Lithium-Ion Battery Development with High Energy Density

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Abstract. With the increasing development of technology, the battery's energy density has improved significantly, which led to improvements in numerous fields, such as the manufacture of electrical vehicles and phones. However, we found out that the battery's energy density is still not as high as expected. For example, electric aircraft are still not ready for mass production as the cost of the production is magnificent. This report will start with the introduction of batteries and how batteries are related to electrical cars to find out the energy density problems of batteries and how to solve those problems. Next, there will be an introduction to electrodes and electrolytes. We will focus on the different properties provided by different materials used to make them up and how to select them.

Keywords: lithium-ion battery; electrode material; electrolyte; energy storage.

1. Introduction

As the technology is developed rapidly, the battery's energy density has been improved significantly, which led to the improvement in numerous products, such as the mileage per charge of the electric vehicles. It seems that infinite energy density will boost the battery's performance extraordinarily. However, we cannot produce batteries with infinite energy density due to many reasons.

First of all, we must understand the definition of energy density. One of the efficient methods to increase the energy density is to promote the potential difference between the anode and cathode and improve the specific capacity of the material. Nowadays, the Ternary polymer lithium battery is one of the most common uses in electric vehicles, the products that are related to our real life. From the graph below, the Ternary polymer lithium battery, Lithium Nickel Cobalt Manganate 111(means that the battery's anode is composed of the Lithium Nickel Cobalt Manganate proportion of nickel, potassium and manganese are 1:1:1) has the lowest energy density. In contrast, that of the Lithium Nickel Cobalt Manganate811 (means that the Lithium Nickel Cobalt Manganate makes up the battery's anode and the proportion of nickel, potassium and manganese is 8:1:1) is increased by 17.32%. It is interesting to figure out that with the increase in the proportion of nickel used in the battery, the energy density goes up respectively (3.93% in NCM523, 7.87% in NCM622, 17.32% in NCM811)

2. Ease of Use

2.1 Construction of Lithium-ion batteries

Multiple modules could be assembled into battery packs. For instance, the 85-kWh battery pack contains 7104 cells. A typical Lithium-ion battery is represented by a cathode and an anode linked by an electrolyte that includes lithium ions.

2.2 Maintaining the Integrity of the Specifications

The chemical energy in the Li-ion battery is finite, and the process of using the battery is the conversion of chemical energy to other energy, so when the chemical energy of the battery is completely converted to other energy or converted to the point where there is not enough chemical energy left to convert it to something else the battery is dead. That is one of the main problems of the Li-ion battery.

3. Lithium-ion battery infrastructure and principles and its unique advantages

3.1 The working mechanism of the lithium-ion battery

- Basic information: The basic working principle of lithium-ion batteries is that the anode and cathode materials have different potential energy separated by a diaphragm, and Li+ moves from the intercalated material electrode with a higher chemical potential to the electrode with a lower potential. Only lithium-ion can move through the membrane in the electrolyte.
- Discharging procession and Charging procession: When a battery is charging, lithium-ion is formed at the cathode and the resulting lithium-ion travel through the electrolyte to the anode. When discharging, Li+ moves from anode to cathode through the diaphragm, and electrons cannot pass through the diaphragm, but they can move to the positive through the negative pole of the outer circuit.

3.2 Advantages of lithium-ion batteries over other batteries

- High energy density: High energy density is one of the significant advantages of lithium-ion batteries. As more and more modern devices and equipment like mobile phones and electronic vehicles require high battery life, there is always a demand for higher battery capacity. One of the most efficient ways to improve battery life is by strengthening energy density.
- Low self-discharge rate: The low self-discharge rate is one of the outstanding characteristics of the lithium-ion battery. The experiment shows that the self-discharge rate of full charge storage for one month is about 10% at room temperature, while the Ni-Cd battery is 25-30%, and the Ni-metal hydride battery is 30-35% under the same conditions. That special condition has accomplished the lithium-ion battery the most advanced battery kind in modern days.
- Environmentally friendly: Another unique characteristic of the lithium-ion battery is that this kind of battery is relatively friendly to the environment. For the production, utilization ion and even scrap of the lithium-ion battery are not polluting, and these processions have not generated any lead, mercury, cadmium and other toxic heavy metals.
- The strong charge holding capacity: allows a wide operating temperature range. It can be stored in an open circuit from 15 °C to 25 °C for 30 days, and its discharging capacity at room temperature is greater than 85% of the rated capacity. At the same time, lithium-ion batteries have good charge-discharge performance in high and low-temperature environments. The charge-discharge performance of -20 degrees Celsius to 60 degrees Celsius is higher than other ion batteries.
- Low cost: Battery life will multiply the competitiveness of appliances. Due to its long circulation, the unit cost will be relatively low [1].

