Research Progress on Graphite Anode of Lithium-ion Batteries

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Abstract. As the new energy vehicles and state-of-the-art portable electronic devices place an ever-increasing demand on high-power energy storage systems, there has been a push to make lithium-ion batteries fast to charge as a research concern. As well as, Lithium plating and dendrite growth of graphite anodes become more likely when charging at a high rate, having a drastic effect on the safety and life cycle of a battery, being the mainstream negative electrode material. The paper review will provide an analytical presentation of lithium plating mechanisms and battery failure processes related to the use of graphite anodes, and their impact on the performance of the battery. Three strategies of modification are highlighted, including using azo-functionalized porous organic framework anodes with adsorption-assisted redox centers, AC preheating lithium-ion battery with suppressed lithium plating and introducing tris (trimethylsilyl) borate (TMSB) into the electrolyte. These strategies not only mitigate lithium plating but also lay a foundation for balancing fast-charging capacity and long-term cycling stability. This review is focused on developing a theoretical point of reference with respect to the creation of safe, stable, as well as high-energy-density lithium-ion batteries. Finally, we propose promising research directions and key perspectives for fastcharging graphite anodes, providing inspiration for further commercialization of fast-charging LIBs.

1 Introduction

As modern science and technology continue to make people life convenient, it has also come to pose the alarming issues of energy crisis and sustainable development. Ensuring that a renewable energy system is put in place is thus necessary as future population and economic development will continue to increase the demand, which will subsequently strain the existing energy supply. The present-day system of energy supplies is still oriented to fossil fuels; nevertheless, the limited nature of their reserves, as well as their impact on the environment problems and greenhouse effect, poses great constraints. In the meantime, as much as the ratio of near-zero-carbon energy sources, such as wind power, photovoltaics, and hydropower, are gradually rising, their use is limited by the nature of natural resources, such as intermittency, volatility, and geographical distribution, and bottlenecks in energy

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storage technology, so that it would become the predominant form of energy. In this regard, the creation of efficient, stable, and mass scale energy storage technologies has become one of the key failures in streamlining the energy structure and making the change and modernization of the energy system possible.

$LiCoO_2$ batteries (Lithium-ion batteries) are a key high-performance electrochemical energy storage platform in this game changing process. The last several years have witnessed the development of LIBs attracting the primary interests of the academic sphere and industry with their excellent characteristics, like high energy density, lightweight construction, compact configuration, and high amounts of cycling, which give this category of energy storage a unique edge of distribution in various application spheres, including distributed energy storage and mobile power systems. Due to their outstanding performance in terms of high energy density, longevity on the cycling stability (more than 1000 cycles), a low self-discharge rate (about 5 per cent monthly), structural compactness, and environment benignity, the use of LIBs has become a solution of choice in storing renewable energy. Moreover, they are today being extensively deployed in a wide variety of applications, such as passing consumer electronics, electric cars and in scalable grid-level energy storage facilities [1]. A Lithium-ion battery (LIB) as one of the categories of secondary (rechargeable) batteries are only run when the lithium ions move between the positive and negative electrodes. In chargeDischarge cycles Lithium ions are in and out of the two electrodes repeatedly. The LIBs are considered superior when it comes to performance, either in terms of high energy density, a high operating voltage, low self-discharge rate, zero memory effect, prolonged cycle lifespan, rapid charge ability, low weight, small size and environmental friendliness relative to other battery systems, such as lead-acid batteries, nickel-metal hydride (Ni-MH) batteries, etc. There has been extensive experimental evidence on anode materials, such as graphitic carbon, amorphous carbon, tin oxides, nitrides, nanostructured oxides and phosphides, which can be used to make secondary lithium batteries since the mid-1970s [2]. But of these candidates, the material that has been widely used in practical activities is only graphitic carbon material. It is worth noting that since its discovery, graphite has been considered as the best anode material in lithium-ion batteries (LIBs) due to its balanced effect on electrochemical properties and affordability [3, 4]. However, it is also known that the graphite anode is also considered a bottleneck that restricts the ability of fast-charging commercial LIBs. Slow kinetics in intercalation of lithium ions to the bulk phase of graphite, together with low redox potential, make lithium plating thermodynamically favourable when rapid charging, or low temperature, is desired. This does not only worsen the electrochemical functionality of the battery, but it is also highly unsafe. Simultaneously, the theoretical potential of the state-of-the-art graphite anodes is close to its maximum, which requires the creation of new high-capacity anode materials that can use lithium-ion batteries [5]. The anode material is essentially the key determinant of the upper limit of the battery energy density as Lithium storage mostly occurs in the anode part of the LIBs. Accordingly, the next-generation high-performance anode materials development is a highly important break-even route and a research direction of overcoming the existing technological bottlenecks in the lithium-ion batteries, which will subsequently contribute to the sustainable achievement of the future energy system and the digital industry.

