity of the Sn/SnSb-Ni composite remains around 450-570 $mAhg^{-1}$ after 50 cycles, which is sufficiently high for practical applications.

1.5. Transition Metal Oxides Anodes (e.g., Fe3O4, Co3O4)

Transition metal oxides are promising anode materials due to their abundance, low cost, and high energy capacities, ranging from 700 to 1200 $mAhg^{-1}$ [20]. Among these, iron oxides, such as Fe_2O_3 and Fe_3O_4, are widely used in Li-ion batteries. For example, Fe_2O_3 has a theoretical capacity of 1007 $mAhg^{-1}$, which is significantly higher than that of graphite (372 $mAhg^{-1}$) [20]. The reaction mechanism is detailed below.

$$Fe_2O_3+6Li^++6e^-\rightarrow 2Fe+3Li_2O \quad (1)$$

Fe_3O_4 is also a suitable anode material for Li ion batteries since it has high theoretical specific capacity about 926 mA h g–1 and are abundant in natural. The reaction mechanism can be generalized as:

$$Fe_3O_4+8Li^++8e^-\rightarrow 3Fe+4Li_2O \quad (2)$$

Despite their advantages, transition metal oxides as anode materials have several drawbacks, including low electrical conductivity, poor ion diffusion kinetics, poor ionic conductivity, significant volume expansion, and high-voltage hysteresis [20]. These limitations result in poor rate performance and power density, while the large volume expansion can lead to pulverization and structural degradation, causing a rapid decline in capacity. To mitigate these issues, scientists have developed strategies such as hybrid materials, doping, and conductive matrix integration. For example, Aminoclay (AC) was used to create SnAC-Fe_3O_4 nanocomposites that can withstand large stresses induced by Fe3O4 volume expansion and maintain structural stability during charge-discharge cycles, as reported by Pham et al.[20].

In addition to structural design, combining transition metal oxides with highly conductive materials is another crucial strategy to enhance electronic conductivity and efficiency. Conductive materials like carbon, carbon nanotubes, graphene, reduced graphene oxide, and multiwalled carbon nanotubes can bear the mechanical stress from volume expansion, stabilize the solid electrolyte interphase (SEI) layer, and inhibit dendrite growth [20]. For instance, Liu et al. prepared Fe_3O_4 composites using crosslinking technology with 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)-oxidized cellulose nanofibrils (TOCN-Na), resulting in a high reversible capacity of about 1635 $mAhg^{-1}$ after 100 cycles at 1 Ag^{-1} [21]. The strong interaction between Fe_3O_4 and carboxylic acid groups in the TOCN-Na matrix ensures uniform dispersion of nano-Fe_3O_4 within a 3D carbon network, promoting efficient lithium-ion transport and storage while preventing agglomeration and excessive volume expansion during Li^+ insertion.

However, significant challenges remain, and further research is needed to advance the development of transition metal oxide anode materials. Future efforts should focus on the following key areas: (1) To enhance the decomposition of metal oxides during battery operation and introduce more active sites, doping transition metal oxides with different elements is necessary; (2) Developing metal-organic framework (MOF)-derived TMO materials, which offer adjustable pores, high specific surface area, and diverse functionalities by coordinating metal clusters and organic ligands; (3) Utilizing self-assembly techniques to design ideal nano-sized structures, which prevent structural damage more effectively than template methods; (4) Creating composites of transition metal oxides with conductive materials to enhance overall conductivity and address the inherent limitations of transition metal oxides[20].

1.6. Alloy-based Anodes (e.g., Si-Sn, Si-Al)

Alloy-based anodes have recently gained popularity as battery materials due to their excellent theoretical energy storage capacities, ranging from 400 to 2300 $mAhg^{-1}$ [22]. These materials offer a good balance of safety, durability across multiple charge/discharge cycles, and high coulombic

efficiency. However, they also have significant drawbacks, including reduced electronic conductivity, substantial volume fluctuations, and capacity degradation [22].

