

The Rate Capability Limitation in High-Energy-Density Lithium-Ion Batteries: Origins and Mitigation Strategies

Chenming Wu *

School of Mechanical Engineering, University of Leeds, Leeds, England

* Corresponding Author Email: WD3079272427@outlook.com

Abstract. In the development of electric vehicles, the advancement of batteries is undoubtedly the most crucial aspect. There are two key indicators that are particularly important for the use of batteries, namely energy density and charging rate. They correspond respectively to the driving range of electric vehicles and the charging time. An excellent battery must possess both high energy density and high charging rate. However, electrode materials that provide high energy density (such as high-nickel positive electrodes and silicon-based negative electrodes) often come with poor rate performance and cycle stability. This leads to problems such as high temperatures during charging or short battery lifespan. This paper systematically analyzes the limiting mechanisms of each component of the battery (with a focus on the positive and negative electrodes) on rate performance, and reviews the latest material-level and system-level improvement strategies. Finally, it summarizes the advantages and disadvantages of existing technologies and looks forward to possible future research directions.

Keywords: Lithium-ion battery; high energy density; fast charging; electrode material; interface dynamics.

1. Introduction

Nowadays, the huge number of electrical vehicles (EVs) plays an important role during control of greenhouse. And the number of EVs is increasing rapidly. IEA's data shows that the global sales share of EVs has soared from about 4% in 2020 to 18% in 2023. One of the limitations of EVs is the battery [1]. The market is dissatisfied with the endurance mileage and charging rate of EVs. Then the energy density and charging rate need to be improved.

The current mainstream lithium-ion batteries' basic working principles are Embedding and Detaching Reaction [2]. In the battery, lithium-ion will move to the anode from cathode through separator and electrolyte when charging (during discharge, it is the opposite). While electronics cannot pass separator, electronics flow through external circuits to form the current.

Energy density refers to the total amount of electrical energy that can be stored in a unit volume or unit mass. It represents how many lithium-ion can move to the anode from cathode during a whole charging or discharging process. The higher energy density a battery is, the longer endurance mileage a EVs can be with the same volume as the battery. Charging rate refers to the speed at which a battery absorbs or releases its full capacity. It represents how fast lithium-ion can move to the anode from cathode. However, high energy density electrode materials (such as high-nickel ternary positive electrodes and silicon-based negative electrodes) often have chemical and physical structures that are not conducive to the rapid insertion and extraction of ions, resulting in a low charging rate. While high charging rate electrode materials (such as lithium iron phosphate positive electrode and lithium titanate negative electrode) have structures that can support the rapid transmission of ions, but they often store less energy per unit mass/volume, meaning their energy density is relatively low [3]. One of the core goals in modern battery research is to overcome this trade-off by means of material innovation (such as nanotechnology, coating, doping) and system optimization (such as battery thermal management, intelligent charging algorithms), in order to achieve batteries that simultaneously possess high energy density and high charging rates.

This article discusses the functions of different parts of battery and how they hinder the development of batteries. And exploring different materials of anode, cathode and separator. Besides, looking forward to possible future research directions.

2. Lithium-Ion Battery Components and Impact on Overall Performance

A battery consists of many components, among which the anode, cathode and separator play a decisive role in the energy density and charging rate of the battery. This section will briefly explain the roles of different components of the battery during charging and discharging and discuss their respective impacts on the overall energy density and charging rate of the battery.

2.1. Anode

Anode is the negative pole of the battery during discharging. And made from active substances, conductive agents and binders are mixed and then coated onto the current collector (which is usually a copper foil). Anode is the receiving end of lithium-ions during discharge. During the charging process, lithium-ions are released from cathode, pass through electrolyte and separator, embedded into the layered structure of the anode material (such as graphite). Additionally, during the first charging process, the negative electrode surface reacts with the electrolyte to form a protective film (solid electrolyte interface, SEI film). This film can prevent the continuous decomposition of the electrolyte in the subsequent charging process, but it also consumes some lithium ions, resulting in irreversible capacity loss [4]. Otherwise, the ability (kinetics) of the negative electrode material to accommodate lithium ions directly determines whether a battery can be charged quickly. Inappropriate fast charging can lead to the precipitation of lithium metal on the surface of the negative electrode (lithiation), forming dendrites that pierce the separator and cause short circuits, thereby posing safety risks.

2.2. Cathode

Cathode is the positive pole of the battery during discharging. Also made from active substances, conductive agents and binders are mixed and then coated onto the current collector (which is usually an aluminum foil). Besides, cathode is the storage source of lithium-ions, which determines the voltage and capacity of the battery (the key to energy density). However, most current cathode materials are lithium-ion compound and a reduction reaction occurred when discharging [5]. Lithium-ions and electrons are released from cathode material during reduction reaction. The potential difference between cathode material and anode material determines the voltage of the battery. There are different working voltages of different anode material. Furthermore, the ability of the cathode material to reversibly incorporate and extract lithium ions is one of the main limiting factors for battery capacity. Thus, the specific capacity and voltage of the positive electrode material are the core parameters for calculating the quality energy density of the battery [6].

