A Comprehensive Review of Health Indicators of Li-ion Battery for Online State of Health Estimation

Wei Liu, Yan Xu, Senior Member, IEEE
School of Electrical & Electronic Engineering
Nanyang Technological University, Singapore
wei.liu@ntu.edu.sg, xuyan@ntu.edu.sg

***Abstract*—Lithium-ion batteries have been widely used in various applications, especially in electric vehicles and battery energy storage systems (BESS). Reliable and accurate estimation of battery online state of health (SOH) becomes increasingly important. To realize this task, a variety of approaches have been proposed and several review papers have been addressed to summarize and classify these approaches. To the best of our knowledge, all current works concentrate on classifying estimation methods while no work has been done to review the health indicators (HIs) that are used for estimation. Classifying the HIs by how they are extracted, however, is of great importance because each HI is only effective in specific application situations. This paper, therefore, is to comprehensively review the existing HIs and make a classification based on how they are extracted and where they can be effectively used.**

***Keywords*—Li-ion Battery, online estimation, state of health, health indicators**

I. Introduction

Batteries, as one type of energy storage systems, have been widely utilized in various areas, e.g. electric vehicles (EVs) and power grids with distributed generation [1]. Among all the types of batteries, li-ion battery is most widely used due to the favorable energy efficiency, high power density, high voltage, low self-discharge rate and relatively long lifetime [2], [3]. To avoid catastrophic failure and prolong battery durability, it is very important to determine battery state of health (SOH), which describes the degree of performance deterioration of a battery compared to its initial or ideal condition [4].

Battery SOH estimation for EVs has been extensively studied with different approaches and several review studies were done [4]-[12] to comprehensively summarize and classify these approaches on the basis of estimation methods. Fig. 1 illustrates the general structure of SOH estimation. As is shown in Fig. 1, an approach for SOH estimation has two important components: 1) health indicators (HIs); 2) methods used to fit HIs with the SOH. To the best of our knowledge, all current works concentrate on the second part, namely the estimation methods. Basically, the major methods used for SOH estimation can be categorized into direct measurement method, model-based method and data-driven method. Little work has been done to review and analysis existing HIs that are used for SOH estimation.

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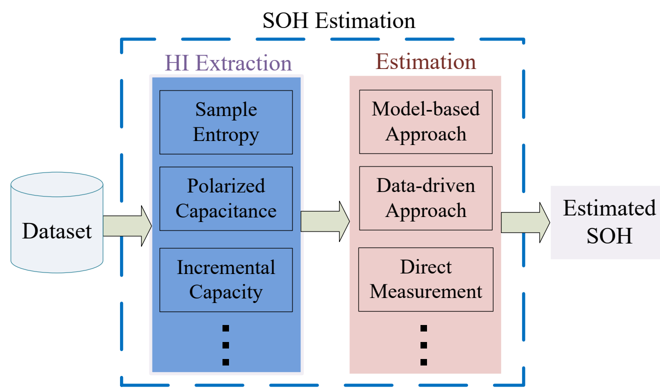

Fig. 1. Schematic diagram of battery online SOH estimation

However, it is of great importance to make a summary on existing HIs because each HI is only applicable to certain situations. Without paying much attention to estimation methods, this review comprehensively explores existing SOH estimation approaches from the perspective of HIs. In addition, the application scenarios of each HI are analyzed based on the extraction process and a comparison is then concluded. This paper aims to accomplishes following tasks:

i.) Identify the extraction processes of existing HIs and analyze their advantages and disadvantages.

ii.) Classify HIs by extraction process and discuss the specific application scenarios of each HI.

iii.) Highlight the major restrains of existing HIs and suggest future research trends.

This paper comprises four sections. Section II gives the commonly used definitions of battery SOH. Section III comprehensively studies the existing HIs. Section IV draws a conclusion and gives some suggestion on future research. The work of this paper would majorly benefit engineers dedicated to online battery SOH estimation in practical applications. Being conscious of the major merits and demerits of HIs studied in this paper, they will be able to efficiently select effective HIs and corresponding estimators that are suitable for their individual situations.

