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Advancements of Applying Nano-Structured Silicon Anode for Next-Generation Energy Storage

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Abstract:
In the advancement of modern technology, lots of innovations have been introduced to civil engineering, transportation and energy systems. Among them, nanotechnology stands out as a pivot with wide-ranging potential. Especially in EVs, nanotechnology involves in improving battery performance. For instance, extending the cycle life, providing faster charging speed, and increasing energy density. Silicon anode gives larger energy capacity which is a good attempt for more efficient lithium-ion batteries. However, the large volumetric change of silicon making this approach unapplicable. Nano-structured silicon and Si/C composites have been proven to have the ability to release the cracking stress through its small size and carbon shell respectively, this offers the opportunity for the further investigation of development of nano-silicon anode. However, many concerns for mass production and manufactural safety have been developed. These problems can be overcome by further research for more safer and cheaper mechanism and machines, proper regulation and sensitive triggers during manufacturing process could avoid the majority of safety issues.

Keywords: Nano-structured silicon, lithium-ion battery, silicon anode, silicon carbon composites.

1. Introduction

Tesla as one of the revolutionary companies for the industry of electric vehicles (EVs) opens an exciting market for development of sustainable transportation with a mission ‘to accelerate the worlds’ transition to more sustainable energy’. Fig. 1 demonstrates the trend of sales for Tesla cars from 2008-2024 (Data from Tesla website). The rising trend marks the outstanding potential for EVs’ market. After Tesla’s pioneering exploration, replacement of gasoline cars with EVs has been a global trend. This is also driven by the urgent of reducing the carbon emission and limitation of fossil fuel resources. However, manufacture of EVs is still hindered by many critical problems: energy capacity, weight management, thermal management for both battery and tires, and environmental concerns for recycling. Nanotechnol-

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ogy comes out to be an effective method which can solve almost all the existing problems faced by EVs. In the past few years, researchers have been increasingly focusing on nanotechnology to find reliable energy sources. For instance, nano-structure silicon for manufacturing anode in lithium-ion batteries (LIBs) to have shorter charging time and longer life cycle [1]. Much research shows that nanoscale particles represent significant differences in both physical and chemical properties compared with their macroscale structure [2, 3]. With length scale ~1-100nm, the small size of nanoparticles leads to large specific surface area which allows more energy storage [2]. This property is vital, particularly in cell production. Compared with bulk materials governed by classical Newtonian physics, nanoscale materials are controlled by quantum physics. With the extreme confinement of electrons, the discrete energy levels get quantified, contributing to unique optical and electrical behavior for nanomaterials. This article explores the benefits by applying nano-structured silicon anode and also the challenges facing during manufacture.