4. Electrode

4.1 Design of electrode materials

According to the description above, lithium-ion batteries are mainly composed of an anode, cathode, separator, electrolyte and container. Figure 1 illustrates the process of battery charging and discharging.

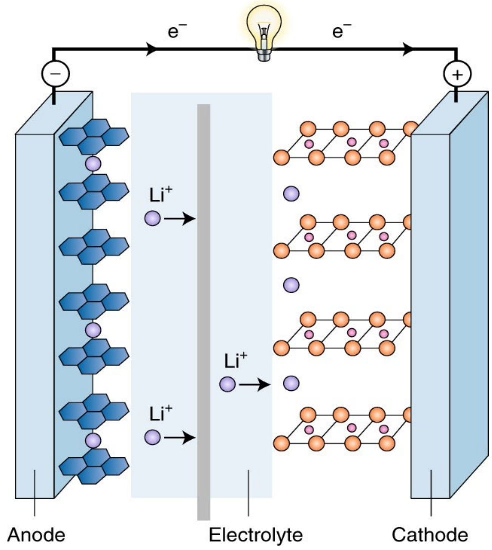

Fig. 1. The process of battery charging and discharging [2].

4.2 Anode materials

A perfect anode material should have low potential, good low-temperature performance, relatively high energy conversion efficiency, etc. [3]. Anode materials can be divided into intercalation-type anode material, conversion-type anode material and alloying-type anode material [4]. Graphite, for example, the most widely used anode material today, which has a relatively low potential, is intercalation-type anode material [5]. Lithium ions do not diffuse through it quickly enough, resulting in a less-than-impressive rate performance [6]. To overcome these disadvantages, multi-channel graphite has been created. This technique allows lithium ions to enter the graphite particles more quickly by etching channels directly into the graphite surface [7]. This increases the coulomb efficiency of the electrode, which, according to experimental results, exhibits an excellent 73% charge rate capacity at 10C [7]. The layer spacing of hard carbon is generally greater than 3.8 Å [8], which facilitates rapid charging and discharging in intercalation-type anode materials. However, this material is not widely used because it has voltage hysteresis and a high initial irreversible capacity. New electrode materials such as graphene have been discovered based on the structure of hard carbon. In contrast, transition metal oxide cathode materials are usually conversion-type anode materials (CTAMs). They will react with lithium ions as [9]:

$$M_xO_y + 2yLi^+ + 2ye^- \leftrightarrow xM + yLi_2O \tag{1}$$

$$M_xS_y + 2yLi^+ + 2ye^- \leftrightarrow xM + yLi_2S \tag{2}$$

However, this reaction with lithium is irreversible at room temperature because the structure of CTAMs does not give a place for lithium ions to insert and extract [10]. Alloying-type anode material has the highest specific capacities. This type of anode material exhibits a strong volume effect in the lithiation reaction, which means that the cycling performance of this material is very low. Using Si as an example, it has the reaction formula [11]:

$$Si + 4.4Li^+ + 4.4e^- \leftrightarrow Li_{4.4}Si \tag{3}$$

The study finds that reducing the size of the Si particles can release internal stresses in the electrode material [12]. In this way, the possibility of the particles being stripped during the reaction is reduced [13]. However, Ge is a rare metal, and the material's cost is too high.

4.3 Cathode materials

The battery's cathode requires a large surface area to allow lithium-ion de-embedding and embedding easier [14]. Nowadays, the ternary polymer lithium battery is one of the most common uses in electric vehicles. Interestingly, the more nickel used in the anode, the larger the potential difference between anode and cathode (voltage larger than 4.5%), the higher the energy density and, therefore, improve the battery's performance. However, if the proportion of the nickel is up to 0.8%, the nickel will react with the water and carbon dioxide in the air to produce the carbonate more frequently. Those carbonates will involve a reaction with the Li-ions, which transfer to the material's surface to produce the $LiCO_3$ and therefore cause the increase in the surface basicity. So, although theoretically, adding Ni can improve the performance of ternary polymer lithium batteries, this approach will face many practical difficulties. LFP has an olivine structure. The two main disadvantages of conventional LFP are the low electrical conductivity and the low migration rate of lithium ions. New LFPs are being prepared by improving the materials' preparation methods and surface coating to improve their electrochemical properties, and modification methods mainly involve surface carbon or metal cladding of LFP materials [3].