II. Definition of State of Health

Due to complex electrochemical reactions shown in Fig. 2, battery usage triggers some irreversible changes in the characteristics of internal components, e.g. electrolyte and electrodes [13]. Such changes as solid-electrolyte interphase (SEI) formation undermines battery performance and are therefore seen as causes of health deterioration. The state of health (SOH), which indicates the extent of deterioration, can be described as the current performance of an aged battery compared to the performance of the battery at initial state or ideal condition [14]. However, there is no consensus on the quantitative definition of SOH. Any feature that changes significantly with battery aging, such as maximum releasable capacity or internal resistance [5] , can be utilized to identify SOH.

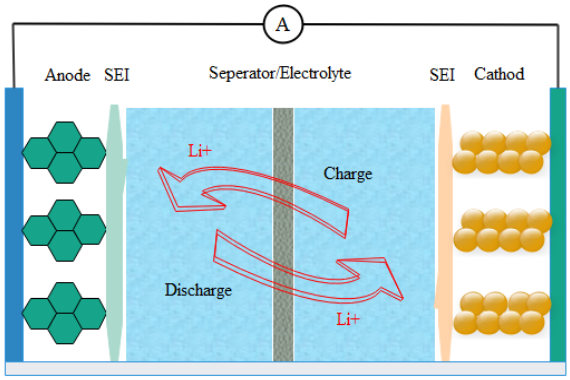

Fig. 2. Internal electrochemical process of charge/discharge

A. SOH based on internal resistance

As the battery degrades, the internal resistance gradually increases which consequently reduces the maximum output current. Dai *et al.* [15] adopted internal resistance to define SOH of batteries used in hybrid electric vehicles (HEVs). In this approach, battery end of life (EOL) is reported when internal resistance rises to 160% of initial resistance. The SOH is therefore expressed as

$$SOH = \frac{R_{EOL} - R_{current}}{R_{EOL} - R_{new}} \times 100\% \tag{1}$$

where R_{EOL} is the internal resistance at EOL, $R_{current}$ and R_{new} are the current and original internal resistances respectively.

B. SOH based on remaining capacity

Compared to internal resistance, remaining capacity is more commonly used to define SOH in literature. Chen *et al.* [14] defined SOH as the ratio of remaining capacity to nominal capacity while Okoshi et al. [16] used the ratio of present capacity to initial capacity to define SOH, respectively shown as (a) and (b) in (2).

$$\begin{cases} SOH = \dfrac{C_{current}}{C_{nominal}} \times 100\% \quad (a) \\ SOH = \dfrac{C_{current}}{C_{initial}} \times 100\% \quad (b) \end{cases} \tag{2}$$

where $C_{current}$ is the capacity at present, $C_{initial}$ and $C_{nominal}$ are respectively the initial capacity and nominal capacity.

In practical applications, a battery is discarded when the remaining capacity decreases to a certain threshold (e.g. 70% or 80%), at which point the battery is reported to reach EOL. By defining the SOH at ideal condition as 100% and the SOH at EOL as 0%, Waag *et al.* [4] proposed to define the SOH as

$$SOH = \frac{C_{current} - C_{EOL}}{C_{nominal} - C_{EOL}} \times 100\% \tag{3}$$

where $C_{current}$ is the capacity at present, C_{EOL} is the predefined capacity at end of life and $C_{nominal}$ is the nominal capacity.

Although different in mathematical expression, both definitions shown in (2) and (3) are based on remaining capacity. Since nominal capacity and discarding capacity are predefined before the battery is in use and initial capacity can be measured by a reference discharge cycle at beginning, estimating battery SOH is equivalent to estimating remaining capacity of the battery.

III. Battery Health Indicators

A. Direct HIs based on offline measurement

Battery capacity can be directly measured by coulomb counting [17], but it requires the full discharge curve from SOC 100% to 0%. As a result, coulomb counting is rarely implemented for a battery in operation. In addition to capacity, the internal resistance can also be directly measured by Electrochemical Impedance Spectroscopy (EIS), which applies a voltage signal over a range of amplitude (e.g. between 5 and 50 mV) and frequency (e.g. between 0.001 Hz to 100,000 Hz) to the study the electrochemical behaviors of the battery [18]-[22]. EIS method, however, can only be conducted offline and is therefore not feasible for online estimation. For a battery in online operation, the capacity and internal resistance are both difficult to be measured directly.

