Progress of State of Health Evaluation Methods for Lithium-ion power Battery

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Abstract. With the wide application of lithium ion battery in the energy storage system, much attention had been paid to the state of health (SOH) evaluation research. In this paper, the research advance of SOH evaluation methods for lithium-ion battery was reviewed. Several main SOH evaluation methods, including defining method, internal resistance method, AC impedance, voltage curve method, model method and some new methods, were discussed in detail. And finally the research direction of further progress in this area was proposed.

1. Introduction

Energy storage technology is emerging in recent years with the development of new energy, electric vehicles and power grid. It can not only provide conditions for large-scale grid-connection of new energy and distributed energy, but also is an important part of the construction of smart power grid, providing guarantee for power grid peak-modulation and frequency scaling, peak filling and power quality [1]. In the energy storage system, the lithium battery energy storage unit is applied after modularization and grouping by a large number of single batteries. Due to the differences in the performance of the individual cells in the group, the charge-discharge temperature and self-discharge rate of the cells are also different, and the energy density and life of the cells after the group are greatly reduced. The normal operation of energy storage system is greatly affected [2]. Therefore, the battery health of energy storage system becomes the most concerned problem. To establish the health status of lithium battery energy storage system evaluation method, real-time monitoring or predict the battery health status in advance, not only for screening and grading of the battery in service portfolio provided the scientific basis, but also can effectively prolong the service deadline, power battery reduce the total life cycle cost of power battery, improve the effectiveness and rationality of the resource utilization.

This paper mainly introduces the research progress of power battery health evaluation methods at home and abroad. This paper mainly discusses several main methods for evaluating the health status of lithium-ion power batteries.
2. Definition of battery health
Battery state of health (SOH) reflect the overall performance of the battery and release electric capacity under certain condition, the characterization of the battery life is an important parameter, refers to the standard conditions, power battery from full state at a certain ratio of discharge to the voltage produced by capacity ($Q_{\text{aged}}$) and new ($Q_{\text{new}}$) the ratio of the nominal capacity of the battery (such as 1-1) [3], with a value between $0 \sim 100\%$, battery SOH value, the greater the said battery performance, the better, the longer cycle life.

$$SOH = \frac{Q_{\text{aged}}}{Q_{\text{new}}} \times 100\%$$  \hspace{1cm} (1)

Where, $Q_{\text{aged}}$ represents the maximum capacity that the battery can currently release, and $Q_{\text{new}}$ represents the nominal capacity of the new battery.

3. Battery health status assessment method
Battery health is affected by many factors and the estimation is complicated. With the aging of battery, the change of SOH is mainly reflected in capacity and internal resistance. When the battery health deteriorates, its impedance will gradually increase, and the capacity, energy and power will attenuate to different degrees. Currently, SOH in lithium battery state of health assessment, mainly from the capacity, internal resistance, power, or cycles of one or more of the following as estimated parameters, according to the parameter change law of mathematical fitting regression, SOH evaluation algorithm is suitable for a particular cell, main evaluation methods: definition method, internal resistance method, ac impedance method, the voltage curve method, model method and some new methods, etc.

3.1. definition method
The definition method, also known as capacity method, is used to evaluate the SOH through the proportional relation of the variation of characteristic quantity such as battery capacity, energy and power [4]. Kong Soon Ng et al. [5] estimated the SOH of battery by using the maximum release capacity ($Q_{\text{max}}$) of lithium battery at SOC~100%. The $Q_{\text{max}}$ is equal to $Q_{\text{new}}$ when the new battery is used. Achmad Widodo et al. [6], when studying the intelligent prediction function of battery health detector, based on capacity method, adopted the ratio between current battery discharge capacity and initial battery discharge capacity as the standard to measure battery SOH.

This method can be used to evaluate the SOH of single battery with simple operation and high accuracy. However, it is not suitable for the evaluation of on-board battery group SOH. Repeated full charging and discharging will cause a certain degree of attenuation of battery performance [7].

