Modelling the Degradation Process of Lithium-Ion Batteries When Operating at Erratic State-of-Charge Swing Ranges

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Modelling the Degradation Process of Lithium-Ion Batteries When Operating at Erratic State-of-Charge Swing Ranges

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***Abstract*— Manufacturers of lithium-ion batteries inform capacity degradation for regular, symmetrical charge/discharge cycles, which is clearly problematic in real life applications where charge/discharge cycles are hardly regular. In this context, this paper presents a methodology that can model the degradation of lithium-ion batteries when these are charged and discharged erratically. The proposed methodology can model degradation of a lithium-ion battery type subject to erratic charge/discharge cycles where degradation data under symmetrical charge/discharge cycles (namely, under a standard protocol) has been provided by the manufacturer. To do so we use the concepts of (i) SOC swing, (ii) average swing range and (iii) Coulombic efficiency to model the degradation process in a simple manner through interpolation techniques. We use both deterministic and Monte Carlo simulations to obtain capacity degradation as a function of the number of cycles.**

Keywords—Degradation, Lithium-Ion Batteries, State-of-Health, State-of-Charge, Depth of Discharge, Coulombic efficiency.

I. Introduction

Energy might be available at times when it is not needed and vice versa. In these situations, an energy storage device (ESD) becomes useful since it will allow the use of energy when really required. In this proposal, a specific type of ESD –a lithium-ion (Li-ion) rechargeable cell– is going to be studied. Some of its characteristics are: high energy density, light weight, no memory effect, and high charge/discharge efficiency, and due to these advantages, this type of battery is used in a wide variety of applications such as consumer electronics, terrestrial and aerial vehicles and power electronics [1].

It is a well-known fact that the capacity of the Li-ion batteries fades while used over an extended period of time. Furthermore, several studies separate the process of degradation into three major groups: capacity fade, power fade and aging factors [2].

A. Basic Concepts

When working with batteries, there are some concepts that need to be properly understood in order to understand the fundamentals. These are explained next.

1) State of Health and State of Charge

The first concept to be explained is the State-of-Health (SOH). As long as the battery is used, its capacity to store energy degrades. This means that at certain point in time, the capacity of the battery is degraded in a certain percentage (with respect to the capacity when the battery was new). It is measured as a percentage, for instance a 100% SOH is used for a new, healthy battery, while a 0% is for a fully degraded battery. Importantly, it is considered in practice that once the SOH reaches a point between 70%-80% of the SOH, the battery is "fully" degraded [3] [4] [5]. In this case, it can be said that the battery reached its End-of-Life (EoL). Depending on the application, different levels of battery life are required. For instance, 15 years might be required for hybrid electrical vehicles, or 10 years for full electric vehicles [2], and these required values can be different for small electronics or power grid applications.

The State-of-Charge (SOC) is associated with the available energy that the ESD is capable to deliver. This corresponds to a short term measurement and is indicated as a percentage. A 100% SOC indicates a fully charged battery, and a 0% SOC corresponds to a fully discharged battery. It is also said, when a battery reaches a 0% of SOC, that it reached its End-of-Discharge (EoD).

2) Depth of Discharge

Another concept is the Depth of Discharge (DoD). The DoD is related to the SOC, since it represents the percentage of how much energy is used by the ESD. For instance, if a fully charged battery is used to a point where the final SOC is 80%, it is said that the DoD is equal to 20%. If a battery starts fully charged and then delivers energy until it reaches a SOC of 70% and then charges up to a SOC of 80%, the DoD will be the difference between the highest and lowest values of SOC; in this case a DoD of 30%. It is established that deeper discharges reduce the life of the ESDs. In this regard, since the starting point is not always a SOC of 100% and the final value is not the lowest value of SOC, two more concepts become useful. The first one is called the SOC swing. This measures the total difference between the starting SOC value and the lowest SOC value in a cycle. For instance, a SOC swing of 40% can represent a change in SOC from 100% to 60% or from 50% to 10%. This is why we need to define the swing range (SR). The SR indicates the range in which the SOC swing varies (indicating explicitly lower and upper bounds of the range). This is important to know because if the SOC swing is equal to 50%, the degradation effect would be one if the SR goes from 50% to 0%, and a different one if it goes from 100% to 50%.