B. Indirect HIs based on online measurement

Since direct measurement is almost impossible for on-board application, indirect estimation becomes crucial and necessary, revealing the importance to study other HIs that can reflect battery degradation and meanwhile are able to be extracted online. Basically, the variables that can be real-time measured by battery management system (BMS) comprise voltage, current and temperature [5]. Any HI for online SOH estimation should be a derivative of voltage, current and temperature. According to the value of output current, battery operation modes are divided into charge mode, discharge mode and rest mode. In this section, HIs that have been developed are categorized and analyzed based on the operation mode when they are extracted.

TABLE I summarizes existing HIs and illustrates a comparison between these HIs. The operation interval represents the length of operation range required for HI extraction. Predefined assumptions during HI extraction are also presented. Such assumptions make HI extraction and SOH estimation easier to achieve, but meanwhile confines the application scenarios of HIs. Complexity incorporates the complexity that HI is extracted and the complexity to map HI to SOH. Practicality for online application signifies the range that HI can be used under practical load conditions.

1) HIs extracted in charge mode

The charge profile of an EV can be controlled at different aging stages, making SOH estimation easier when battery is charging. Ref. [23] proposed a model-based method to estimate the SOH using the voltage curve of CC charging stage at different life cycles. The length of the constant current charge time (CCCT) and the constant voltage charge time (CVCT) were extracted as the health indicators to demonstrate the capacity degradation [24], [25]. With Gaussian Process regression, a vector of time spots [26] at specific voltages were employed to measure the capacity of a battery in CC operation. The battery is set to charge with a constant current over short periods and the time values at several equispaced voltage points are used as HIs to predict capacity. The details of abovementioned HIs extraction process are presented in Fig. 3.

The CCCT and CCVT are only applicable when the battery is charging at CC stage from low cut-off voltage to high cut-off voltage or CV stage until current drops to a predefined threshold, while the HI proposed in [26] can be extracted with only partial charge process. Generally, a desirable accuracy can be achieved with a short period of galvanostatic charge (as short as 10 seconds), which guarantees the extensive application range of this HI. The weakness is that the estimation accuracy is highly sensitive to the defined starting voltage.

