The design of high-energy-density Li-ion batteries

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Abstract. Future energy storage device research should focus on increasing energy density (ED). Over the past few decades, lithium-ion batteries (LIBs) have been commonly employed as high-performing energy storage systems. Due to the growing demands on the performance of LIBs in terms of size, weight, and energy storage, researchers continue to experiment with various methods to increase the ED of LIBs by adopting battery structures, novel materials, and systems. Before their actual deployment, however, a number of concerns, such as the issue of electrolyte instability under high voltage, still need to be resolved. In order to better understand the design of high ED lithium-ion batteries. This paper focuses on three key areas: compression of the proportion of inactive material, augmentation of the proportion of active materials, and mitigation or compensation of film formation losses of solid electrolyte interphase (SEI). With the development of LIB technology, it is anticipated that in the future, lithium-ion batteries will find usage in more applications, and their future will be even more promising.

Keywords: energy density, design, materials, film formation, lithium-ion batteries.

1. Introduction

LIBs with high ED have become more prevalent as the market for mobile electric vehicles has grown quickly. The ED of ternary lithium batteries is between 200 and 300 Wh/kg, while the ED of common lithium iron phosphate batteries is expected to be less than 200 Wh/kg. The ED of lithium-ion batteries is far from reaching the requirements of major advancements, which restricts the use of numerous scenarios. For unmanned aircraft and other gadgets to travel farther and faster, there must be a major improvement in the energy and power density of batteries.

The first step is to improve the ED of the battery system. This includes the design of high-capacity high-voltage cathodes and high-capacity low-voltage cathodes. The choice of cathode materials will range from lithium cobaltate to lithium iron phosphate, to ternary materials with a high nickel content, and eventually to materials with sulphur and oxygen elements. In the choice of negative electrode materials, from the existing graphite through silicon to lithium metal. However, using high-voltage cathodes and lithium metal cathodes will also present safety concerns that must be addressed before they can be used in practical applications. Some of these concerns include electrolyte instability at high voltage and electrolyte decomposition brought on by the formation of the SEI film during the forming process [1].

The impact of structural and chemical factors on LIBs' ED will be examined in the article that follows. The drawbacks of various materials will be addressed with solutions.

2. Compression of the proportion of inactive substances

2.1. Thick electrode design

The thick electrode design approach can develop the ED of the battery while reducing the cost by significantly increasing the active material loading and decreasing the proportion of inactive components.

As shown in Figure 1(a), considering the three components of electrode, collector and diaphragm, increasing the electrode thickness from 25 μm (active material loading 8 mg/cm^2) to 200 μm (active material loading 64 mg/cm^2) and reducing the ratio of inactive material from 44% to 12% significantly improves the electrode active material ratio and effectively increases the overall battery ED. However, increasing the electrode thickness will lengthen the electron and lithium ion transfer path, which increases the battery impedance, poor battery multiplier performance and electrode reaction kinetics, and a series of problems such as low adhesion strength of electrode coating and easy to fall off. Therefore, when the electrode thickness is increased infinitely, the material utilization rate decreases and the battery ED decreases instead. As shown in Figure 1(b), the electrode thickness needs to be optimised, which is the thick electrode performance improvement opportunity, and Figure 1(c) is the challenge faced by thick electrode [2].

