A new way to determine the optimal remanufacturing point of lithium ion batteries for electric vehicle has been proposed in this paper. The proposed optimal remanufacturing point can avoid the sharp degradation stage of battery and ensure most of active materials covered in electrodes reused in remanufacturing process with modest cost and energy. In order to find out the optimal remanufacturing point in our experiment, the charge-discharge cycle of lithium ion batteries was carried out by using battery testing system and internal resistance meter, which can obtain enough data such as the degradation of capacity, the change of internal resistance, the charging and discharging rate and the cycle life of battery for analysis. Then the optimal battery’s remanufacturing point about 500-550 cycle times has been found.

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1. Introduction

Lithium-ion batteries, which have high energy density, low self-discharge, rapid discharging and charging capability, excellent cycle life, wide operating temperature range and no harm to our environment, are increasingly used in worldwide [1]. Because of their relatively high-power density, rapid discharging and charging capability, lithium-ion batteries are also attractive as energy storage devices for hybrid electric vehicles (HEV) and electric vehicle (EV) [2]. Due to the worldwide shortage of oil resources, climate warming, economical use of petroleum products, reducing emissions, many governments around the world have taken some constructive methods including funding, regulations and restrictions to encourage both automakers to study and produce EV and HEV, and customers to purchase and use them, particularly the Chinese government has launched new regulations on environment protection and financial providing in the recent decades. So EV and HEV will increasingly used in all over the world in the near future. However, we will face new problems and challenges. For example, how to properly deal with so many these degraded batteries removed from these electric vehicles?

Many studies on spent lithium-ion batteries have been done in the area of recycling and remanufacturing those batteries, and developed lots kinds of physical and chemical methods to solve the problem [3]. The physical processes include mechanical separation process, thermal process, mechanochemical process and dissolution process. For example, Tenorio have reported the mechanical separation techniques, which can separate materials according to different property like density, conductivity, magnet behaviors, and so on. Dissolution process, which can make LiCoO2 get separated from their support substrate easily and recovered effectively, was present by Contestabile [4]. The chemical processes, however, which basically consist of acid leaching, bioloeaching, solvent extraction, chemical precipitation and electrochemical process, are connected to leaching steps in acid or alkaline medium and purification processes in order to dissolve the metallic fraction and to recover metal solutions that could be used by chemical industry. The leaching agents adopted in the process of
lithium-ion batteries leaching were H\textsubscript{2}SO\textsubscript{4} \cite{5}, HCl \cite{4}, and HNO\textsubscript{3} \cite{4}, and so on. Aiming to the treatment of recycling spent lithium-ion batteries, a process which was composed of sorting, crushing and riddling, selective separation of the active materials lithium cobalt dissolution and cobalt hydroxide precipitation as shown in Fig. 1 was developed by Contestabile \cite{4}. This process can really deal with these spent batteries, but it will bring severe problems, such as severe environmental pollution, hazardous working conditions, expensive cost and huge energy consumption.

![Flow-sheet of metal recovery processes](image)

Fig. 1. Flow-sheet of the metal recovery processes.

So the remanufacturing technology is really a good choice for end-of-life of spent lithium-ion batteries. According to the auto industry, end-of-life of lithium-ion batteries is clarified to occur when either the net DST delivered capacity or peak power capability at 80% DOD is less than 80% of rated. In other words, a battery is said to have reached its end-of-life if the capacity degrades by 20% of its original capacity \cite{7}. With such a high capacity still retained, directly recycle for end-of-life of spent lithium-ion batteries is really an unwise decision. An indication shows that the bulk materials in the spent batteries are still active, so the spent batteries can be remanufactured by using appropriate technology. So the remanufacturing process for end-of-life of spent lithium-ion batteries has been investigated by Ramoni and Zhang \cite{6}. They studied on end-of-life strategy for spent batteries and developed a remanufacturing process included the complete disassembly of those batteries, during which each component was cleaned thoroughly, examined for damage and reprocessed to original equipment manufacturer specifications as shown in Fig. 2. Remanufacturing, to some extent, has already resolved most environmental pollution, saved large quantity of energy and cost, and prolonged battery’s life. The remanufacturing point can exert greatly influence on the quality, the cost, energy consumption of the remanufactured product. An optimal remanufacture point can avoid the sharp degradation stage of battery, and ensure most of active materials covered in electrodes reused in remanufacturing process with a modest cost and energy. So it is very important to find out the optimal battery’s remanufacturing point.

![Flow-sheet of end-of-life of spent lithium-ion batteries](image)

Fig. 2. Flow-sheet of end-of-life of spent lithium-ion batteries \cite{6}

In order to pre-determining the optimal remanufacturing point of lithium ion batteries, a series of experiments was designed and experimental platform was built in this paper. And the experimental apparatus is an on-line lithium-ion battery monitoring system which includes a computer, a high-precision battery resistance meter, a battery testing and controlling software, and so on.

2. Experimental

2.1. Mechanism

In order to find out the optimal battery’s remanufacturing point, an on-line lithium-ion battery monitoring system which is composed of control system and data acquisition system was built. The diagrammatic layout of battery control system is shown in Fig. 3. At the same time all data such as battery’s capacity, charging/discharging time and rate, cycling times, current and voltage in these processes can also be recorded by the system. The transformation of data and directions can be exchanged between the computer and the testing equipment by RS232. The proposed optimal battery’s remanufacturing point depends on mainly two parameters, namely, the battery’s capacity and resistance. A thoroughly study be carried out on the two mainly factors and on the relationship between them, then the optimal battery’s remanufacturing point can be determined.
2.2. Materials and equipment

The battery in the study is of LiFePO₄ cathode and carbon anode, with LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte. The battery is 1000Ah 3.2V with dimensions of 140mm×88mm×8mm, as shown in Fig. 4.