3) State of Health Degradation Models

We are going to focus on one particular type of degradation model based on the concept called the Coulombic efficiency, denoted with the Greek letter η. It is defined as the fraction of the prior charge capacity that is available during the following discharge cycle [3] (also, we can define one efficiency for charging and a different one for discharging). This efficiency is affected by the depth of discharge, the extracted current, and the temperature at which batteries are placed and operated. Datasheets provide information regarding the trend of the capacity degradation after a certain amount of cycles, as shown in Fig. 1, which is reconstructed from the datasheet of the Panasonic NCR18650B Li-ion battery. This is the degradation effect when batteries are discharged at nominal current, with a SOC swing of 100% and charged by using the defined protocol defined by the datasheet.

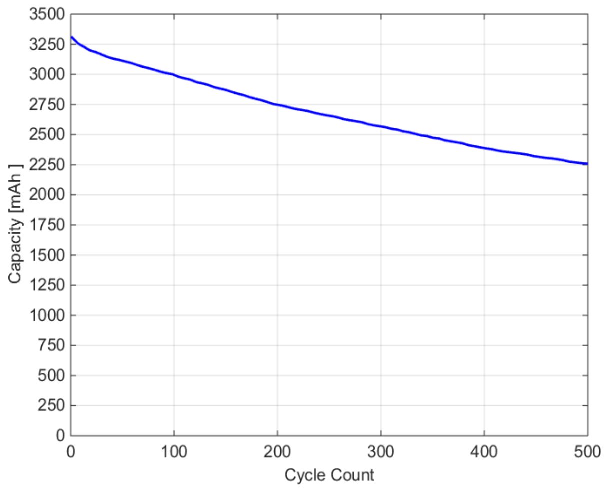

Fig. 1. Panasonic NCR18650B lifespan characteristics

Even though the degradation is caused by multiple effects, the Coulombic efficiency can be used to simplify and explain the entire degradation phenomenon by only one term.

Fig. 2 shows an example of the degradation of battery capacity for different values of Coulombic efficiency, after 100 cycles of use.

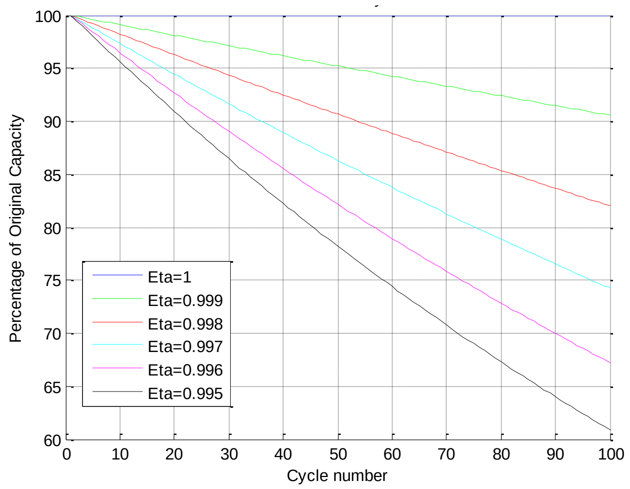

Fig. 2. Coulomb efficiency effect during cycling [3].

Basically, the higher the value of η, the less degradation per cycle a battery will have. Since most Li-ion batteries have a lifespan of a several hundreds of cycles, it is imperative to work with several decimal points in order to obtain the most appropriate value of the Coulombic efficiency.

4) Cycle Definition

The most common definition battery cycle can be established as the process of discharging a fully charged battery and then charging it again. Clearly, the amount of total cycles before full degradation occurs will depend on the manufacturer and the type of battery. Also, transforming number of cycles in time (measured in hours) is complex and a number of considerations need to be taken into account, for example: temperature, depth of discharge, actual state of health of the battery, etc.