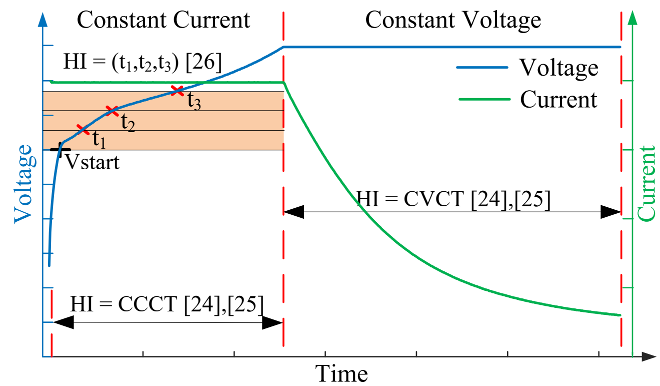

Fig. 3. Schematic diagram of HI extraction based on charge process

TABLE I
COMPARISON OF EXTRACTED HIS

HIs	Ref.	Operation mode	Operation interval	Assumptions	Complexity	Practicality for online estimation
CCCT/CVCT	[24],[25]	Charge	Full Cycle	Constant Current/Voltage	Low	Medium
Voltage & current series	[27]		Full Cycle	None	High	Low
dQ/dV at IC peaks	[28],[29],[30]		Cover IC peaks	Constant Current	Low	Medium
SOC positions at IC peaks	[31]		Cover IC peaks	Constant Current	Low	Medium
Time spots at specific voltages	[26]		10 seconds	Constant Current	Low	High
Sample entropy	[32]-[34]	Discharge	Full Cycle	Constant Current	Low	Low
TIEDVD	[35]		3.80-3.87 V	Constant Current	Low	High
DVDETI	[36]		500 seconds	Constant Current	Low	High
Voltage & current series	[37]		Full Cycle	None	High	Medium
Voltage & current series	[45]	Charge & discharge	Full Cycle	None	High	Low
Voltage series	[43]		Full Cycle	Constant Current	High	Medium
Internal ohmic resistance	[41]		SOC 30-80%	None	High	Medium
Polarized resistance	[41]		SOC 30-80%	None	High	Medium
Diffusion capacitance	[48]		3.5-4.05V	None	High	Medium
Fusion of multiple HIs	[42]		3.9-4.1V, etc.	Constant Current/Voltage	Medium	High
Voltage, current & temperature series	[47]		SOC 10%-90%	None	Medium	Medium
Aging cycles	[49]-[53]	Others	N.A.	Constant Current	Low	Low

Considering the characters of battery electrode materials, Li *et al.* [27] built a model to fit voltage vs charged capacity curve at different aging stages. The parameters that need to be identified have clear physical meanings including the charged capacity and voltage corresponding to each phase transition process inside the battery. Variation of identified parameters can then be used to calculate degraded capacity. Voltage and current during charging process are used in this approach to identify parameters and the charging process must enclose all the phase transitions. Incremental capacity analysis (ICA) and differential voltage analysis (DVA) techniques based on charging curve are also widely used for SOH estimation [28]-[31]. ICA or DVA builds the IC or DV curve, which describes the relationship between open circuit voltage (OCV) and dQ/dV or dV/dQ. The peaks on IC or DV curve reflect significant information of the SOH and are therefore used as solid HIs [28]-[30]。

Apart from peak values, it was also concluded [29], [30] that the voltage location of peaks on IC curve can be used as a strong indicator of capacity degradation. Zheng et al. [31] replaced OCV with SOC and concluded that SOC positions of IC curve peaks rarely change at different aging cycles. Battery SOC can therefore be directly decided based on IC curve. Simultaneously, battery capacity can be calculated according to the relationship between maximum releasable capacity and charged capacity given SOC variation. An example of IC curves at different aging cycles is illustrated in Fig. 4. As is shown, the SOCs at two marked feature points rarely vary with battery degradation, therefore the estimated capacity can be computed as

$$C = \frac{\int_{t(1)}^{t(2)} I(t)dt}{SOC(2) - SOC(1)} \quad (4)$$

where C is the current capacity, $SOC(1)$ and $SOC(2)$ are respectively the SOC at first and second feature point.

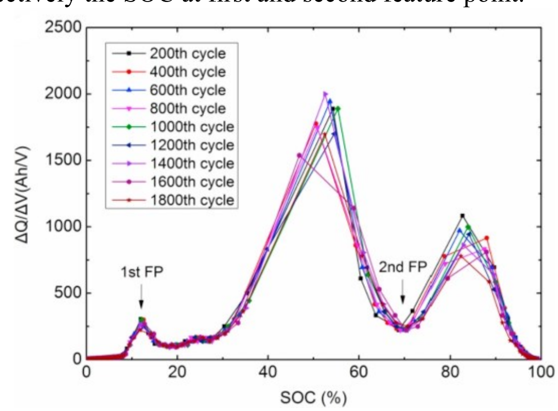

Fig. 4. IC vs SOC at different aging cycles of a LiFePO4 battery [31]

Mathematically, ICA based approaches compute the derivatives of charged capacity with respect to OCV. Due to the differential process, a diminutive error of BMS measurement may lead to highly undesirable results. In addition, the battery must operate in a certain range of voltage or SOC that encompasses the peaks on IC curve. Therefore, ICA or DVA may be suitable for SOH estimation of EVs but it is not appropriate for SOH estimation of BESS in power grids.

2) HIs extracted in discharge mode

Compared to charge mode, discharge mode of an EV is more arbitrary and dependent on ambient conditions. It is therefore more difficult to develop HIs from discharge curve. Many current approaches make an incautious assumption that the battery discharges with a constant current.