Silicon anodes, in particular, have gained significant attention because of their abundant resources and high theoretical capacity. However, the large volume changes inherent in silicon during charging and discharging have limited their widespread application in lithium-ion batteries. Silicon anodes are produced by leaching aluminum from rapidly solidified aluminum-silicon alloy ribbons using a single-roll melt-spinning process. For example, silicon anode ribbons made from 50Al-50Si alloys, composed of micron-sized primary silicon and nano-sized eutectic silicon, demonstrate low volume expansion during lithium insertion and can achieve capacities of up to 3000 $mAhg^{-1}$ [23]. Scanning electron microscopy (SEM) reveals that the pore structure formed during this process effectively suppresses electrode expansion. Even without the use of binders or conductive carbon additives, the electrode exhibits excellent cycling stability at a C/10 rate, maintaining an initial capacity of 2070 $mAhg^{-1}$ with only a slight decrease to 1970 $mAhg^{-1}$ after 10 charge/discharge cycles [23]. The findings offer a new approach to designing low-expansion silicon anodes that are suitable for high-capacity energy storage devices.

Various strategies have been devised to deal with the significant volume variation in alloy anodes, including the use of materials in nanosized, engineered alloys (binary or ternary), heterostructures (hybrids with other types of anodes), and compositions incorporating buffer materials [24]. The development of binary or ternary alloys has become a promising strategy for mitigating severe volume expansion and improving the electrochemical reaction kinetics of anode materials over the past few years. Metal and metalloid elements are combined with electrochemically active or inactive components to form these alloys, with examples including SnSb, SnTe, SbBi, Sb_2Se_3, $BiSbSe_3$, $FeSb_2$, and NiSb. Furthermore, these alloys can be enhanced by integrating additional techniques such as carbon coating, nanostructure design, and electrolyte optimization to improve the cycling stability of anode materials [24]. The creation of these alloys can be achieved using a variety of synthesis methods, including sol-gel, selenization, ball milling, spray methods, electrospinning, precipitation, hydrothermal processes, and carbonization [24].

4. Future Directions and Challenges

In response to the demand for higher energy density in batteries, researchers have explored various anode materials. Current research highlights the use of nanosized and composite materials in next-generation anodes, largely due to their unique properties, such as high specific surface area. However, achieving the ultimate energy density in batteries remains a distant goal. Most of the innovative materials discussed are still at the laboratory stage and face significant challenges in commercialization. The primary hurdle lies in the inability to produce these materials at low cost and on a large scale. Additionally, each material has its own limitations. There is often a trade-off between energy density and battery longevity—materials with high theoretical capacity tend to have shorter life cycles, with rapid capacity degradation after repeated use.

When considering all critical factors, including low cost, thermal stability, conductivity, energy density, capacity, and lifespan, no single material currently meets all these criteria. The battery industry is grappling with the challenge of achieving a balance between these properties. Potential solutions include the development of composite materials and improving battery performance by optimizing the cathode and electrolyte components.

5. Conclusion

The innovations in anode materials aimed at boosting energy density have been summarized above, along with the challenges these materials face in achieving higher energy density in Li-ion batteries. Each anode material comes with its own set of challenges. Conventional materials like graphite suffer from low energy density, while lithium metal poses significant safety risks. Innovative anode

materials, including silicon, Sn/SnO_2, transition metal oxides, and alloy-based anodes, primarily struggle with extreme volume expansion. To address this, scientists have largely focused on nanosizing these materials, which has proven effective in managing volume changes and enhancing energy density. Other strategies include structural design, composite synthesis, and doping.

However, these new materials also present drawbacks, such as low thermal stability and poor cycle performance. Given these challenges, it is evident that there is still a long road ahead for battery innovation. The ideal electrode material has yet to be discovered, and new types of lithium-ion batteries require further research. Despite these hurdles, promising directions remain, particularly in the development of composite materials and the application of nanotechnology. The potential for advancing Li-ion batteries is immense.

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