

# Rational Design of Nanoelectrodes for Highly Efficient Lithium-Ion Batteries

Yizhou Gu\*

University of California Santa Barbara, Santa Barbara, United States

\*Corresponding author: yizhou\_gu@ucsb.edu

**Abstract.** Li-ion battery is a very promising market. Researchers and scientists are trying to improve further the function of all Li-ion batteries on the account that they still cannot meet the customers' requirements and may not be as competitive as the internal combustion engine on traveling distances. The Nanotechnology application of Li-ion battery electrodes affects the general performance such as capacity, energy density, charging and discharging speed, etc. At the atomic scale, the pulverization problem caused by lithiation also limits the growth of batteries. Nanotechnology may be one of the solutions because the strain the material can sustain at the nanoscale is extremely large. The working mechanism of Li-ion helps to have an overall understanding of how batteries work. Replacing graphite with silicon can greatly enhance the battery's performance, but there are still some problems with replacing the electrode material. There are three different types of applications of nanotechnologies that can solve the problems like pulverization: 0D nanoparticles, 1D nanowires, and 2D nanofilms. Nanotechnology is no longer at a laboratory scale and has taken part in the mass production industry.

**Keywords:** Li-ion battery; electrodes; nanotechnology.

## 1. Introduction

### 1.1. Background of Electrification

The world is suffering a large amount of greenhouse gas emissions from burning fossil fuels. Burning fossil fuels provide energy. It is noticeable that in the past century, the vast majority of the facilities in our house are powered by steam or using coals. Most of the lamps are ignited oils. However, with the development of technology, most of the facilities inside our house are powered by electricity. This is a spreading trend that is happening to the world, including factories and vehicles. If energy resource like fossil fuels is replaced by electricity, a large amount of pollution can be avoided.

Electrification of vehicles is one of the most important regions that people are looking at. As reported by the United States Environmental protection agency, greenhouse emissions from transportation account for about 27 percent of total U.S. greenhouse gas emissions, the largest sector of U.S greenhouse gas emissions [1]. Obviously, with the electrification of vehicles, many emissions can be reduced, which is one of the most important reasons scientists are trying to explore and develop the electrification of vehicles.

### 1.2. Problems and Main Challenges of Electrical Vehicles

Electrical vehicles are developing rapidly, but there are also some problems. The first problem is safety. Most of the batteries use group 1 elements – alkali metals. Themselves are very reactive elements. It is in group 1 alkali metals of the periodic table. It is extremely rare to find pure forms of alkali metals naturally. The  $2s^1$  electron for alkali metals can be easily lost, making them a strong reducing agent [2]. Take lithium as an example; when lithium is exposed to the air, it will react with nitrogen, carbon dioxide, and oxygen to form lithium nitride, lithium carbonate and lithium oxide. It is noticeable that the reaction of lithium and oxygen is combustion, which is extremely dangerous when it happens on electrical vehicles (EVs). As a result, the application of alkali metals is often in its compound form.

The second problem will be traveling distance or, in other words, energy density. Lithium ion is not the most reactive compared to other alkali metals like sodium. However, it has the highest energy density. Since lithium ion is at the top of the group 1, it only has 2 electron shells, making it extremely small. As a result, Lithium-ion (Li-ion) battery has the highest capability of handling high voltage and charge storage per mass and volume. But even though the lithium battery has the highest energy densities compared to any battery today (100-265 Wh/kg or 250-670 Wh/L), it is not enough to satisfy customers' traveling distance needs [3].

The third problem will be charging speed and lifecycle. Although the average operating time of EV batteries is 14.7 years, the customers are still worried about the expense of exchanging the batteries in the future [4]. Their concerns are mainly contributed by the preference of choosing a date in the advertisement by the car manufacturers. Charging speed is another problem. It takes Tesla Model X roughly 7 hours to be fully charged from 0% to 100% compared to internal combustion engine cars. That is a big disadvantage. It means a limitation of traveling and potential problems when the car is out of power.