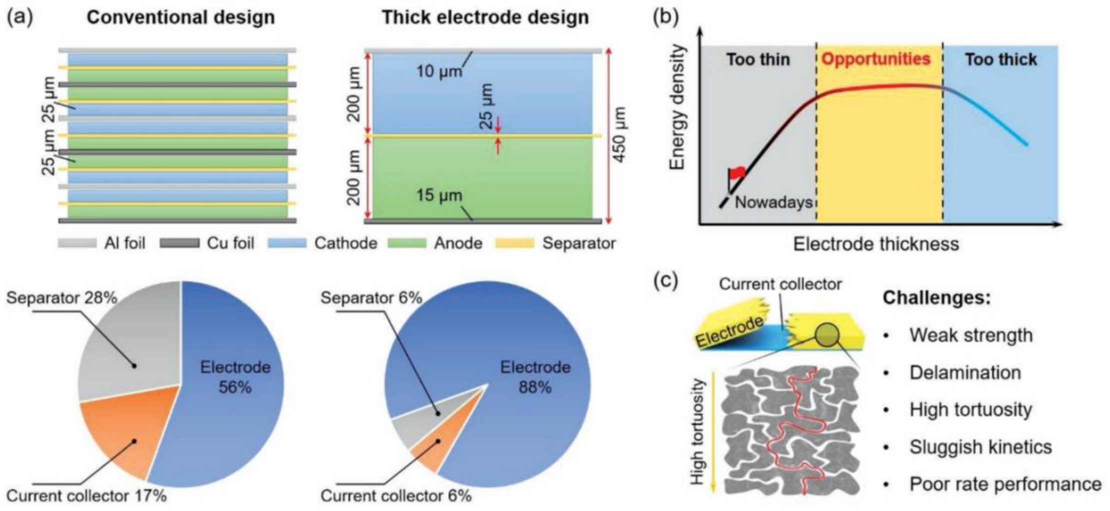

Figure 1. Illustration of the advantages and disadvantages of thick plate design. a) The connection between thick plate and stacked thin plate designs. b) The possibility; and c) the difficulties of thick plate design [2].

2.2. Reduction of the diaphragm thickness

Diaphragms are mainly low-density polypropylene or polyethylene materials, and reducing the thickness is not obvious for reducing the weight of the battery. However, it can increase the amount of active material in the battery and improve the volumetric ED of the battery. The use of functional coated composite membrane can compensate for the degradation of mechanical properties caused by the reduction of membrane thickness. For example, 9 μm polypropylene (PP) base film +3 μm aluminium oxide coated ceramic membrane compared with 12 μm PP film, the membrane surface density increased from 6.1 g/m^2 to 8.6 g/m^2, but compared with 20 μm PP film surface density of 10.2 g/m^2, the weight and thickness of ceramic coated membrane are reduced. At the same time, the electrolyte retention capacity and thermal stability are increased. However, it is not recommended to further reduce the thickness of the diaphragm to improve the ED of the power cell based on the current 9 μm base film, as this will increase the self-discharge rate and safety risk of the battery.

2.3. The electrode binder

The electrode binder plays a crucial role in preserving the electrode's integrity and greatly enhances the battery's specific capacity (SC) and cycle stability. In addition to polyacrylic acid (PAA), polyacrylonitrile (PAN), and polyacrylate, the three primary types of LIB binders that are frequently employed are carboxymethyl cellulose (CMC), polyvinylidene fluoride (PVDF), and styrene-butadiene rubber (SBR) emulsion. Due to its higher polarity and water solubility, PAA is frequently employed as an anode/cathode bonding agent in lithium batteries [3]. The bonding agent, which joins the conductor and collector as well as the positive and negative active elements, is a crucial part of lithium batteries. It is also in charge of the electrodes' morphology and structural integrity [4].

2.4. Coating volume

The motor's amount of coating and the percentage of active materials was increased to boost the ED, but this lowers performance. Particularly, as illustrated in Figure 2, if the electrode is excessively thick, the kinetic conditions of the electrode's Li+ diffusion will decrease, which will impact the multiplicity and cycle performance of the LIBs.

A type of high-performance thick electrodes is invented with graded porosity utilising a capillary suspension and a multilayer electrode technique to solve this issue [5]. In the surface layer away from the copper foil, a capillary suspension slurry was used with the addition of 1-octanol, resulting in a significant increase in porosity and improving the kinetic conditions of the electrode, resulting in porosity from the bottom up. The use of a standard slurry in the lower layer close to the copper foil results in low porosity and good electrical conductivity. As a result, the thick electrode's kinetic conditions and electrochemical performance are greatly enhanced, which raises the cell's weight and volumetric specific energy (SE) without compromising cycle performance.