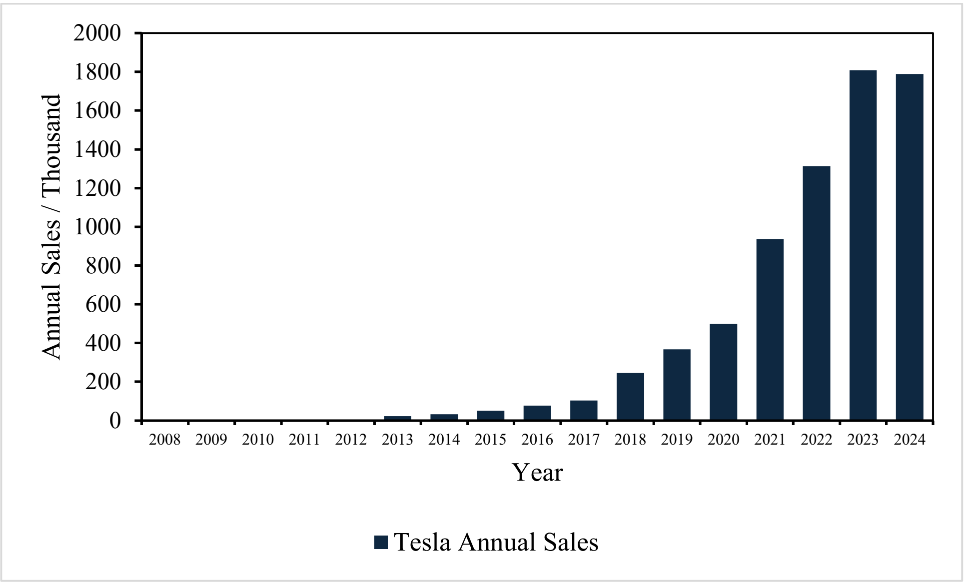

Fig. 1 demonstrates the different sales of Tesla cars from 2008-2024

2. Novel Application of Nano-Structured Silicon Anode in LIBs

2.1 Basic Principles of LIBs

For the increasing demand of more environmentally friendly, economically feasible, and large capacity energy source, LIBs turn to be a wise suggestion. LIBs have been widely used as great power source in laptops, phones, and many other portable electric devices for many years. But there are still many issues for the application of LIBs to the modern society. Among them, low capacity and short life cycle are more severe, if LIBs are considered to be used in EVs.

The charging and discharging mechanism for LIBs is due to the oxidation and reduction of lithium. Lithium atoms from its metal oxides are oxidized to form lithium ions during charging process, the electrons from lithium creating the current. Lithium ions travel through the electrolyte and are accepted by anode waiting for reduction during discharging process. Thus, for the development of a higher capacity LIBs, more acceptance of lithium ions in anode is important. Fig. 2 shows the charging and discharging working principles for LIBs.

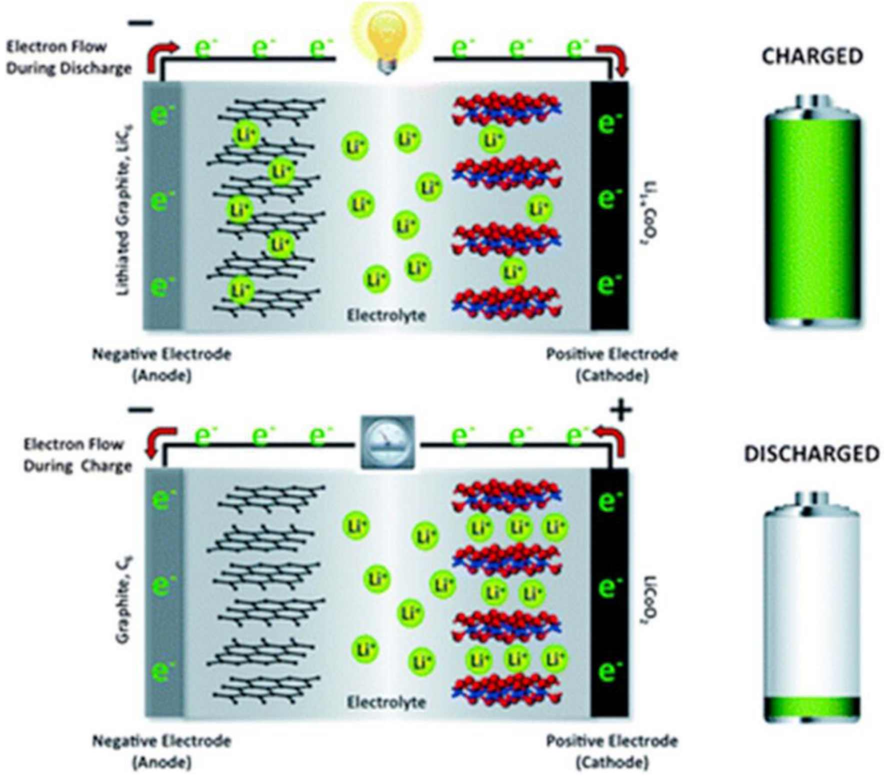

Fig. 2 demonstrates the charging and discharging mechanism for LIBs [4]

2.2 Comparing Graphite Anode with Silicon Anode

In traditional LIBs, graphite comes out to be the most commonly used anode material due to commercial consideration [5]. However, the stoichiometry ratio between graphite and lithium is 6:1 (LiC6), leading to the low efficiency of energy storage (~372 mAhg-1) [6]. Compared with silicon anode which accepts 4 lithium ions to form a fully alloyed form of Li22Si5. This silicon anode meets the highest theoretical capacity of ~4200mAhg-1 which is almost ten times larger than that of graphite [7]. In addition, Si anode shows stable discharge potential ~0.5V, compared with ~0.05V for graphite. This property averts deposition of lithium due to overcharge of cells.