### 1.3. What is the 'Life Cycle of Battery'?

As the battery is being charged and discharged, its capacity decreases. The life cycle of a battery means the number of charges and discharge processes a battery can have before it loses its function. There is no general agreement on when the battery can be defined as 'low function'. Usually, when the battery cannot reach 80% of its capacity, it is already underperforming, and the rest of the cycles cannot be considered anymore. A new concept is taking part—Depth of Discharge (DOD). For example, if a 5000 mAh battery is discharged to 2500 mAh, 50% of its capacity is lost so the DOD will be 50%. However, this is indeed a tricky part. Most manufacturers assess their batteries with 80% DOD. A full charging and discharging cycle are also tested with 80% DOD. However, the customers do not have this information, so they will fully discharge their EVs and charge them back, which may damage the battery and the life cycle of the battery will be significantly less than the data provided by the manufacturer [5].

## 2. Working Mechanism of Lithium-Ion Battery

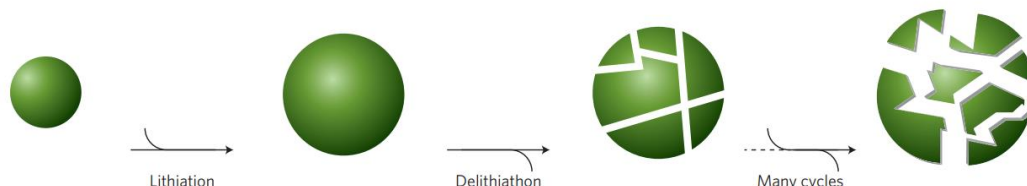
The battery comprises electrolyte, anode, cathode, anode, negative current collector, and positive current collector. The cathode is made of metal oxide, and the anode is made of graphite. Both of them can store Lithium ions and electrons. When an external power supply is applied, the electrons in the metal oxide will move to the positive current collector, be transported to the negative current collector, and be stored in the anode. The lithium will also be repelled and transported by the electrolyte. There is a separator between the cathode and anode, which only allows lithium ions to pass through. When the temperature is too high, the electrolyte will be burnt. All the lithium ions will be crushed into the cathode the battery can be on fire. This separator can prevent the explosion or being on fire. A reverse process will happen when discharging, and lithium ions return to the cathode from the anode. Electrons will also return to the cathode through the external circuit [6].

### 2.1. Replacing the Graphite Anode with Silicon Anode

For Li-ion batteries, the Li-ions will be stored on the anode after charging and move back towards the cathode while discharging. The number of Li-ion stored on the anode largely determines the capacity of the batteries. The Li-ions will be stored at the center axis of a 6-carbon ring and between each layer for the usual cathode material- graphite. Electrons are stored at the center axis of the 6-carbon ring but instead stored between the layers. They are stored in the layer at the same plane as the carbon atom layer [7]. So, Li-ions are adsorbed per 6 carbon atoms, which gives it up to 372 mAh/g capacity. However, silicon is much beyond this value since each silicon can exceed 3.75 Li-ions and reach 3600 mAh/g capacity. This is one scale more than the value of graphite. But there is

an issue caused by this high capacity. The process of bonding silicon with Li-ion is called lithiation. During lithiation, the volume of the anode will be up to three times larger than the original value. Additionally, the volume will return to the original during the discharging process. As a result, it expands and shrinks each life cycle. Finally, result in a crack of the anode and pulverization of the anode ultimately.

Material pulverization



**Fig. 1** Pulverization of the particle [8]

Electrode failure

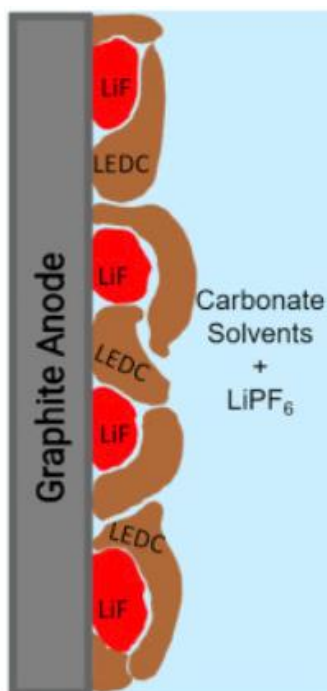


**Fig. 2** Pulverization of the Electrode [8]

As a result, many researchers focus on reducing the pulverization effect and improving the life cycle. The nanoscale is indeed one of the focuses.