The cycling was carried out at 25°C which is controlled by air-conditioner, the charging/discharging process at C/3 and C/2, separately, through battery testing platform integrated with charging and discharging system, with a computer equipped with battery testing system software to monitor the cycling of the battery and acquire the data, as shown in Fig. 5. According to the auto industry, the battery reaches the limit of life when its capacity has dropped to 80%. So the cycling was carried out until the capacity dropped by 20%, at the same time lots of cycling data had been obtained. By analyzing these data, the optimal battery’s remanufacturing point can be found before the battery reached to end-of-life.

In the process of cycling, the internal resistance of the battery was measured at the state of discharging 3.2V by high-precision internal resistance meter, as shown in Fig. 5.

3. Results and discussion

3.1. Capacity fade analysis

The cycling induced capacity fade of a LiFeO₄ battery was studied and cycle-life models were established by Wang [1]. The function form of that model can be expressed as: Ψ_{cyc} = f(t, T, DOD, Rate). Which t is the cycling time, T is the test temperature, DOD is the depth-of-discharge, and Rate is the discharge rate for the cycle testing. However, in our experiment the DOD equals 90%, the discharge rate is C/2, T is a constant value, so the relationship between cycling number and capacity fade can be studied and the optimal battery’s remanufacturing point can be found. Fig. 6 shows the discharge curve obtained at a 90% DOD, C/2 rate with different number of cycles. The relationship between capacity fade and cycling number is represented in Fig. 7.

In Fig. 6, the discharge curve of the battery cells cycled at different cycling number shows that the battery’s performances become worse with the increasing of cycling number. When the capacity decreased to 80% of the original capacity, its performance can’t meet electric vehicle’s need, so it will be removed from electric vehicle. So the optimal battery’s remanufacturing point should be found before it.
capacity decrease to 80%. In Fig. 7, the overall curve can be divided into three parts, and make linear regression for data fitting, as shown in Fig. 8. There are two turning points and three curves represent the three working stages of the battery. Before the first turning point of A, the decrement rate of capacity fade is very fast, because the forming of SEI will largely increase the impedance of moving ability of Li⁺; after that, a slower capacity fade process was appeared, in this process the thickness of SEI will increase at a normal speed until the second turning point of B is coming up; after the second turning point, there are many other factors including electrolyte decomposition, current corrosion, severe film action and smaller hole can collapse the battery. So the second point (about 500-550 cycle number) can be used as the optimal battery’s remanufacturing point, it will largely decrease our remanufacturing cost and increase material reuse rate.

3.2. Impedance changing analysis

Based on the principle of electrochemistry, the basic equations of energy and power of Li-ion battery are [8]:

\[ W = nEF \sum R \]  \hspace{1cm} (1)

\[ P = \frac{VI}{\sum R} \]  \hspace{1cm} (2)

where, \( W \) is specific energy of battery cell; \( P \) is specific power of battery cell; \( E \) is electromotive force; \( F \) is Faraday constant (about 96500C/mol); \( \sum R \) is internal resistance; \( V \) is the working voltage; \( I \) is the working current.

From Eq. (1) and Eq. (2), increasing in \( \sum R \) means reduction in both specific energy and power. Therefore the direct measure of the capacity depreciation in the Li-ion battery is the increasing in internal resistance, which results from interfacial reaction and growth of a passive SEI layer at the electrode surface upon cycling [8, 9]. The change of internal resistance of Li-ion battery is shown in Fig. 9. When using equations to express the tendency of impedance, three fitted curves can be obtained, as shown in Fig. 10, which represent three working stages of Li-ion battery. Before the first turning point, the impedance increases rapidly, because of the fast forming SEI layer; then a modest increasing process was appeared, in this stage the battery is working at normal condition till the second turning point was coming up; after the second turning point the impedance of the battery was sharply increased, because of lots of severe damages such
as the electrolyte decomposition, current corrosion, severe film action and smaller hole in the battery. So the second point (about 500-550 cycle number) can be used as the optimal battery’s remanufacturing point.

From Fig. 8 and Fig. 10, the fitted curves on the tendency of impedance are very similar to the fitted curves on the tendency of capacity. There are also two remarkable turning points, and appeared at the same cycle number. There are must have a very close relationship between the two parameters, which has been shown in Fig. 11. Given they have also two turning points in Fig. 8 and Fig.10, a hypothesis that there is a linear relationship between the key parameters can be derived. At last, the experimental results have demonstrated it. So impedance increase of the Li-ion battery must be a key factor leaded to the discharge capacity fade, and eventually made it into a spent one.

4. Conclusion

In this report, we have presented the cycling testing results from an accelerated cycle life study on commercially available LiFeO4 batteries though battery testing system and internal resistance equipment. The relationship between cycle number and discharge capacity, impedance was investigated and described. The results show that the tendency of the discharge capacity and impedance of Li-ion battery are very similar at 90% DOD, C/2, 25°C. Two turning points are discovered, divided the whole change curve into three parts, which represents three different working stages. After the second turning point, the discharge capacity decreases largely, and the impedance increases sharply, the comprehensive result is Li-ion batteries are quickly reach to its end-of-life with severe collapse in electrodes, electrolyte decomposition and current corrosion. All these will increase the remanufacturing difficulties and even un-remanufactured, so it is very important to choose an appropriate remanufacturing point, and the optimal battery’s remanufacturing point (the second turning point about 500-550 cycle times) has been found.

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