2.3. Separator

Separator is a porous insulating film placed between the positive and negative electrodes, usually made of polyethylene or polypropylene materials. Its main function is to physically isolate the positive and negative electrodes, preventing them from coming into direct contact and causing a short circuit. At the same time, its microporous structure allows lithium-ions to pass through freely. Besides, the porous structure of the diaphragm can absorb and retain the electrolyte, ensuring smooth ion transmission. When the battery temperature is too high, the separator material will melt and close the micropores, thereby blocking the ion transmission and stopping the battery reaction. This is an important safety protection mechanism, called thermal insulation effect of closed pores.

2.4. Electrolyte

Electrolyte is a medium in a battery that plays the role of ion conductivity. It is a liquid formed by dissolving lithium salts in an organic solvent. In liquid-state lithium-ion batteries, it penetrates the positive electrode, negative electrode and separator, and fills all the pores within the battery. And as the organic solvent, to dissolve the lithium salt and provide a transmission channel for lithium ions. In addition, a small amount of additive is added to significantly improve a specific performance.

2.5. Current Collector

The current collector is a metal foil that covers the layer of electrode active material. The positive electrode uses aluminum foil, while the negative electrode uses copper foil. The main function is to collect the current generated by the electrode active substances and conduct it to the external circuit. Conversely, during charging, the external current is uniformly conducted to the active substances. It also provides mechanical support for the fragile electrode material coating. In current lithium-ions battery, aluminum foil is usually used as the current collector for the anode because aluminum forms a dense oxide layer at the high potential of the positive electrode, which ensures stability and makes it less prone to oxidation and corrosion. Moreover, the current collector of cathodes usually uses copper foil, because copper is stable at the low potential of the negative electrode and has good conductivity. Aluminum, on the other hand, will form an alloy with lithium at low potential and is therefore not suitable for use as the negative electrode current collector.

2.6. Packing

Packing is the process of housing all the internal components of the battery (electrodes, separators, electrolyte) and providing a protective outer shell that isolates them from the external environment. It encapsulates the internal components into a single unit to prevent the leakage of electrolyte, the intrusion of external moisture, air or other impurities. Providing structural strength is one of the functions of packing, to protect the fragile internal battery cells from external mechanical shocks and pressures. If there is not extra heat dissipation, packing transfers the heat generated inside the battery to external environment as part of the heat dissipation. Packing is usually externally insulated to prevent electric shock. At the same time, a safety valve is equipped (especially in cylindrical and square hard-shell batteries), which will release pressure when the internal pressure abnormally rises, preventing explosion.

3. Mechanism Analysis of Rate Performance Limitation of High Energy Density Electrodes

In electrochemical batteries, interface kinetics refers to the rates and difficulties of a series of complex processes that occur at the interface between the electrode material surface and the electrolyte. Its essence is the process of charge transfer and material transformation. This section will explore the process of lithium ions entering the electrode material from the electrolyte and the influence of high energy density materials on interface kinetics.

Lithium ions do not "run freely" in the electrolyte. They are surrounded by a layer of solvent molecules (such as EC, DMC), forming a "solvent shell". To reach the electrode, they must first break free from this solvent shell when a lithium ion moves from the electrolyte to the electrode material (the opposite occurs during discharge). This step requires energy consumption and is a major bottleneck during high-speed charging, also called desolvation.

Then whether it is the SEI (solid electrolyte interface membrane) on the negative electrode or the CEI (cathode electrolyte interface membrane) on the positive electrode, lithium ions must pass through this protective layer. The ion conductivity and thickness of this layer directly determine the ease with which ions pass through. After that is the most important electrochemical reaction step, charge transfer, At the electrode/ electrolyte interface, lithium ions gain or lose an electron, transforming from "ions" to atoms (when being inserted), or vice versa. The speed of this reaction is measured by the charge transfer resistance. For the last step, interface diffusion, lithium ions/atoms may first

undergo a brief two-dimensional diffusion on the electrode surface, searching for suitable embedding sites, before entering the electrode matrix [7].