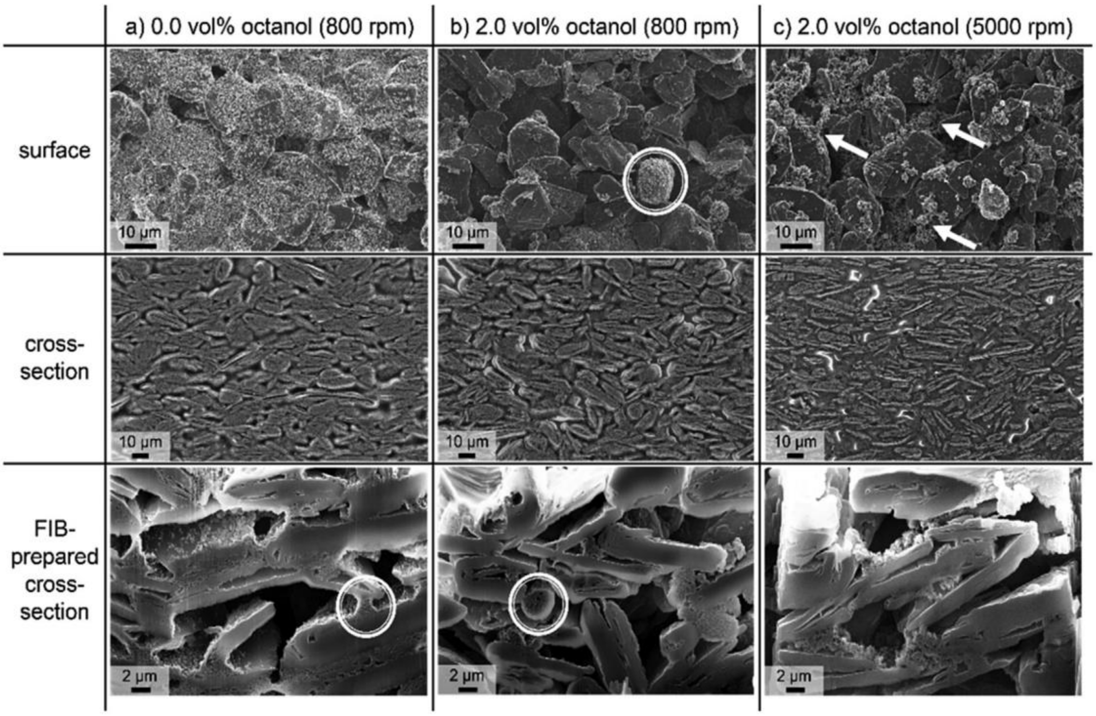

Figure 2. Ultra-thick SLP 30 electrodes made from slurry at various octane levels and mixing rates are shown in scanning electron microscope (SEM) images (quantification in parenthesis) [5].

2.5. The amount of electrolyte

Another crucial step in improving LIBs' SE is controlling the electrolyte content. A medium is used in

LIBs by the electrolyte. Both positive and negative Li+ diffuse through the electrolyte. The formation of the SEI film during the formation process degrades the electrolyte, and its ongoing consumption is brought on by the oxidation of the positive electrode during the circulation process, which also degrades the electrolyte. Enhancing the electrolyte solvent system, the electrolyte additive system, and the stability of the electrolyte are crucial for reducing the amount of electrolyte while maintaining the performance of the battery. In order to increase the stability of the electrolyte, a small amount of fluoroethylene carbonate (FEC) additive to the electrolyte along with traditional ethylene carbonate (EC) and ethyl methyl carbonate (EMC) is added as the solvent (weight ratio 3:7) [6]. Researchers found that the FEC additive in $LiNi_1/3Mn_1/3Co_1/3O_2$ (NMC 111) batteries may significantly improve cycle stability, improve initial coulomb efficiency, and effectively prevent electrolyte breakdown. based on Figure 3.