Observing that the discharge curve is gradually distorted as the battery ages, sample entropy of discharge voltage curve [32]-[34] was therefore applied as the HI to demonstrate battery degradation. Sample entropy is calculated as

$$SampEn = -\ln\left(\frac{\sum_{i=1}^{N-m} A_i^m(r)}{\sum_{i=1}^{N-m} B_i^m(r)}\right) \tag{5}$$

where m , r and N are parameters predefined, $A_i^m(r)$ and $B_i^m(r)$ represent the probability that two sequences match for m and $m+1$ points, respectively.

Current and temperature are not embodied in sample entropy of discharge voltage. Hence it can be used in limited situations where a reference full discharge is conducted. The time interval of equal discharging voltage difference (TIEDVD) [35] was proposed to quantify capacity degradation. Afterward, Liu *et al*. [36] proposed to extract a new HI named discharge voltage difference of equal time interval (DVDETI) to identify SOH. The results both suggest a strong relationship between remaining capacity and extracted HI, indicating that SOH can be estimated using TIEDVD or DVDETI. The details of HIs extraction based on discharge process are presented in Fig. 5. Current is not demonstrated with voltage because it is assumed to be a constant.

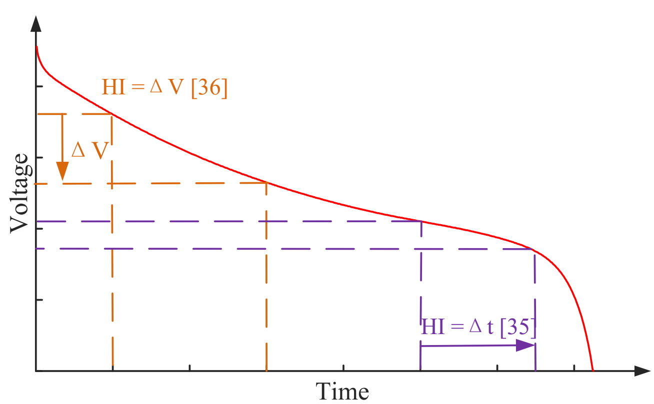

Fig. 5. Schematic diagram of HI extraction based on discharge process

The superiority of TIEDVD and DVDETI over sample entropy is that they are extracted from only partial discharge curve. The range of time interval and discharge voltage difference are predefined subject to the demand of users as well as the available data acquired by BMS. However, the proposed HIs take into account voltage variation while ignores discharge current profile and temperature. The application scenario is therefore limited because they only function when load profile in operation must be the same as that of offline training.

Based on both discharge voltage and current curves, Zou *et al.* [37] proposed a model-based approach to simultaneously determine SOC and SOH. Sample entropies of both voltage and current were collected as multiple HIs [38] to index SOH with the help of a data-driven approach. Both voltage and current are used for SOH estimation, so these HIs are well applicable to dynamic load profiles.

3) HIs extracted in charge and discharge mode

Some HIs that can be used both in charge and discharge mode were also proposed. Ref. [39] applied recursive least squares (RLS) method to identify parameters of Thevenin model of a battery, which is the best battery model considering the complexity, accuracy and robustness [40]. The diagram of Thevenin model is shown in Fig. 6, where V_{oc} and V_o represent the open circuit voltage and terminal voltage, respectively. I is the output current, C denotes the polarization capacitance, while R_0 and R_1 are respectively the ohmic internal resistance and polarization resistance. The identified ohmic internal resistance is then used to indicate battery SOH and compared to the SOH defined by capacity.

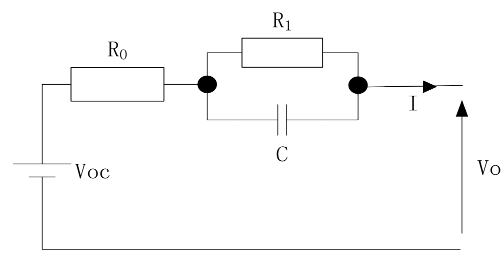

Fig. 6. Diagram of Thevenin model

Pan *et al.* [41] also used Thevenin model to simulate battery dynamic characters and RLS was applied to identify model parameters. Differently, both ohmic internal resistance and polarized resistance are utilized as multiple HIs to estimate battery SOH. These approaches are applicable to dynamic load profiles because ohmic internal resistance or polarized resistance are used as HI and they can be obtained under dynamic load profiles with the help of ECM. The drawback is that the battery SOC must range between 30% and 80% because the internal resistance is the average value during this range. Moreover, the accuracy of estimation is highly dependent on the precision of constructed ECM.