4.4 Comparison and selection of various electrode materials

For the selection of battery electrodes, we should focus on the application scenario of the battery. Sometimes the excessive pursuit of high energy density will bring other risks. For example, a perfect battery should have good low-temperature performance and high energy density. However, these two good qualities are usually not achieved simultaneously. Although the ternary lithium battery has a higher battery energy density, due to the NCA in a high-temperature environment when the structure is unstable, resulting in poor safety at high temperatures and a low-temperature environment, it also does not perform as well as lithium iron phosphate batteries. These are batteries with lower energy density chosen for practical applications. Safety considerations are more important. Alloying-type anode material has the highest specific capacities, but due to the significant volume effect, it is not more widely used than graphite which has more mediocre performance. Graphene has good electrical conductivity, dissipates heat quickly, and is extremely thin. So, it is an excellent material for electrodes. Carbon nanotube, based on nanotechnology. To obtain the required internal resistance of the battery, it is usually necessary to add 2-5% to a lithium battery if a carbon black-based conductive agent is added; unlike this, the addition of a carbon nanotube conductive agent usually requires only 0.4%-1.0% to be added to a lithium battery [15]. The cathode material in lithium batteries will repeatedly expand, contract and even crack and split during the charging and discharging process. In the long run, some of the cathode material will break away from the conductive network inside the battery and fail, resulting in the degradation of the battery's performance and life. Carbon nanotubes, as a high aspect ratio conductive additive, can build up a conductive network inside the battery on a large scale, thus avoiding the above problems. Conventional zero-dimensional carbon black-based conductive agents do not provide similar functionality. However, these new materials generally face several problems, such as the difficulty of industrial mass production and high price. This is fatal for practical applications.

5. Electrolyte

5.1 The effect of the electrolyte on the energy density of the battery

Electrolytes are chemicals composed of soluble salts, acids or organic compounds. Their main function is allowing the flow of ions between cathodes and anodes and ensuring the processes inside the battery are reversible. However, whichever substance is chosen as the electrolyte, they all occupy a huge percentage by mass in the battery, which causes the decrease in energy density.

5.2 Electrolyte selection in Li-ion battery

We can divide the electrolytes used in Li-ion batteries into molten salt electrolytes and solid electrolytes. Next, I will describe the selection of these two electrolytes in turn.

5.3 Molten salt electrolyte

The molten salt electrolyte for lithium-ion batteries consists of three components, organic solvent, lithium salt and additives [16]. The main reason for choosing an organic solvent but not the aqueous solution is that the presence of an aqueous solution reduces the potential difference between two electrodes, which leads to a decrease in the stability of the electrodes. Since the lithium salt is the major source of lithium ions inside the battery, to ensure enough lithium ions for reversible reaction, the electrolyte we selected must not involve any reactions with electrodes [17].

5.4 The choice of organic solvent

Four organic solvents are chosen - carbonate esters, ethers, carboxylic acid esters and organic compounds containing sulfur [17].

1）Carbonate esters

Carbonates are widely used in the production of electrolytes due to their high electrochemical stability, low melting point (around -73 °C) and high flash point. We can divide the carbonate esters used in electrolytes into two types according to their structure, cyclic carbonates and chain carbonates. Propylene carbonate (PC), a kind of cyclic carbonate, is the most commonly used in electrolytes due to its relatively high electrochemical stability and difficulty in decomposing during distillation. In addition, the boiling point of propylene carbonate is approximately 242 °C, and the melting point is almost 48.8 °C, allowing propylene carbonate to work at low and high temperatures. Remaining in a liquid state for nearly 290 °C is an extremely rare property in organic solvents. Another interesting characteristic of propylene carbonate is its strong solubility to carbon dioxide. Specifically, each liter of propylene carbonate can dissolve 8.5 liters of carbon dioxide in its standard state. Therefore, it has an industrial use for absorbing carbon dioxide and thus preventing the bulge of batteries. However, the very high viscosity of propylene carbonate leads to a negative effect on the transfer of lithium ions. As shown from the table1, the viscosity of propylene carbonate is 2.53, which is much higher than the 1.40 of EC. The consequence of this situation is a difference in lithium-ion concentration between the electrodes, which leads to polarity. As a result, the cell's performance will be lower [18].

Table 1. the viscosity of different solvents [18]

Solvent name	Viscosity cp
Methyl propionate	0.43
Ethyl acetate	0.45
Ethyl acetate	0.53
Diethyl carbonate	0.75
Vinyl carbonate	1.4
Propylene carbonate	2.53
Butylene carbonate	3.2

2）Carboxylic ester

Carboxylic acid esters are mostly intended to improve electrolytes' performance at low temperatures. For example, ethyl acetate (EA) can improve the interphase of solid electrolytes. In terms of MF, one of its advantages is that its purification is simple. In addition, due to the high dielectric constant, electrolytes made from MF show strong electrical conductivity, high resistance to low temperatures and a large range of electrochemical stability. Though the addition of carboxylic acid esters has many benefits, the high activity leads to an increase in sheet resistance, resulting in poor cycling efficiency performance [17].