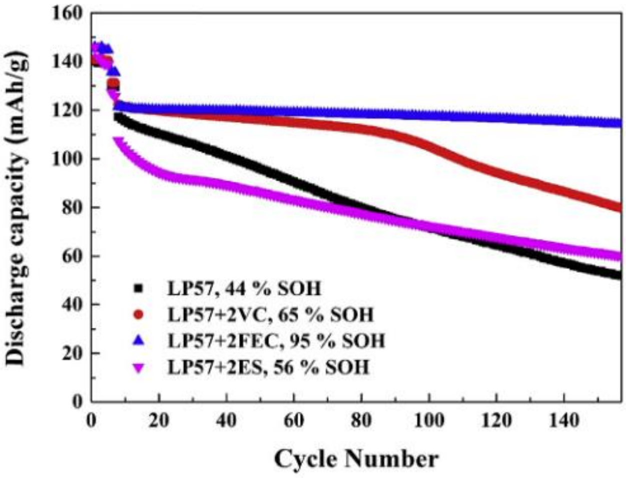

Figure 3. The long-term cycle performance of cells using four electrolyte systems shows capacity retention in SOH values of 44, 65, 94, and 55% SOH for LP57, vinylene carbonate (VC), FEC, and ethylene sulphite (ES) systems, respectively, at 0.1 C for 5 CC blasts and 1 C for 150 CC/CP blasts [6].

3. Increase of the proportion of active materials in the electrode

3.1. The selection of positive and negative active substances

There are two broad paths to increase the ED of LIBs: 1) Raise the operating voltage of LIBs; and 2) Boost the capacity of the materials used to make positive and negative electrodes.

3.1.1. Increase the working voltage. The voltage differential between the positive and negative electrode materials determines the working voltage of LIBs. The following samples represent the majority of the current high-voltage cathode material selection:

1) High voltage $LiNi_{0.5}Mn_{1.5}O_4$ spinel lithium nickel manganate. The material has a working voltage of 5.0 V, a voltage platform of around 4.7 V, a theoretical capacity of 147 mAh/g, and an actual capacity of more than 138 mAh/g [7].

2) Olivine high voltage materials, such as $LiMnPO_4$ and $LiCoPO_4$ materials. Their voltage platforms may reach about 4.1 V for $LiMnPO_4$ materials and approximately 4.8 V for $LiCoPO_4$ materials, respectively [8].

3) Li-rich material, which theoretically has a capacity of more than 200 mAh/g or even 300mAh/g. However, in order to effectively use the benefits of this high capacity, a higher operating voltage, even as high as 4.8V, is required.

The electrolyte is quickly oxidised and destroyed at high voltage, which makes the electrode unstable and renders the battery dangerous. There are two things to think about in order to solve this issue. First, starting with the electrolyte solvent system, a more stable ionic liquid electrolyte and a novel electrolyte salt may be used to increase the electrochemical stability window of the electrolyte.

The surface coating of high voltage materials, on the other hand, can be used to separate the electrolyte from the active material. In order to surface coat lithium-rich layered materials, Li_3PO_4 was employed, as seen in Figure 4(A). Transition metal element dissolution was decreased, the change of layered structure into spinel structure was delayed, and the cycle performance of lithium-rich materials was greatly enhanced [9].