3.2. Internal resistance method
To estimate the health status of the battery by internal resistance, the resistance value in the battery should be measured as accurately as possible, and then the correlation between the aging degree of the battery and the internal resistance should be determined. In order to obtain the internal resistance value of battery, the equivalent circuit model of internal resistance of li-ion battery is usually established, and the resistance value in the model is calculated by means of recursive least square method, so as to realize real-time identification of the internal resistance of battery. Equivalent circuit models mainly include time domain model and frequency domain model.

The time-domain model is usually used for estimating the internal resistance of battery SOH by the internal resistance method, of which the PNGV model is most commonly used [8], as shown in figure 1. Among them, OCV is the battery open circuit voltage, $R_0$ is the battery ohm internal resistance, $R_p$ is the polarization internal resistance, $C_p$ is the polarization capacitance, $C_b$ is the large capacitance representing the charge accumulation effect, and $U$ is the load voltage. The parameters of the model can be obtained by collecting the data of the composite constant current pulse experiment. However, the
frequency domain model is usually used to estimate the internal resistance of battery SOH by ac impedance method, and the specific content will be introduced in 3.3.

\[ R_{i,\text{new}}(\theta) = a e^{-b \theta} + c \]  
\[ R_{i,\text{act}} = k_d R_{i,\text{new}}(\theta_{\text{act}}) \]

The internal resistance method realizes the online evaluation of the power battery's health status, but the implementation conditions of this method are not easy to meet. It not only requires the high-precision control of some parameters, but also ignores the influence of one or several parameters, which may bring inevitable estimation error.

### 3.3. Alternating current impedance method

Ac impedance spectroscopy is a frequency domain measurement method. More dynamic information and interface structure information can be obtained by studying the electrode system by measuring the impedance spectrum in a wide frequency range. The change of electrode structure is closely related to battery performance, so it is feasible to apply the ac impedance method to the study of battery state detection.
Researchers at home and abroad used the ac impedance method to estimate the battery SOH. First, the equivalent circuit in the frequency domain was established. The most commonly used Randles model [11] is shown in figure 2, where $R_0$ is the ohmic impedance, $R_{ct}$ is the electrochemical impedance of the charge transfer process, $C_{ct}$ is the dual-layer element, and $Z_w$ is the Warburg impedance of the diffusion and mass transfer process. Nyquist plots of the battery model were obtained through electrochemical impedance spectroscopy experiments, and the model parameters of the battery with different aging degrees were identified. Then fuzzy theory or neural algorithm were used to analyze the collected data information to determine the battery health.

In 2010, Bharath Pattipati et al. [11] established the Randles model of battery. The experimental results show that the medium and low frequency impedance increases with the increase of cycle times of battery. 2013, Zhang CP[12] by electrochemical impedance test of lithium ion battery, such as pilot use lithium ion battery electrochemistry impedance model is established, impedance model parameters are studied along with the change of battery aging degree properties, the results showed that the electrochemical impedance and diffusion resistance increases with the increase of the cell cycle significantly, while the ohmic resistance is almost the same, this conclusion is further verified the battery health status and their internal impedance relationship.

Anyhow, ac impedance test battery internal impedance of components can be obtained, compared with other methods for battery information more comprehensive, and current research of ac impedance spectrum method to evaluate SOH is not mature enough, not only need a large amount of data collection and analysis to get the battery characteristics, and equipment demand is higher, so the method is not suitable for on-board battery and online evaluation.

3.4. Voltage curve method
Voltage curve method is through the external characteristics of the battery charge or discharge curve to determine SOH, Dong MZ[13], such as the guiding thought of pattern recognition, think that the battery charge and discharge characteristics consistent also has same chemical properties, on this basis, using statistical pattern recognition method, set up according to the battery charge and discharge pressure characteristic curve for waveform recognition, the mathematical model to evaluate the battery capacity and SOH. Xu WJ [14] used the characteristics of voltage difference when the battery was charged or released with the same power under different health levels, and established the voltage curve fitting method to estimate the current SOH of the battery. Based on the single battery cycle test, the voltage reference curve is fitted by neural network and the adaptive method is added to estimate the SOH.