2.3 Challenges faced by Traditional Silicon Anode

While there is a problem for silicon-based anode. The massive intake of lithium ions contributes to the severe volume change of silicon. During the repeating process of lithiation and de-lithiation, loads of stress will be applied on the silicon atom leading to cracking and pulverization [1,8,9]. Finally, the continuous cracking of silicon atoms leading to mechanical failure of anode and fading of the capacity. Apart from that, the massive volume change also causes the broken of solid electrolyte interphase layer (SEI layer) on the surface of the silicon anode. The expose of the fresh anode to the electrolyte leads the formation of more thicker SEI layer and irreversible capacity loss (Longer diffusion distance for lithium ions. Thus, the higher resistance and low conductivity were caused), and the continuous assumption of anode will extremely reduce the life cycle of the battery [1]. Fig. 3 illustrates the cell failure mechanism of silicon and the generation & regeneration process of SEI layer.

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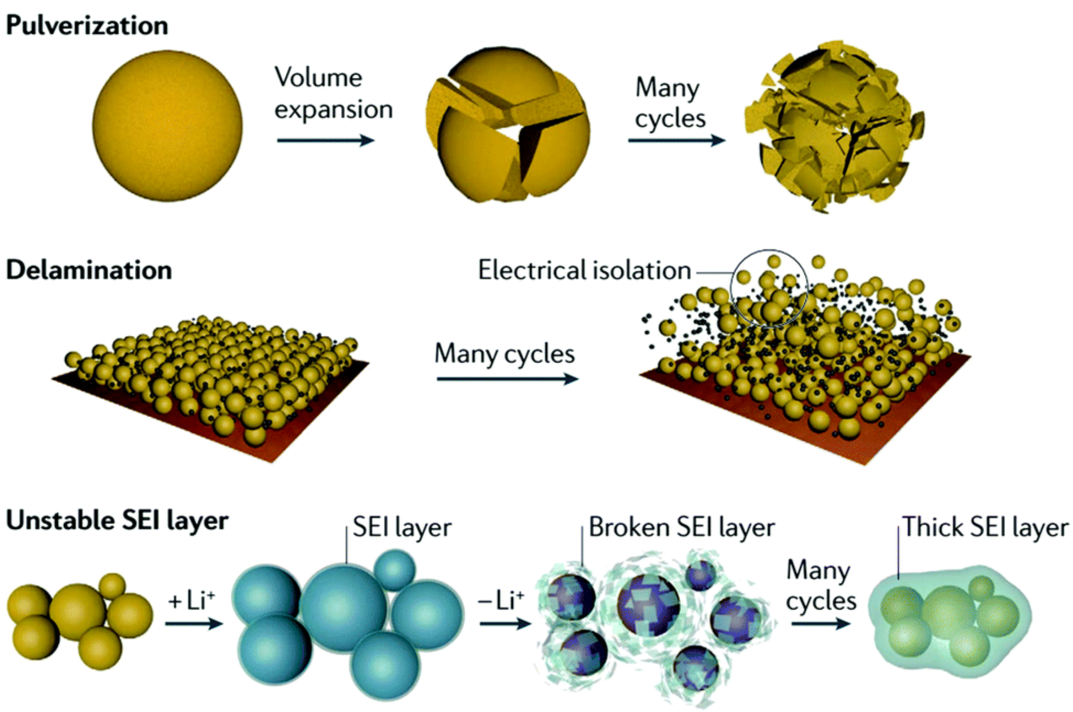

Fig. 3 machoism for the pulverization process of silicon atom and the formation of SEI layer [9]

2.4 Benefits of Applying Nano-Structured Silicon

These situations above are the reasons why nanotechnology has been applied for the silicon anode manufacture. Previous research has proven that nanoparticles show high reversible capacity due to their ability to avoid pulverization tendency [10]. Nano-structured silicon with diameter lower than 150nm will not suffer from cracking anymore [11]. Two kinds of nano-structured silicon, namely silicon nanowires and silicon composites, can be applied and both of them have been proven to have attractive ability for improving LIB performance.

Before turning silicon anode from macro state to nano structure. The change of crystal silicon (c-Si) to amorphous silicon (a-Si) is critical. For crystalline silicon, the atoms are regularly ordered (anisotropic), the pathway for lithium ions is restricted which leads to low conductivity. But in the amorphous structure, different grains are randomly stacked together (isotropic), and each grain has its unique electrical potential. The change of electrical potential between grains gives higher ionic conductivity and faster charging speed for the entire battery system [12]. Research has also proved that a-Si undergoes less volumetric expansion compared with c-Si due to lots of grains and grain boundaries inside the structure [5]. According to the Hall-Petch equation, smaller grains leading to higher tensile strength. During the volumetric expansion, dislocations appear inside the anode structure. Grain boundaries act as barriers to stop the dislocation. Thus, the a-Si is more tolerant to the cracking than c-Si.