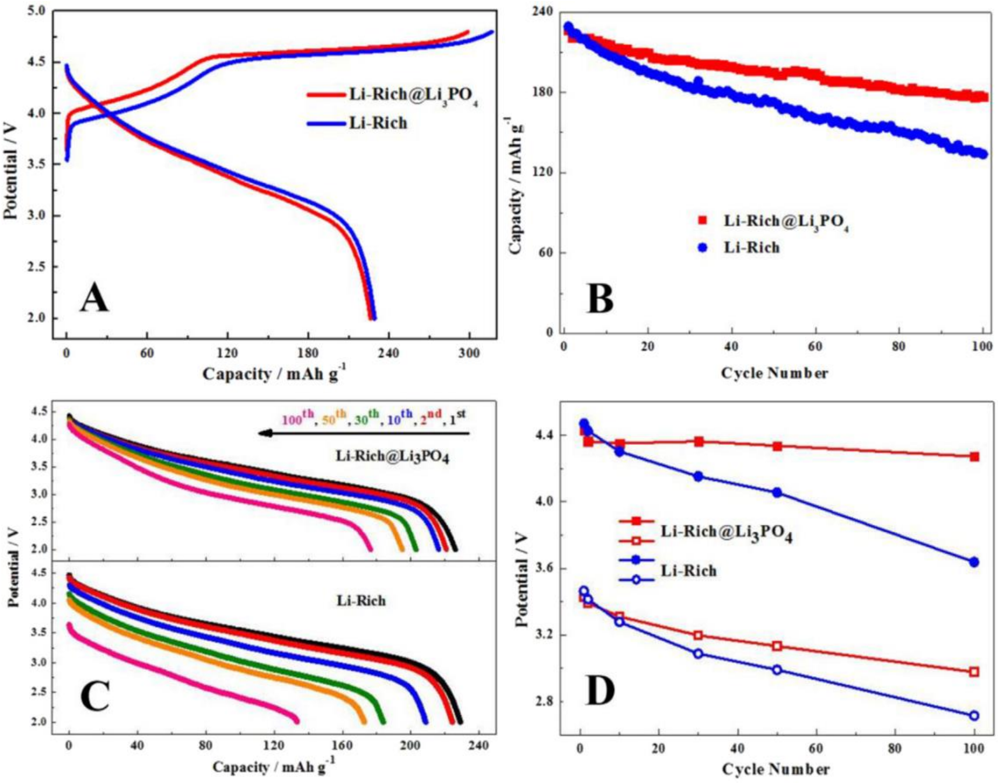

Figure 4. Initial charge and discharge curves, cycling results, and the discharge cu discharge potential (open circle) of Li-Rich@Li_3PO_4 and Li-Rich are shown in (A), (B), and (C), respectively [10].

3.1.2. Increase the capacity of positive and negative materials. To boost both positive and negative active materials' particular capacities, there exists two primary kinds of high-capacity cathode materials from which to pick in terms of anode materials:

1) Ternary materials, such as high nickel NCM811, are currently the most developed high performance cathode materials. The SC can be as high as 200 mAh/g, which appears to be a lot greater than $LiCoO_2$ materials. The SC of high-nickel NCA materials can also be as high as 190 mAh/g. Lithium-rich materials have particular capacities that can exceed 200 mAh/g or even 300 mAh/g.

Lithium-rich materials remains rather uncommon on the market, primarily for the following reasons: High irreversible capacity, voltage drop, and poor cycle performance are the three factors in terms of high-capacity cathode materials, which mainly have the following options:

1) Crystalline silicon has a SC of more than 4200 mAh/g, making it the most developed and dependable high-capacity anode material on the market, but it has a huge expansion and poor cycle performance.

2) Since N atoms have an electronegativity of roughly 3.5, adding N elements to graphite might greatly increase its SC [11]. In recent years, research on high-capacity anode materials has centred on N-doped graphite materials. The SC of the graphite anode may be significantly growth following the doping of N elements into the graphite. The electronegativity of the N atoms is around 3.5. N-doped mesoporous carbon hollow sphere materials were created using a stencil method, and their SC can reach 931 mAh at a current density (CD) of 0.1 A/g at a CD of 0.5 A/g. Here, 1100 cycles at a CD of 0.5 A/g resulted in the maintenance of a SC of 485.7 mAh/g. seen in Figure 5 [11].

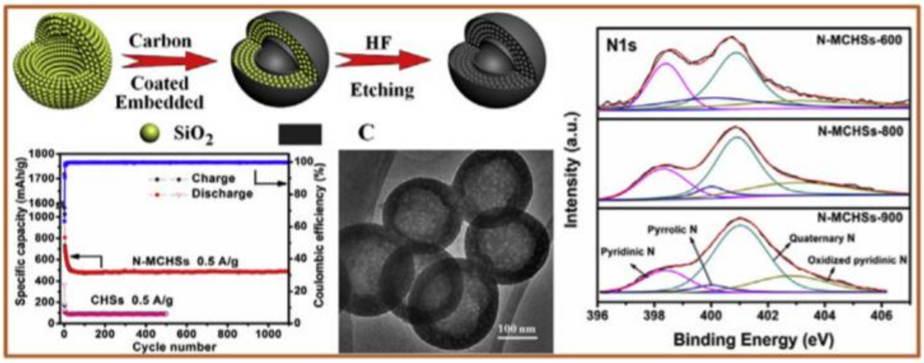

Figure 5. N-doped mesoporous carbon hollow sphere materials [11].

3) The reversible capacity is substantially larger than that of graphite at 1290 mAh/g, however performance is hindered by the low electrical conductivity and low ion diffusion rate. The SC of this material, which exhibits strong electrochemical performance, can still reach 915 mAh/g even at an extreme CD of 10A/g, as shown in Figure 6 [12].