Ref. [42] extracted and fused 10 HIs to indicate battery capacity, where 4 HIs are extracted from CC discharge curve, 4 HIs from CC charge curve and 2 HIs from CV charge curve. The similarity derived from gray relational analysis between each HI and capacity is above 0.5, implying that every HI is effective to represent capacity. Through the kernel principal components analysis algorithm, one fused HI is generated and turns out to have a higher similarity with capacity. The major advantage of the fused HI is that it is easy to extract when battery works at CCCV charge or CC discharge conditions. The idea to incorporate multiple HIs as one final HI is another important contribution, resulting an improvement in estimation accuracy at the same working conditions.

Assuming that battery works at CC charge or discharge profile, probability density function of voltage data [43] was proposed to estimate battery SOH. The mathematical basis of probability density function approach is identical to that of ICA/DVA methods, but it avoids the computation of derivative. The restrain of this method lies on the assumption of CC charge or discharge. You *et al.* [44] used the real-time measured voltage, current and temperature to fit the capacity with neural network. This method is tested in various dynamic load profiles corresponding to realistic driving patterns. Using voltage and current curve, a particle filter based on Monte Carlo sampling [45] was developed to estimate battery SOC and SOH at the same time. This approach is also viable for SOH estimation dynamic load profiles. Looking deep into the internal electrochemical properties of degraded batteries, two model-based approaches were presented [46], [47] for capacity estimation with the help of real-time current, terminal voltage and temperature.

Given the observation that diffusion capacitance is highly correlated to the SOH, Chen *et al.* [48] applied diffusion capacitance to estimate battery SOH. The diffusion capacitance is calculated based on a resistance-capacitance circuit model and voltage and current curves of either charge or discharge process. The diffusion capacitance can be obtained in dynamic load profiles, making it suitable for SOH estimation when battery is randomly charged or discharged.

4) *Others*

Without exploring the details of battery performance at different aging cycles, some literatures applied distinguished algorithms to map capacity directly to number of cycles [49]-[53]. The commonality of these approaches is that the batteries are repeatedly charged and discharged with reference profiles. It is worthy pointing out that the proposed methods [50], [51] are both capable to indicate battery capacity without offline aging test. However, these approaches neglect the random working conditions of batteries in practical use and are therefore only effective with restrained load schemes.

IV. Conclusion and Future Research

In this paper, existing battery HIs used for online SOH estimation are comprehensively reviewed and following few conclusions can be drawn:

1) Most HIs and estimators are developed specifically for EV applications, while little work has been done to extend the research field to other applications.

2) More studies propose to estimate battery online SOH using HIs extracted from charge process than discharge process.

3) Model-based approaches are often capable to estimate online battery SOH with random load profiles, while data-driven approaches sometimes have a strict constrain on the load conditions.

4) Generally, the complexity of HIs used for data-driven approaches are relatively lower and that of HIs used for model-based approaches are higher.

Based on the abovementioned conclusions, this review also gives some suggestions in terms of future research. Firstly, since data-driven approaches are superior to model-based methods in simplicity and better accuracy, further study is needed to extract novel HIs that are suitable for data-driven approaches. To achieve a better adaptability, predefined assumptions like CC are not preferred. Therefore, all the operation factors should be considered when extracting HIs. To extract valid HIs, a more thorough understanding into the intrinsic electrochemical principals of battery degradation should be accomplished for different battery types, which may also contribute to the construction of a more accurate ECM and therefore achieving better estimation accuracy

Moreover, techniques of denoise filters and intelligent algorithms are developing rapidly in recent years. More advanced denoise techniques can be introduced to reduce the noise of raw data from BMS and novel intelligent algorithms can be applied to improve the estimation accuracy or deal with situations with less input data. With the same available information, multiple HIs will also contribute to enhancing the estimation performance.

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