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Entropy-induced temperature variation as a new indicator for state of health estimation of lithium-ion cells

Yao Wu*, Andreas Jossen

Institute for Electrical Energy Storage Technology, Technical University of Munich, 80333, Munich, Germany

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ABSTRACT

Conventional state of health (SoH) estimation is often based on the capacity or resistance of lithium-ion cells. However, online capacity or resistance measurements are rarely achievable in electric vehicles. An alternative indicator should replace capacity and resistance to make online SoH diagnosis more manageable.

In this paper, we introduce a novel SoH indicator, which is extracted from the cell temperature variation rate curve during the constant current charge process. There are two observable cooling areas in the temperature variation rate curve. The distance between these two areas, defined as t_{min}, could serve as a gauge for cell SoH if electrode active material loss is negligible during the operation. In order to validate the assumption, test data from both calendar aging and cycle life tests on a commercial lithium-ion pouch cell is utilized. From the 544 aging data units, a linear correlation is observed between t_{min} and SoH with a product-moment correlation coefficient of 0.954. The same correlation is found for all the tested cells under different aging conditions, which makes t_{min} a promising indicator for SoH estimation.

1. Introduction

With high energy and power densities and a long life span, lithium-ion batteries have been used in various industrial areas. In an earlier phase, their application is mainly limited to small portable devices. In recent years, however, a growing number of lithium-ion batteries are used in electric vehicles (EV) [1]. Whatever the application, lithium-ion batteries suffer from inevitable degradation mechanisms, which leads to poor performance and even safety issues. Battery management systems (BMS) are therefore developed to monitor battery state of health (SoH) and state of charge (SoC).

SoH quantifies the performance difference between the present condition and the initial condition of a battery cell or module [2]. The generally accepted SoH definition is the ratio of the actual capacity (C_{actual}) and the initial capacity ($C_{initial}$), which suits for applications where the battery energy plays a more important role [3].

$$SoH = \frac{C_{actual}}{C_{initial}} \tag{1}$$

SoH can be alternatively defined with battery resistance increase. However, due to different operational conditions and battery materials, capacity loss and resistance increase may develop at different relative paces, causing incomparable health evaluation based on capacity and resistance [4]. Additionally, it is almost impossible to conduct online capacity measurement in EVs due to the dynamic workload and expensive cost [5]. Hence, it is beneficial to find an alternative indicator for SoH estimation with online implementation potential.

According to Ref. [6], SoH estimation methods can be categorized into experimental techniques and adaptive battery models. The former stores the lifetime data and relies on the previously gained knowledge about the operation performance of the lithium-ion cell. The latter determines SoH through calculation from degradation-sensitive parameters of the lithium-ion cell, which requires usually a high computational load. Kalman Filters and Neural Networks are typical examples of adaptive battery models [7–9]. In the experimental techniques, some features of the lithium-ion cell have been suggested for SoH estimation. In Ref. [10], open circuit voltage (OCV) is reported as an optional indicator for SoC as well as SoH estimation. However, the OCV measurement requires an extremely low current and thus takes much time. Incremental capacity analysis [11] and differential voltage analysis [12,13] have also been utilized for SoH estimation, but they

* Corresponding author.
E-mail address: yao.wu@tum.de (Y. Wu).

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need a low operation current as well and vary a lot with cell chemistries. Eddahech et al. [14] have investigated the constant voltage (CV) charge step of cells in a calendar aging study and correlated the current and duration of CV with SoH. This correlation, however, has not been validated with cells from cycle life tests. Zhou et al. [5] have introduced mean voltage fall during discharge as a new indicator for SoH determination. To achieve a satisfactory linear correlation, the indicator needs to go through mathematical transformation, which makes the experimental method more complex.

In this work, we offer a novel SoH indicator, which can be easily obtained from a cell surface temperature measurement during a constant current (CC) charge process. Temperature monitoring is commonly included in any BMS to prevent accelerated battery degradation and thermal runaway due to extreme temperatures. A combination of temperature monitoring and SoH estimation is optimal for BMS.

The rest of this paper is organized as follows: Section 2 provides a theoretical background for the new SoH indicator. Section 3 describes the experimental work used to validate the assumption. Section 4 depicts why the new indicator is proposed for SoH estimation and the validation results with our experimental data. Finally, the conclusions are drawn in Section 5.

2. Theory

The heat generation of a lithium-ion cell during operation includes four sources, i.e. the Joule heat, the reversible reaction heat, the side reaction heat and the mixing heat. Since the aging effect during one cycle is usually indistinctive and the mixing process is not significant during CC operation, the last two sources can be neglected. Hence, Eq. (2) describes the heat generation of a cell under CC charge or discharge [15].

$$\dot{Q} = \dot{Q}_{jou} + \dot{Q}_{re} = I^2R + \frac{IT}{nF}\Delta S \tag{2}$$

where $\dot{Q}$ is the heat generation rate, $\dot{Q}_{jou}$ is the Joule heat, $\dot{Q}_{re}$ is the reversible reaction heat, I is the current, R is the charge or discharge resistance, T is the cell temperature, n is the number of exchanged electron per mole, F is the Faraday constant (96485 C/mol) and ΔS is the entropy change.