3.5. Model law
Model method is based on the study of the cell aging mechanism, through the analysis of a large number of experimental data, build capacity attenuation and inside the battery parameters, the parameters such
as temperature, ratio, depth of discharge, self-discharge function relationship, to realize the estimate of the battery state of health, including electrochemical model, empirical model and equivalent circuit model, etc. The electrochemical model describes the aging law of battery through the electrochemical reaction mechanism inside the battery. The empirical model takes the external factors that affect battery performance as input and capacity as output. The circuit model is the direct equivalent of the battery, which can be embedded into the battery management system and has achieved online SOH prediction.

In 1994, Fuller et al. [15] used the “first principles” electrochemical model to estimate the capacity of li-ion polymer batteries. Spotnitz et al. [16] introduced the growth of SEI film resistance into Fuller model to study the relation between the change of battery impedance and capacity attenuation. In the same period, Ramadas et al. [17] comprehensively considered the influence of two factors of battery charge-discharge ratio and reduction of active substances on battery performance. Based on the electrochemical reaction inside the battery and the increase of SEI film resistance in the circulation process, a semi-empirical model of battery capacity attenuation was established.

2005, B.Y. Liaw[18] studied the capacity attenuation based cycle life model, on the basis of the analysis of large amounts of data, quantitative research is the battery SOC, SEI film resistance and internal factors such as lithium ion diffusion coefficient of the effects on the cell cycle capacity attenuation, and quantitative analysis of the external factors such as temperature, ratio and maximum charge voltage and discharge depth capacity caused by the recession, and predicts the experience model of battery capacity decline.

Li HL et al. [19] comprehensively considered the influence of temperature and multiplier on the attenuation of battery capacity, and conducted the accelerated life test for 18650 lithium-ion batteries. On the basis of Arrhenius formula and the existing experience formula of acceleration life, the experimental data were fitted and regression analysis was conducted, and the power-function relation between temperature, multiplier and battery capacity attenuation was obtained (as shown in equation 1-4), and an empirical model of lithium ion battery capacity degradation was established.

\[ Cr = \frac{C_0}{(1 + AT)^N_c} \]

Where: Cr is capacity attenuation rate; T is the absolute temperature; I is the discharge current; Nc is the number of cycles; All the others are constants, which can be obtained by the acceleration test data fitting. Using the external factor input model greatly reduces the complexity of the model.

In conclusion, the model method takes multiple factors of battery aging as input simultaneously, and realizes the comprehensive effect of multiple parameters on battery capacity attenuation. The estimation accuracy is relatively high, but it is mainly limited to laboratory evaluation. Although the circuit model realizes the SOH online prediction of on-board batteries, the prediction accuracy is not high.

3.6. Other methods

In recent years, in terms of the estimation of battery health, scholars at home and abroad have developed some new estimation methods while studying the traditional estimation methods, and combined them with the traditional methods to improve the estimation accuracy of battery SOH.

In the process of qualitative or quantitative analysis of battery SOH, some mathematical tools will be used, including kalman filtering method [20], fuzzy logic [21], artificial neural network method [22], probability density function [23], support vector machine method [11] and so on. Among them, kalman filtering method can use considerable measurement to correct the estimation error, which has achieved certain achievements in estimating battery SOC, and has attracted much attention in estimating battery SOH. Dai haifeng et al. [24] of tongji university estimated the life state of the battery on the basis of collecting current, voltage and other data in the experiment by using double-kalman filtering algorithm, and the estimation accuracy is relatively high.

4. Conclusion

Large energy storage systems such as electric vehicles, energy storage power station's developing, the lithium ion battery health status evaluation research, much attention has been paid a lot of researchers both at home and abroad to establish various SOH assessment methods, including the definition, internal resistance, ac impedance method, the voltage curve method, model method and some new methods,
such as different methods has its advantages and disadvantages and application fields. However, at present, most of the domestic and foreign research on battery SOH is in the laboratory stage, especially the definition method, impedance method and model method with higher precision, and the actual application environment of power battery cannot meet the estimation conditions. Even if the internal resistance method realizes the real-time estimation of vehicle battery SOH, the accuracy is low.

Therefore, from the perspective of combination of multiple evaluation methods, organic combination of two or more evaluation methods to achieve the unity of evaluation accuracy and application function will be the research direction of future power battery health evaluation methods.

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