By analyzing the movement process of lithium ions through interface dynamics, important factors affecting battery performance can be identified. During high-rate (high-current) charging or discharging, a large number of lithium ions pass through simultaneously within a very short period of time. If any step in the interface, especially the desolvation and charge transfer processes, is too slow, the ions will accumulate at the entrance. Therefore, in order to maintain high current, the system must apply a greater voltage to "push" the ions through this slow channel. This will result in an increase in charging voltage, a decrease in discharging voltage, and thus cause energy efficiency loss and heat generation. Additionally, at the negative electrode, if Li^+ cannot enter the graphite in time due to blockage, it will directly obtain electrons and release as metallic lithium (lithium dendrites), thus posing a risk of short circuits. Moreover, excessive voltage will cause the electrolyte to decompose on the electrode surface, making the SEI/CEI membrane thicker, consuming active lithium and electrolyte, and thus leading to a permanent reduction in capacity [8].

In the present EVs designing, high energy density is regarded as the first one. However, high-energy-density materials often come at the expense of interface dynamics. One of widely used anode material, High-nickel NMC, the surface of it is unstable and will react vigorously with the electrolyte, forming a thick and uneven CEI film [5]. The ionic conductivity is poor, hindering the transmission of Li^+ [6]. Similarly, at high potentials, structural phase changes and oxygen release are prone to occur, which further catalyze the decomposition of the electrolyte and increase the interface impedance [9].

Furthermore, cathode material's volume expands and contracts by 10%-300% [9]. This will continuously damage and tear the original SEI membrane. The freshly exposed silicon surface will continuously react with the electrolyte to form a new and thicker SEI film. This process will continuously consume lithium and electrolyte, resulting in a continuous increase in interface impedance and a gradually blocked ion channel.

4. Improvement Strategies and Research Status for Enhancing Resolution Performance

Shortage of materials, high costs, significant pollution and difficult processing have all hindered the development of electric vehicle batteries. However, the rapid advancement of nanotechnology in recent years has brought about new breakthrough directions. This section will separately explore new materials for the three key components - the positive electrode, the negative electrode, and the separator. And it will also analyze the feasibility of these new materials.

4.1. Anode

For the anode material, the volume changes during charging and discharging lead to particle pulverization, electrode structure damage, and unstable solid electrolyte interphase membrane (SEI), making it difficult to achieve both high performance and safety. A silicon-carbon composite negative electrode material with porous and carbon-coated layers is expected to solve these problems. Researchers were inspired by the resilient structures in nature and adopted a "bottom-up" hierarchical design strategy to prepare this material [10].

The core design concept of this improvement scheme is to reserve buffer space for the volume expansion of silicon and construct an efficient and stable conductive network. Specifically, the researchers used a chemical vapor deposition method to uniformly coat a layer of carbon on the surface of the porous silicon clusters formed by the self-assembly of silicon nanoparticles. This design achieves multiple functions: the internal porous structure provides valuable internal space for the volume expansion of silicon during lithiation, greatly alleviating macroscopic mechanical stress and structural deformation, and preventing electrode rupture. The external continuous carbon coating layer forms a strong and highly conductive shell.

This carbon shell is crucial: first, it efficiently connects all silicon nanoparticles, forming a three-dimensional electron conduction network, significantly improving the conductivity of the electrode; second, it acts as a physical barrier, separating silicon from the electrolyte, helping to form a thinner and more stable SEI membrane, reducing the continuous consumption of active lithium and electrolyte; third, it effectively constrains the silicon nanoparticles together, maintaining the structural integrity of the composite particle even if the internal silicon expands or contracts.

After 100 cycles at a 0.5C rate, the reversible specific capacity of this composite material still remains at approximately 1950 mAh/g (based on the total mass of the silicon-carbon composite), with a very high-capacity retention rate. What is more notable is that its mass-specific power (power density) reaches 5 to 10 times that of silicon-based negative electrodes reported in the literature, demonstrating excellent rate performance. This work combines the high-capacity advantage of silicon with the stability and conductivity advantages of carbon materials through exquisite micro-nano structure design, providing a highly valuable blueprint for the development of next-generation high-performance lithium-ion battery negative electrodes.

4.2. Cathode

The existing cathode materials, high-pressure spinel nickel-manganese oxide lithium, suffer from poor cycle stability and manganese dissolution issues. However, a new improved solution has been developed through a unique synthesis process, resulting in a microsphere-shaped, aluminum-doped, and surface-coated with zirconium oxide $\text{LiN}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material [11].

Firstly, the researchers synthesized a precursor with a microsphere morphology, eventually obtaining secondary microspheres formed by the agglomeration of nano-primary particles. This structure has two advantages: Firstly, the nano-sized primary particles significantly shorten the diffusion path of lithium ions, enhancing the material's rate performance; Secondly, the micrometer-sized secondary spherical structure provides a higher compaction density, facilitating the improvement of the electrode's volumetric energy density and enhancing the material's processing performance.