### 2.1.1 Advantages of Li-ion battery

As aforementioned in Section 1, the high energy density is an advantage of lithium batteries, which can increase the capacity and life cycle. Additionally, the functioning voltage of the Li-ion battery is quite high compared to the other batteries, which can be up to 4.2 V, while all the others are only half the value or 1/4 of the value. So, a large amount of current can be delivered. Additionally, Li-ion has no memory effect, which is a significant benefit compared to the other types of batteries. There is no poisonous containment. This makes it easier to deal with in manufacturing and dispose of. All these factors make Li-ion stand out in the market and take the vast majority of the market in the past few years [3].



**Fig. 3** SEI layer [9]

Additionally, the Solid electrolyte interphase SEI layer is easily formed on the surface of the anode during the first charging cycles. It is like a passivation layer that inhibits further decomposition of the anode, resulting in more lifecycles and increasing the Li-ion batteries' performance [9].

### 2.1.2 Disadvantage of Li-ion battery

The performance or capacity of the Li-ion battery drops dramatically when it is completed, discharged or overcharged. To achieve this, an additional circuit should always be inside the battery to avoid those two circumstances. Like all the other batteries, aging is also the main problem for Li-ion batteries. This limits their life cycle, limiting the performance and age of the device. Price is also a problem. The cost to manufacture a li-ion battery is much higher than all the other batteries. The data I gathered is roughly 45% more than nickel-cadmium batteries. This may prohibit its application in some industries with a low-profit percentage [3].

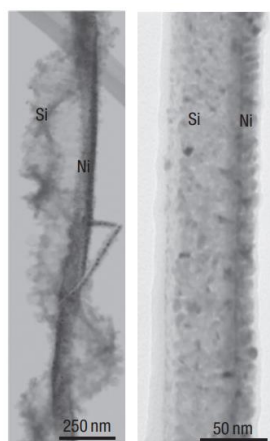
## 3. Application of Nanotechnology

There are indeed other methods like combing silicon with other materials like carbon to make the anode. But the amount of Li-ion that can be stored or charged into silicon anode is much higher than all the other elements. Researchers indeed find the solution to maximize the amount of lithium by using nanotechnology. Indeed, when the size of the particles decreases, they can sustain a higher amount of stress. If the silicon is reduced to the nanoscale, such as silicon nanoparticles or nanowires, it can withstand higher mechanical stress and avoid the pulverization effect [7].

### 3.1. 0D Nanoparticles

There are various types of nanoparticles like the most common spherical shape, cubic shape, tetrahedral shape, pyramidal shape, icosahedral shape, pyramidal shape and so on. They can be manufactured physically, chemically, or biologically to control these shapes. Electron beam lithography can be applied to reduce bulk material into powers and further into nanoparticles. Nanoparticles will behave differently and perform unique properties according to the charge, polarity, and other factors. Their shapes are controlled by adding different additives such as ligands (amines), polymers and hydrophobicity/hydrophilicity. Since their will affect the formation of coordinative bonds. By experimenting, specific additives cause coordinate bonds to accumulate on several parts of the nanoparticle instead of accumulating at the same speed. The rate of growth difference results in the formation of different shapes [10].

### 3.2. 1D Nanowires



**Fig. 4** Nanowire before and after lithiation [11]

Nanowires have a similar function as nanoparticles, increasing the battery capacity massively without damaging the electrode. Additionally, researchers found that the length of the nanowires will extend during lithiation. They made an experiment to evaporate 25-nm Ni upon the nanowire. During

lithiation, the Nanowires roll up the Ni in 3D. It is because of the strain between the Ni and the nanowire. The nanowire does not grow freely but wraps into a helical shape. The small diameter enhances the strain that those nanowires can sustain. To grow these kinds of nanowires, the basic function is the same as growing different shapes of nanoparticles. The catalyst is placed at one end of the nanowire, so it becomes a more favorable site for crystallization and adsorption. The growing direction and diameter of the nanowire can be defined then.

### 3.2.1. Nanowires application on Li-ion battery electrodes

Each nanowire is directly connected to the current collector. As a result, the requirement for a binder is eliminated. This also eliminates the separation between the current collector and the electrode. Furthermore, the elimination of the binder reduces the weight of the battery. The 1D transportation route will be from the surface of the nanowires to the center of the nanowire. Surprisingly, nanowires also increase their size in all dimensions instead of mainly focusing on the diameter. It is indeed because of the huge change in the atomic structure during lithiation when charging [11].