This review presents a summary of the problem of lithium plating and battery failure experienced in the process of fast-charging batteries using graphite anodes in lithium-ion batteries. Three modification strategies are put forward, including the use of azo-functionalized high-potential organic anodes utilizing adsorption-assisted redox centers, AC preheating lithium-ion battery with suppressed lithium plating, and introduction of tris (trimethylsilyl) borate (TMSB) to the electrolyte, as viable methods of overcoming these difficulties.The article offers research objectives and critical thinking towards the design and creation of high-power anode materials in lithium-ion batteries.

2 Introduction to lithium-ion batteries

2.1 Principle of operation of Lithium-Ion Batteries

Working of Lithium-Ion Batteries as presented in Fig. 1. Mostly, the lithium-ion batteries contain a cathode, a separator, an electrolyte, an anode and current collectors. The saparator is an insulating and porous membrane which is crucially important in avoiding direct contact between the cathode and the anode to prevent short circuits whereas, the lithium ions are free to move freely through its little porous membranes. During charging the lithium ions are extracted off the cathode material and flow through the electrolyte to the anode with the applied voltage. These ions are then intercalated at the anode crystal structure following surface desolvating of electrolyte interphase (SEI) film surface. The protective layer formed (SEI film) during the initial several charging cycles is fundamental and plays an essential role in stabilizing an anode-electrolyte interface, boosting cycle life, and safety of the battery. At the same time, the external circuit moves electrons between the anode and the cathode leaving the battery at a high-energy state with a lithium-rich anode and a lithium-depleted cathode. This will be achieved through transforming electrical energy into a storage chemical energy. During the discharge process, the lithium ions are set free by the anode material and relocated to the cathode through the electrolyte by the internal potential difference thence to the cathode material where the lithium ions intercalate. Meanwhile, these electrons will be passed between the cathode and the anode employing the external circuit; since it is the same charge that is transferred, chemical energy will be changed into electrical energy, and made available to the external load, e.g. smartphones, electric vehicles, or grid energy storage systems and a complete cycle of energy release is accomplished [6].

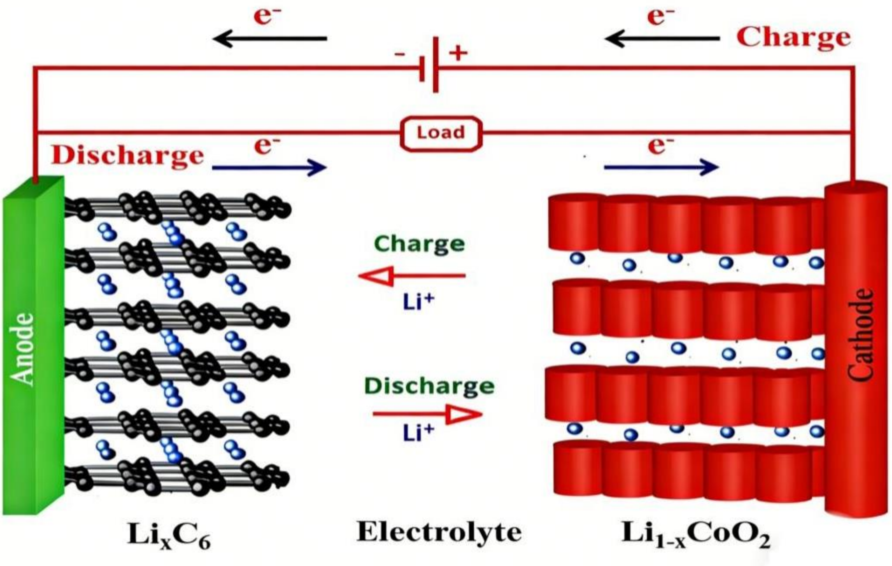

Fig. 1. Schematic of the operating mechanism of a lithium-ion battery.