3）Ethers

Ether has a relatively low dielectric constant and viscosity, which is the major advantage when used as part of an electrolyte. However, ether is quite easy to oxidize due to its high activity. Hence, ether is mostly used as an additive to carbonates rather than the main organic solvent [17].

6. Organic compounds that contain sulfur.

A solid under the standard condition, Sulfone is the most common use of sulfur-containing organic compounds in the electrolyte when mixed with other organic solvents. These kinds of organic solvents are extremely stable. Also, their Coulomb efficiency of them is high. Both properties improve the battery's endurance and ensure the user's safety [17].

6.1 Lithium salt

Generally, inorganic lithium salts are the major use in lithium-ion batteries due to their high stability, low price and ability to withstand high potentials. Lithium hexafluorophosphate is the most common use in lithium-ion batteries due to its poor binding ability, which contributes to high electrical conductivity. In addition, when lithium hexafluorophosphate is used as an electrolyte, the voltage across the battery's cathode is 5.1 Volt, which is much higher than the standard voltage for lithium-ion batteries, 4.8 Volt. This property leads to the stability of lithium hexafluorophosphate. And it involves the decomposition reaction with air even at the condition of high purity. The decomposition product of lithium hexafluorophosphate, gaseous PF5, acts as a strong Lewis acid, which accepts a lone pair on the oxygen atom in the solvent molecule and participates in further decomposition. The products of further decomposition - carbon dioxide and other gases increase the pressure inside the cell, creating problems related to safety [19].

6.2 Solid electrolyte

The solid electrolyte used in the Li-ion battery transfers Li-ions between the electrodes in solid form and plays both the diaphragm and electrolyte roles. In general. Due to the properties of non-flammable and high compressive, the disordered growth of lithium crystals on the surface of the negative electrode can be controlled during charging, effectively preventing the formation of dendritic crystals [20].

6.3 Solid polymer electrolytes

All solid means the solid polymer electrolytes are formed by the composition of lithium salts such as $LiPF_6$, $LiBF_4$, $LiCLO_4$, $LiAsF_6$ and polymer matrix such as PEO and PAN PVDF, PVDC AND PMMA [21, 22]. Unlike all solids, inorganic composite polymer solid electrolytes are composed of inorganic particles such as Li_3N, SiO_2, TiO_2, $LiALO_2$ and Li-Al-Ge-P-O with the polymer electrolyte [23]. The polymer electrolyte shows flexibility and a relatively good contact surface with the electrode, contributing to processability.

6.4 Inorganic solid electrolytes

Inorganic solid electrolytes consist of two types of materials, solid-phase crystalline materials and glassy non-crystalline materials. Both materials have high conductivity towards ions, low conductivity towards electrons and relatively low activation energy. The solid-phase crystalline materials allow the transfer of lithium ions through the interstitial defects of coordinating polyhedron structure, while the glassy non-crystalline materials provide interstitial defects that establish expansive pathways for the movement of lithium ions [24, 25]. Overall, inorganic solid electrolytes exhibit high electrical conductivity and a wide electrochemical stabilization window, facilitating the rapid formation of solid electrolyte interphase.

6.5 Organic-inorganic composite solid-state electrolytes

Organic-inorganic can be deemed the complex of solid polymer electrolyte and inorganic solid electrolyte as they show both enormous flexibility and high mechanical strength properties. However, the conductivity of the polymer matrix is relatively low. Furthermore, it tends to crystallize at low temperatures

7. Conclusion

The challenges of energy density with lithium-ion batteries and the selection of materials used in electrolytes and electrodes have been summarized above. In general, the challenge of energy density is related to the chemical processes within the battery. To be specific, the sources used to promote reaction in the battery have to be limited to reduce the negative effects of some overly chemical processes. Also, the efficiency of some procedures is still not as high as the expectation. In addition, different choices of materials used in electrodes and electrolytes can result in different battery performance and variations in energy density. In addition, the reports talk about nanotechnology concerning electric vehicles themselves, tires, and lubricants. Overall, the general direction of research is very promising, although the energy density of batteries is still not as high as expected at present. At the same time, there is still much space for progression, as many materials for electrodes and electrolytes have not yet been developed.

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