### 3.3. 2D Nanofilms

Nanofilms have a range of different shapes. The classical one will be rectangular. However, other shapes are also circular or triangular films [10]. Originally, the bulk film will not perform well under cycling. The lithiation and delithiation break the atomic structure and cause the particles to detach from each other. Finally, result in damage to the whole electrode. So, it tends to pulverize during charging. By reducing the length in one dimension-thickness, the stain that films can sustain is largely improved. During manufacturing, substrates are seeded to make the incoming precursor units form at the same line [10, 11].

#### 3.3.1. Nanofilm application on Li-ion battery electrodes

The nanoscale scale thickness reduces the length for lithiation and decreases the volume-to-surface area ratio. Same as all the other applications of nanotechnology on electrodes. The capacity and energy density are increased dramatically. However, its area increase may not be as large as the nanowire and nanoparticle. Additionally, some scientists try to make holes in the nanofilms, which can further increase the capacity of the Nanofilms. The films have more electrocatalytic sites [10].

## 4. Real Application of Big Companies

### 4.1. Amprius

Amprius takes the lead in the anode manufacturing of high-density Li-ion batteries. It is built upon the research of Stanford University and solved the problem of low-performance silicon nanowire batteries. Instead of keeping the silicon nanowire batteries at the experimental level, it is keen on bringing them to real-world application.

#### 4.1.1 More data about the evolution of campus battery

##### 320 Wh/Kg EV BATTERY CELL

Amprius 320 Wh/Kg (680 Wh/L) EV battery cells have over 1400 cycles at 100% DOD (4.2-2.5 V) charge and discharge at 25 degrees and 1000 cycles with >80% capacity retention at 45 degrees. The cycles were achieved without clamping. This cell supports 3C discharge with 94.5% capacity retention based on its 0.2 C discharge capacity and fast charge rate of 15 mins to 80% SOC. The cell can also sustain 90-day 100% SOC (4.2 V) storage at 60 °C and >80% discharge capacity retention at -20 degrees.

##### 350 Wh/Kg EV BATTERY CELL

Amprius 350Wh/Kg (800Wh/L) EV cells currently have over 700 cycles at 100% DOD (4.2-2.5 V) charge and discharge at 25 °C and 500 cycles of 100% DOD with >80% capacity retention at

45 °C. Again, the cycles were achieved without clamping. 350Wh/Kg EV cells also displayed excellent performance in rate capabilities, 60 °C and 30-day storage and -20 °C discharge.

**Table 1.** Milestones and Timing of Amprius [12]

Jan-16	Milestone/Deliverable: More than 750Wh/l energy density and more than 350Wh/kg specific energy, DST life is more than 750.	Complete
Jan-17	Milestone/Deliverable: More than 850Wh/l energy density and more than 400 Wh/kg specific energy	Complete
Jul-17	Milestones: Achieve $\geq 850$ Wh/L, $\geq 400$ Wh/kg and $\geq 1,000$ cycles in a $\geq 2$ Ah cell Achieve $\geq 875$ Wh/L, $\geq 415$ Wh/kg and $\geq 850$ cycles in a $\geq 10$ Ah cell Achieve $\geq 850$ Wh/L, $\geq 400$ Wh/kg and $\geq 750$ cycles in a $\geq 40$ Ah cell	Partially complete
Sep-18	Deliverable: Deliver 30 pouch cells with a capacity $\geq 40$ Ah, energy density $\geq 937.5$ Wh/L, specific energy $\geq 437.5$ Wh/kg, and DST cycle life $\geq 1,000$	On track

These data from Amprius show the evolution of the silicon nanowire battery cycle life. Originally, in Jan 2016, its cycle life was less than 750. At that time, those nanowire batteries from Amprius are probably as good as the normal 18650 Li batteries in life cycles. However, from the attachment above, Si nanowire batteries' cycle life is rapidly revolutionizing. In Jan 2017, it was significantly better than a normal Li-ion battery. In some of the recent updates by Amprius Nanjing, it has over 1400 cycle life at 100% DOD (4.2-2.5 V) 25 degrees. Those silicon nanowire batteries have better overall performance now since the specific energy is much higher than the other batteries [12].