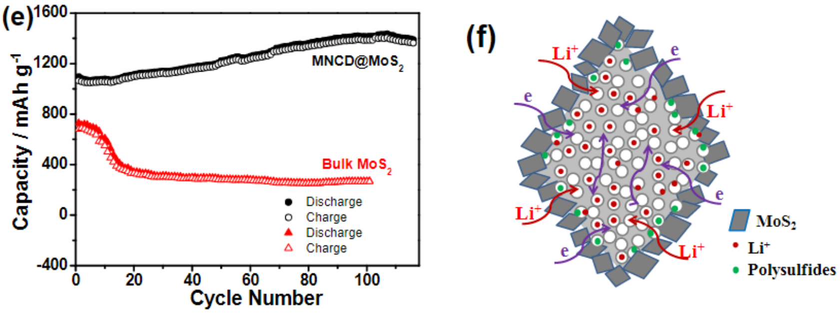

Figure 6. (e)Long-term cycling behaviour of bulk MoS_2 and MNCD@MoS_2 at constant current densities of 100 mA g^{-1}, (f) Schematic illustration of MNCD@MoS_2's structural benefits [12].

4) Li metal anode, with a SC of up to 3860 mAh/g, is the best anode material for LIBs due to its low potential and high conductivity. There are several methods to stop the increase of lithium dendrites, stop the volume expansion of metal Li in charging and discharging process, increase the safety of the metal Li anode, and enhance cycle efficiency. According to estimates, replacing the negative electrode of LIBs with lithium metal would raise their ED to around 440 Wh/kg, as seen in Figure 7 [13].

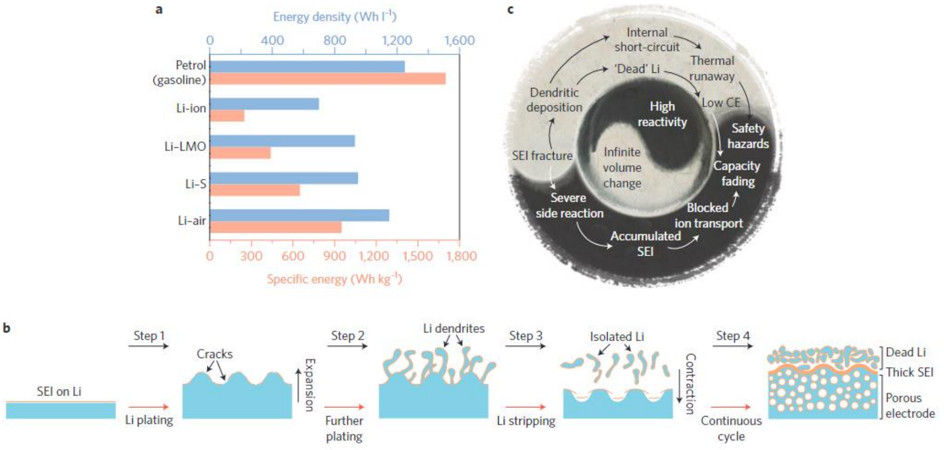

Figure 7. A bar graph displaying the realistic SE (pink) and EDs (blue) of standard Li batteries and petrol, section a. Relations between the different problems in the Li metal anode, section c [13].

4. Conclusion

In summary, this paper gives a basic assessment of the challenges and accomplishments in the development of high-energy-density LIBs from the structural and active materials perspectives. This evaluation also predicts the research route and problems, such as the low SE induced by continual electrolyte intake during the film-forming process, which results in excess. Furthermore, the Li^+ diffusion kinetics of the electrode decrease with increased electrode thickness, which affects the multiplicity and cycle performance of the LIB.

The market will determine whether or not 300 Wh/kg high nickel system lithium batteries are commercialized. In the interim, development efforts will be focused on critical components and technologies for the 400 Wh/kg next-generation high ED batteries. In the framework of sustainable energy mobility and energy storage, new system batteries with higher EDs and longer lifetimes will also be studied. As LIB technology advances, it is expected that LIBs will be widely used in more fields and have even better prospects.

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