Most datasheets provided by manufacturers include information of the lifespan under regular, symmetrical discharge cycles and controlled temperature settings. Usually the amount of total cycles is given to a full discharge or a fixed DoD. Some studies regarding the electrochemistry of the batteries demonstrate that there is a major impact on the capacity fade when the DoD is larger, or even when the starting point is different. In other words, if a datasheet establishes certain amount of total cycles under a given DoD (different to 100%), the manufacturer may be assuming that the initial capacity is 100%. Clearly, the amount of cycles will be different if the initial capacity is, for example, 90% or 80%. This means that if the battery has the same SOC swing but different SR, degradation may differ. Since most of the applications have different DoD and power requirements, determining the real SOH of a battery might become a difficult task.

II. Proposed Method

This method was previously used in [6], although we provide much more details next. In the proposed method, the cycles are characterized by using its associated Coulombic efficiency $\bar{\bar{\eta}}_k$. In this sense, the storage capacity is degraded through each cycle k, by using (1).

$$\bar{\bar{E}}_{k+1} = \bar{\bar{\eta}}_k \, \bar{\bar{E}}_k \tag{1}$$

This proposal includes a methodology that uses information of the battery, regarding the amount of operating (regular) cycles and the values of SOC swing and SR. Using data provided by the manufacturer, it is possible to calculate the value of $\bar{\bar{\eta}}_k$. In this case, 11 SR (100-0%, 100-25%, 75-0%, 100-50%, 75-25%, 50-0%, 100-75%, 75-50%, 62.5-37.5%, 50-25% and 25-0%) and the total number of cycles for each of these SR is known. If we observe Fig. 1 and Fig. 2, we can calculate a value for the Coulombic efficiency if we consider a constant decay rate. By using the known amount of total cycles, and assuming that a cycle is complete after discharging the battery at nominal current between the defined values of SR, the following equation simplifies the calculation of the Coulombic efficiency, through (2).

$$\bar{\bar{\eta}}_k = (\%Degradation)^{1/\#cycles} \tag{2}$$

In this case, the percentage of degradation should be defined as a value between 0 and 1, since it would be equal to the percentage of the nominal capacity where the user or manufacturer defines the threshold to be considered as fully degraded. For instance, if a battery is rated to work for 5000 cycles, with a final nominal capacity of 80% (of its original value), the value of the Coulombic efficiency would be 0.99995537; but if this percentage is considered as 75% (of its original value), the value of $\bar{\bar{\eta}}_k$ would be 0.99994246. This procedure is performed for all the eleven cases mentioned before, so each one has associated a value of $\bar{\bar{\eta}}_k$. Even though we have a good amount of operating cases, this does not cover all the possible combinations of SR. For this reason, using Similarity Based Model (SBM [7]), it is possible to interpolate and obtain an appropriate value of the Coulombic efficiency. Using the known SOC swing and the average SR value, we are able to create a scatter plot as that shown in Fig. 3, where the asterisks represent the known conditions and the black circle represents a particular operational condition. Equivalent Coulombic efficiency will be determined as described next.

Since the scatter plot presents a triangular shape, we use SBM and K-nearest neighbors (3 neighbors in this case due to the triangular shape). By weighting the inverse of the distances to the known conditions (3 of them), it is possible to determine the value of an approximate Coulombic efficiency for all possible operating conditions.

Common datasheets for Li-ion batteries provide information about the lifespan of a batteries when used between 100% and 0% SOC, as shown in Figure 1. From this information it is possible to estimate a value for the Coulombic efficiency by using (2).

Having all the SOC swing and SR information is not always possible. For this reason, this paper proposes a method for extrapolating the previous results in order to be used with other Li-ion batteries. Assuming that Li-ion batteries have similar behaviors, we propose that the Coulombic efficiency can be escalated using the known previously described case where the 11 SR values are known.

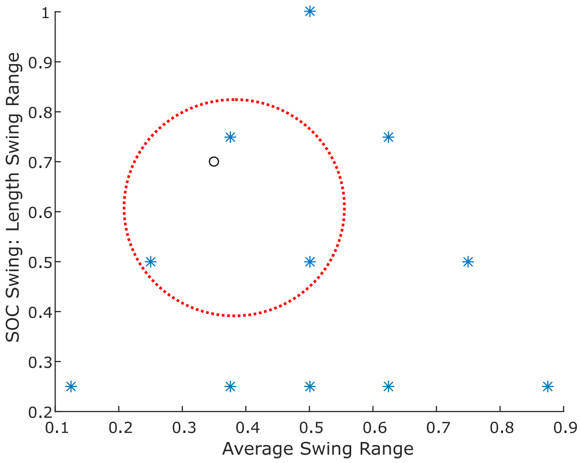

Fig. 3. K-Nearest neighbor scatter plot.