## 4.2. OneD Battery Sciences

It is one of the few manufacturers that successfully commercialized the production of Nanowire batteries. They are concerned about the technical drop-in for businesses and the business drop-in. Technical drop-in means the following: The anode material has to meet the requirements of EV factory acceptance criteria (impurities; batch to batch variations; BET; etc.) currently used in Tier 1 factories. The electrode designing specifications can be met with the existing commercial binders, conductive additives, electrolytes, separators, and cathodes in all-electric vehicle cell formats. Business drop-in means the following: The existing suppliers can be leveraged. The electrode and cell costs are reduced. The technology is patent protected and has reasonable assurance of freedom to use [13].

### 4.2.1 More about their technology

In order to meet their business strategy, they choose to improve the battery's performance and participate in the industrial chain. They are using the technology of growing nanowires upon the graphite electrode to fill the defects of the graphite. Filling the defects can decrease the surface-to-volume ratio since the upper sides of the nanowires form an even layer. The diffusion route of the electrons is also reduced, resulting in a higher charging speed. The volume, in general, increases because the nanowire layer grows upon the electrodes, so more electrons can be stored in the electrode. As a result, the energy density of the electrodes increases as well [13].

## 5. Conclusion

Back then, the nanowire batteries may not be as good as normal 18650 Lithium-ion batteries on life cycles. However, the cycle life of nanowire batteries is rapidly revolutionizing. Some recent

updates published by Amprius Nanjing are over 1400 cycle life at 100% DOD (4.2-2.5 V) 25 degrees. With the development of nanotechnology, the production of Nanoelectrodes Li-ion batteries can likely be commercialized and put into mass production. Silicon is an ideal product since it may take the battery's capacity to another level. However, the pulverization problem limits its development. Nanotechnology helps solve this problem because the material at the nanoscale can withstand more changes in its shape during lithiation. Like arranging material in an S shape, its tensile strength is promoted.

However, the big graphite market needs to be considered because of the market value. The solution provided by OneD battery is applicable since it becomes of the graphite market and successfully improves the battery's overall performance to a quite large scale. Except for the product by OneD battery, all the other products are still at their experimental level. Much more work is required to move to the industrial level since many problems will be produced when the scale increases. The nanowire battery industry has just started, but this market has much potential. The huge increase in capacity may also influence the pace of electrification of the whole world.

## References

- [1] EPA. Transportation and Climate Change. United States environmental protection agency, 2020.
- [2] Katherine Szelong (UCD), Kevin Fan. Chemistry of Lithium. Chemistry Libretexts, 2020
- [3] Institute, University of Washington Clean Chemistry. Lithium-ion Battery. University of Washington, 2022.
- [4] Storage, Circular Energy. The lithium-ion battery life cycle report, Circular Energy Storage Research & Consulting, 2020.
- [5] Energy, Dragonfly. What Is a Battery Life Cycle? dragonflyenergy.com, 2021
- [6] Energy, Office of Energy Efficiency & Renewable. Lithium-ion battery, How does it work? Office of Energy Efficiency & Renewable Energy, 2017.
- [7] Richardson, Melodie, Increasing battery capacity, 2020.
- [8] Prof. Colm Durkan, Nanotechnology & Electric vehicles technologies, University of Cambridge Department of Engineering.
- [9] Monday, Battery. What is the SEI, and what effect does it have on the battery? | Battery Monday. Grepow Blog, 2021.
- [10] Advances in and prospects of nanomaterials' morphological control for. Ayman A. AbdelHamid, Adriana Mendoza-Garcia, Jackie Y. Ying, 2022, 96: 2-14.
- [11] High-performance lithium battery. Candace K. Chan, Hailin Peng, Gao Liu, Kevin, Mcilwrath, Xiao Feng Zhang, Robert A. Huggins, Yi Cui. Nature Nanotechnology, 2007, 3: 31-35.
- [12] (Nanjing), Amprius. HESO Anode Materials System Enables High Energy Density EV Batteries. Nanjing: Amprius (Nanjing), 2021.
- [13] The limiting factor, Low-Cost Silicon Nanowire Coated Graphite for OEMs, YouTube, 2021.