More importantly, the researchers carried out synergistic modification of the bulk phase and interface. Aluminum doping entered the material's crystal structure, effectively stabilizing the spinel framework and inhibiting phase transformation and lattice distortion during charging and discharging, thereby enhancing the structural stability at the bulk phase level. At the same time, the zirconium oxide coating on the material's surface played a crucial role. This inert and robust protective layer directly isolated the active material from the electrolyte, significantly inhibiting electrolyte catalytic decomposition under high pressure (especially $> 4.5 \text{ V vs. Li/Li}^+$) and manganese element dissolution loss.

The key data strongly support the improvement effect: At a high-temperature condition of $55 \text{ }^\circ\text{C}$, the unmodified LNMO material showed a sharp decline in capacity retention rate to approximately 58% after 100 cycles. While the samples with synergistic modification (Al-doped and ZrO_2 -coated) demonstrated excellent stability, with a capacity retention rate of up to 89%. Moreover, at a high current density of 10C, the modified material still released a considerable capacity of approximately 100 mAh/g, far superior to ordinary materials, demonstrating its excellent fast-charging capability. This work profoundly indicates that through the "combination punch" strategy of morphology design, bulk doping, and surface coating, it is possible to collaboratively solve the inherent problems of high-energy-density cathode materials from multiple dimensions, which is an effective way to realize its commercial application.

4.3. Separator

The separator material requires a certain thickness to prevent lithium dendrites from piercing and causing short circuits, but increasing the thickness of the separator will also slow down the rate of lithium-ion passage [12]. To address the problems of poor wettability, insufficient thermal stability, and low porosity of commercial polyolefin separators (such as PP/PE), a solution was proposed to

prepare a polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) composite fiber separator using electrospinning technology. This solution made fundamental improvements at both the material and microstructure levels [13].

Firstly, at the material level, PVDF-HFP polymer was selected. The C-F bonds in its molecular chain have extremely strong polarity and have a natural affinity for common carbonate-based electrolytes, significantly enhancing the electrolyte wettability and retention of the separator. The high electrolyte retention directly translates to higher ionic conductivity, reducing the internal resistance of the battery. Secondly, PVDF-HFP material itself has a higher melting point (about 170 °C) and thermal stability, compared to commercial PE separators (melting point ~135 °C), its thermal shrinkage has been significantly improved, thereby enhancing the thermal safety of the battery.

Secondly, at the structural level, electrospinning technology creates a three-dimensional network structure composed of randomly stacked nanometer to micrometer fibers. This structure endows the separator with an extremely high porosity (up to over 80%) and interconnected pore structures, much higher than commercial separators (~40%). The high porosity provides more and more unobstructed paths for ion transmission, further enhancing the ionic conductivity. At the same time, this fiber network structure has a larger specific surface area, capable of adsorbing more electrolyte.

Key data confirm its superiority: The electrospun fiber separator exhibits an excellent electrolyte absorption rate (>250%), with an ionic conductivity of up to 1.5 mS/cm, significantly superior to commercial Celgard separators (~0.7 mS/cm). In thermal stability tests, after 1-hour thermal treatment at 150 °C, the commercial PP/PE separator undergoes severe contraction and even melting and cracking, while the PVDF-HFP fiber separator maintains its size without significant contraction. Based on this separator assembly, the battery shows a capacity retention rate over 15% higher than that using commercial separators after 200 cycles at 1C rate, thanks to its stable interface and continuous efficient ionic transmission capability. This work demonstrates that by innovating traditional battery components through advanced materials and preparation processes, the electrochemical performance and safety of batteries can be comprehensively improved.

5. Conclusion

This article discusses the components of batteries, explains their definitions and functions. It elaborates on the reasons and principles that limit the energy density and charging rate of batteries. During the use of high-rate performance batteries, interface dynamics is a crucial research method. This article describes the process of lithium-ions detaching from the electrolyte and embedding into the electrode materials. Through interface dynamics analysis, the factors affecting battery performance are obtained: the insufficient rate of lithium-ions passing through. This leads to the need to increase the voltage to improve the rate of lithium-ion passage. This results in energy efficiency loss and heating. Moreover, the accumulated lithium ions will precipitate lithium dendrites on the electrode surface, puncture the separator or the packaging, leading to safety issues.

Finally, there are three improvement schemes corresponding. The $\text{LiN}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material for the cathode has a capacity retention rate of up to 89% at high-temperature harsh condition. At a high-rate, the modified material can still release a considerable capacity, the silicon-carbon composite anode for the anode has a high-capacity retention rate. The power density reaches 5-10 times that of silicon-based anodes; likewise, the polyvinylidene fluoride-hexafluoropropylene composite fiber separator remains stable after heat treatment at 150 °C for 1 hour. After 200 cycles at a 1C rate, the capacity retention rate is higher than that of batteries using commercial separators. The rate limitation of high-energy-density electrode materials mainly stems from slow ion/electron transmission and unstable electrode-electrolyte interfaces. The solution requires multi-scale, multi-component collaborative innovation.

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