Silicon nanowires have attracted lots of researchers for their unique property. One dimensional structure of the Si nanowires allows only one pathway for the transportation of electrons. The particular structure of Si nanowires also offers the opportunity of direct connection with current collector without the help of specific binders. Both of them act together offering faster charging process. Furthermore, the large surface area to volume ratio also accelerates the charging/discharging speed.

Moving on to the Si/C composite, formed by holding a layer of porous carbon around the nano-structured silicon, also offers excellent life cycle for the LIBs. The porous carbon shell around nanostructure silicon accommodates the stress from pulverization of silicon. The voids on the porous shell allow the free movement of lithium ion. Thus, the carbon shell (yolk-shell) structure protects silicon from cracking without influencing the ionic conductivity. What's more, the additional layer of carbon shell between anode and electrolyte protects the anode from overreaction with electrolytes. As the SEI layer will form outside the carbon shell, it has also been protected. It will not be broken and reformed every cycle which offers a uniform and thin layer. Uniform and thin SEI layer formed around the outer carbon shell act as a double barrier to extend the lifespan of cells without influencing the rate of transmission of ions.

3. Application Challenges for Nano-Structured Silicon Electrodes

3.1 Concerns about Mass Production

With the fast innovation brought by nanotechnology, various concerns for the application have also been considered. One of them is mass production. In laboratory, the common method for the conversion from c-Si to a-Si is chemical vapor deposition (CVD). However, this process is slow and costly for the accurate experimental environmental control. The product formed is also in a small amount which is not efficient. For the large scale and more affordable production, the popular way is ball milling of c-Si with citric acid [11]. After the process of spray pyrolysis, Si/C composites were formed. This process is simple, but the quality of the final product is not ideal. Research for better manufacture method or even brand-new approach for greater LIBs with large energy density is still undertaken. Lots of educated people with advanced equipment are needed for the development of nanotechnology. This is a long-term process, and the cost loads of time and money are unavoidable.

3.2 Safety Concerns in Industrial Production

Safety concerns are also significant problems. Nanomaterials like nano-structured silicon, are famous for their high reactivity due to larger surface area to mass ratio. The high reactivity and smaller size create a higher reacting probability between human cells and nanomaterials [13]. Reactive oxygen species (ROS) introduced by nanomaterials are also reported as an important trigger for lung injury [14]. Inhalation of these nanomaterials and ROS during the manufacture process could cause the pulmonary inflammation or even influence the biological function of tissues. Through coating and passivation of human tissue, the cellular uptake function of cell is strongly affected. This leads to the denature of the cell and finally causing cell death. Thus, the smaller size of the material the higher risk of suffering pulmonary diseases. To avoid the risk of nanomaterials exposure to workers. Each nanomaterial should be tested and labeled with their hazardous clearly. Unique protecting methods should be applied to unique nanomaterials. Always wearing gloves, protecting clothes and efficient respirators is one of the good ways to reduce the direct contact between human bodies and nanomaterials. Detecting devices should be equipped inside each room of the industry to alarm any possible contamination.

4. Conclusion

Nanotechnology is rapidly reshaping the future of EVs by offering innovative approaches. Especially in enhancing the battery performance. Nano-structured silicon shows high energy capacity, excellent lifespan, stabler SEI layers after introducing composites and its plentiful resources. With the construction of nanowires and nano-structured silicon composites, both demonstrate their unique advantages making silicon anode more suitable for LIBs.

However, with the continuous growth of nanotechnology industry. A set of challenges have also been brought. Safety concerns for human exposure with nanoparticles, especially during the process of manufacture and disposal must be carefully accessed. Additionally, the development and implementation of novel nanomaterials requires educated people with long-term research and experiments. Maintaining consistent quality during large-scale production, as well as addressing recycling and environmental concerns, remain critical hurdles. Challenges are inevitable, especially for every novel invention. But the exceptional properties of nanomaterials justify the effort to overcome these challenges. The nano-structured silicon anode and its composite will undoubtable shape the next generation of LIBs, and even for the innovation of EVs. Nanotechnology is not just a tool; it offers the opportunity for creating a more sustainable and environmentally friendly future.

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