2.2 Lithium-ion battery anode

Lithium-ion batteries are based on the anode as the basic lithium storage host, so the material characteristics of anode are the major determinants of energy density, rate capability and cycle life of the battery. The graphite type is the most utilized commercial anode today because it is less expensive, generates high levels of lithium intercalation, and boasts of consistent electrochemical operation. Nevertheless, graphite anodes are especially problematic under conditions of rapid charging, in which case kinetic constraints can slow down lithium-ion diffusion and lithium plating can take place, when lithium metal gets deposited on the anode surface rather than inserted into the graphite structure. This not only decreases the charging effectiveness but it also presents a safety hazard and decreases the overall life of the battery.

3 Graphite anode

3.1 The drawbacks of graphite anode as a fast-charging anode are as follows.

The speed of charging a graphite-based battery is frequently slowed down by the kinetics of Li intercalation within graphite layers, which are impossible to match the current transferred to the battery. Consequently, not all Li ions can get intercalated within the desired time and instead act as metallic Li locally on the electrode surface.

In addition, the lithiation potential of graphite (0.1 V vs Li/Li +) is quite similar to the lithiation potential of metallic Li (0 V vs Li/Li +). The charging current becomes too large, the Li+ concentration on the graphite surface reduces drastically and leads to the effect of overpotential that is, the electrode potential is lower than the metallic Li deposition potential. This effect also facilitates the bulk deposition of Li + to metallic Li on the graphite surface. The problem of Li deposition on the surface of the graphite is a critical problem in fast charging. Though graphite has enough interlayer spacing which can allow the depositing Li to access, the metallic Li is deprived of diffusion ability and cannot be involved in the further reaction. Through repeated charge-discharge cycles, the increased current densities lead to Li being concentrated in preference at such points of deposition to form progressive Li dendrites and eventually damage the effective functioning of the battery [7]. Besides the lithium dendrite problems, lithium-ion batteries have other problems of failure. Lithium-ion battery failures can be broadly divided into two different categories during failures, which include performance-related failures and safety-related failures. The performance-related failures include the inability of the battery to sustain the usage requirements and meet the stated technical standards, which is reflected in the capacity decadence, decreased cycle life, and deterioration of the rate capability, among other problems. In comparison, safety-related failures are those types of failures that have the possibility of having a hazard, stemming either out of incorrect operation or misuse or missuse in using the battery. Common symptoms comprise thermal runaway, battery swelling, leakage of electrolytes, lithium dendrite growths, and internal short circuit [8].

3.2 Strategies of fast charging anode modification.

3.2.1 Inhibition of lithium plating on graphite anodes.

High-potential anode materials with azo groups as redox-active sites should be used. In this design, azo groups function as reversible redox-active centers capable of binding lithium ions, while neighboring oxygen atoms act as lithiophilic adsorption sites, thereby facilitating charge transfer between Li^+ and the redox centers. The adsorption-assisted three-atom redox centers synergistically improve Li^+ adsorption and intercalation, reduce surface polarization of the negative electrode, and enhance Li storage capacity and cycling stability [9]. POF-AN is synthesized from phloroglucinol and diarylamines via diazonium coupling, and the POF-AN||Li half-cell demonstrates high Li-storage capacity. The azo-functionalized organic anode exhibits a relatively high lithiation potential compared to graphite, providing a wide margin against Li plating onset and effectively suppressing metallic Li deposition on the electrode surface during cycling [9]. This structural design, leveraging the adsorption-mediated action of three-atom redox centers, further facilitates Li^+ adsorption and intercalation to increase Li storage capacity and cycling stability.