The Biot number (Bi) is the ratio of the internal thermal resistance of a body to its boundary layer thermal resistance [16]. It is defined as:

$$Bi = \frac{hL_C}{k_b} \tag{3}$$

where h is the heat convection coefficient, L_C is the characteristic length, which equals the quotient of the body volume and the body surface area and k_b is the thermal conductivity of the body.

If the $Bi < 0.1$, the resistance to conduction within the body is much less than the resistance to convection across the surface fluid boundary layer. Therefore, the temperature distribution inside the body can be considered as uniform at any time during a transient process [17]. In our case, the cell is a thin pouch cell with a L_C of 0.00285 m. The cross-plane thermal conductivity $k_b = 3.4$ W/m/K is obtained from Ref. [18]. A forced convection is applied to the cell in a climate chamber at 25 °C. The heat convection coefficient $h = 24.927$ W/m^2/K is extracted from Ref. [15]. With the above conditions, the tested cell has a Biot number of 0.021, which is smaller than 0.1. Therefore, the lumped capacitance method can be applied to the examined cell.

The temperature variation rate dT/dt of a cell can be expressed in Eq. (4) with the lumped capacitance model. It is influenced by the Joule heat, the reaction heat and the heat dissipation to the environment.

$$\frac{dT}{dt} = \frac{\dot{Q}}{mc_p} - \frac{hA}{mc_p}(T - T_{env}) \tag{4}$$

Combining Eq. (2) and Eq. (4), the temperature variation rate can be described with Eq. (5).

$$\frac{dT}{dt} = \frac{1}{mc_p}\left(I^2R + \frac{IT}{nF}\Delta S\right) - \frac{hA}{mc_p}(T - T_{env}) \tag{5}$$

where m is the cell mass, c_p is the cell heat capacity, A is the cell surface area, T is the cell temperature and T_{env} is the environmental temperature. If the cell temperature change is limited to 5 °C, the heat capacity c_p and the heat convection coefficient h could be assumed as constant [15,19].

3. Experimental

Lithium-ion pouch cells of the type SLPB50106100 with a nominal capacity of 5 Ah from the manufacturer Kokam were investigated for both calendar aging and cycle life aging. The active materials of the cell are composed of graphite at the negative electrode and blended material $LiCoO_2/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (LCO/NCA) at the positive electrode.

Table 1 provides an overview of the calendar aging test. The cells were charged to 50% SoC and stored at 25 °C, 40 °C and 55 °C, respectively. Table 2 shows the cycle life test with stress factors, temperature and discharge rate. In the cycling profile, cells were charged with 1C (corresponding to 5 A) CC to 4.2 V and then switched to a CV charge at 4.2 V until the current dropped below 0.05C. Thereafter, a 1C, 3C or 5C CC discharge procedure was applied to the cells until the voltage reached 2.7 V. After 5 min rest, the next charge step began. The cycle life test was conducted at 25 °C and 40 °C for 1C discharge cycling. At least two cells were tested under each aging condition in Tables 1 and 2.

Performance tests were carried out every two weeks to examine the capacity of the cells. The cell actual capacity was measured as follows: cells were charged with 1C CC to 4.2 V and then switched to CV at 4.2 V. When the current fell below 0.05C in the CV phase, cells were considered as fully charged. After 10 min rest, a 1C CC was employed to discharge the cells to 2.7 V, followed by a CV phase to further discharge the cell until the current declined to 0.05C. The total capacity from the CC and CV discharge steps was regarded as the cell actual capacity, to minimize the influence from resistance increase on the capacity. Before and after the aging tests, a 1C pulse test was carried out on each cell to measure its 10s-charge/discharge resistances at various SoCs. Cycle life tests, performance tests and pulse tests were all conducted with a Cell Test System (CTS) by BaSyTec. Performance tests and pulse tests were performed in a climate chamber at 25 °C. During cycle life tests and performance tests, a negative temperature coefficient (NTC) thermistor from EPCOS AG was attached to the surface center of each cell to monitor its surface temperature (see Fig. 1). The NTC thermistor has a resistance tolerance within ±1% between 0 °C and 60 °C. The measurement was intended for temperature analysis as well as protection against cell overheating during the test. For

Table 1
Calendar aging test for investigating the stress factor temperature.

	25 °C	40 °C	55 °C
50% SoC	×	×	×