3.2.2 AC preheating lithium-ion battery with suppressed lithium plating

The Lithium-ion batteries that utilize graphite anodes presently show a major decline in performance in low temperature settings and low-temperature preheating is a sensible solution to the low-temperature service efficiency. Unlike external preheating methods, internal alternating current (AC) preheating achieves preheating control based on self-generated heat in the battery itself that is not only able to rapidly and effectively increase battery temperature but also create a homogenous temperature field inside the battery cell. Moreover, sizable parameters optimization may avert lithium plating in lithium- ion batteries throughout the internal AC warming of the battery [10]. AC preheating system was set and preheating tests were performed under AC current conditions which practically inhibits lithium plating. The temperature-dependent nature of the impedance of lithium-ion batteries was used to design a temperature-controlled AC preheating protocol: at the preheating stage, the preheating current parameters are dynamically changed according to the change in battery temperature. This thermal feedback mechanism enables the battery to maintain high temperature elevation rate during the entire preheating process thus providing a better preheating capability [10]. In this work, the maximum amplitudefrequency clusters of the AC preheating current in lithium-ion batteries preventing lithium plating at various temperatures were outlined and it was extended by way of the temperaturefeedback AC preheating protocol on the basis of the above findings.

3.2.3 Enhancement of failure behaviour in lithium-ion batteries

Gas formation in the lithium-ion batteries can be suppressed at high voltages by the addition of 5% tris(trimethylsilyl) borate (TMSB) to the pure electrolyte used in the batteries. The test outcomes during three-electrodes experiment show that TMSB is capable of properly enhancing the potential of the battery anode. Electrochemical impedance spectrophotometers indicate that the introduction of TMSB to full cells results in the rise of cathode impedance and slight impact on the anode impedance [11].

In the meantime, it has also been reported through experiments, that addition of TMSB containing electrolyte can increase the anode potential during the process of overcharge. This implies that, to some degree, TMSB will minimize the possibility of a lithium deposit in batteries, thus enhancing the safety performance of the batteries [11].

Moreover, galvanostatic charge-discharge experiments of coin cells indicate that TMSB is able to improve the rate performance of the coin cells as well as cycling stability over a given concentration range. This is an innovative way of quenching lithium plating in lithiumion batteries.

4 Future research directions for lithium-ion batteries

Considering the critical limiting factors that afflict graphite anodes in the high rate charging, optimal anode materials in fast charging would have low ion intercalation barriers as well as low ion transport barriers to allow fast lithium-ion (Li +) insertion/extraction. Thus, it is essential to increase the rate of lithium ions (Li +) migration in the bulk anode materials, decrease interfacial impedance between the electrolyte and the anode, and improve the structural stability of the anode in the cycling process, which are the main prerequisites of achieving credible fast-charging behavior of advanced anode materials.

The theoretical lithium-ion battery energy density using graphite as the anode has now reached its natural limit and the impractical increase in energy density is highly constrained by its low specific capacity and low lithiation potential. In the meantime, they are challenged by a lack of rapid fast-charge kinetics, lithium plating evident, and safety risks which are prominent that inhibit their use in high-power electric vehicles. The relevant optimization strategies can be mainly categorized into two groups: The former is to increase the ionic and electronic conductivity of graphite through structural engineering (e.g. porous design, heteroatom doping), facilitate the efficient movement of lithium ions and electrons between particles, and reduce the diffusion distance of lithium ions within the graphite crystals, effectively increased ion migration rate in graphite particles and overcoming the issue of inadequate fast-charging kinetics. The second is to create homogenous, strong solid-electrolyte and interphase (SEI) coating on the anode surface using the formulation of electrolytes and interface engineering, and streamline the process of battery assembly technique, in order to homogenize the concentration of lithium ions reaching the anode surface and to minimize the incidence of local potentials more negative than the lithium plating potential, to induce the effect of suppressing lithium plating and ensuring the safety of lithium in the long-term operation of a battery.

5 Conclusion

This paper provides a comprehensive review of the lithium plating issues and corresponding failure mechanisms in graphite anodes during fast charging of lithium-ion batteries. It is emphasized that the rapid charging characteristics of graphite anodes are established by nature as limited with slow lithium intercalation kinetics and potentially potential dependent electrochemical performance. Such strategies as rational material structure design (e.g., azo-functionalized high-potential organic anodes with adsorption-assisted redox centers and lithiophilic adsorption sites) and selective electrolyte design (e.g. adding additives such as TMSB) have been shown to reduce lithium plating and improve the stability of batteries through cycling to some extent. In the next phase, the focus in future research activities ought to be on enhancing ion transport efficiency, interfacial stability between electrodes and electrolytes, and preventing lithium dendrite growth, which eventually seeks to enhance the real-world application of lithium-ion batteries that are safe and high-rate.

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