Table 1 shows the corresponding escalating factors that can be used to characterize the efficiency when the batteries are operated at different SR. Also, it considers different degradation percentages since they can differ among manufacturers.

TABLE 1. Escalating factors for three degradation cases.

	Degradation Percentage		
SR	**0.7**	**0.8**	**0.85**
100-0	1.000000	1.00000000	1.00000000
100-25	1.000003	1.00000266	1.00000193
75-0	1.000024	1.00001860	1.00001354
100-50	0.999989	0.99999203	0.99999420
75-25	1.000019	1.00001521	1.00001108
50-0	1.000037	1.00002874	1.00002093
100-75	1.000027	1.00002146	1.00001563

75-50	1.000011	1.00000881	1.00000642
62.5-37.5	1.000008	1.00000620	1.00000451
50-25	1.000043	1.00003347	1.00002438
25-0	1.000054	1.00004184	1.00003047

For example, let consider two types of commercial Li-ion batteries. The first case is the Samsung ICR18650-22P. Using the information provided by the manufacturer it is possible to calculate the Coulombic efficiency. In this case, we have a value of 0.9992869 after 500 cycles since after at that point the capacity of the battery has degraded to 70% of the nominal capacity, meaning that there is a 30% loss of the original capacity.

The second case corresponds to the Panasonic CGR18650, as seen in Fig. 4. Calculating the same parameters as the first case, we obtain a Coulombic efficiency of 0.9995538, considering a degradation of 20%, since the available capacity at that point will be 80% of the original capacity, after 500 cycles of use.

Using the obtained value of η for each case, it is possible to calculate an approximate value of Coulombic efficiency when working at different SR. Table 2 shows the escalated values for the Coulombic efficiency for each of the SR.

With these results, the user can replicate the previously explained methodology in order to characterize in a better way the degradation effect when another type of Li-ion battery is operated under any SR conditions.

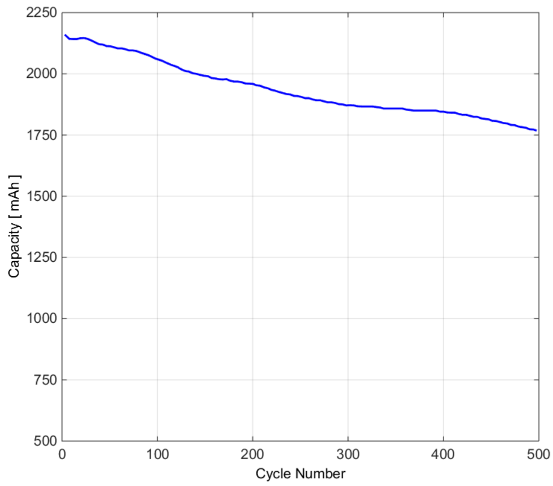

Fig. 4. Panasonic CGR18650 lifespan characteristics

III. Simulation Example

In this example we model the degradation process of the Samsung ICR18650-22P Li-ion battery using the results of Table 2. We performed a Monte Carlo simulation of 50000 realizations and operating the battery under any SR combination. Also we model the degradation process in a deterministic way by using a fixed value of eta. For the deterministic part, we consider three values for eta: a constant value of eta (obtained from the datasheet -and equal to the 100-0% SR-, and the maximum and minimum value of eta obtained from the Table 2. For the constant value of eta, we are going to consider the extracted information from the datasheet, which gives a value of 0.9992869, the maximum value is 0.9993409 and the minimum is 0.9992759. For the Monte Carlo simulations, the corresponding value of eta is calculated by the K-NN method explained in the previous section and using as a reference the values obtained in Table 2. In this sense, it is possible to simulate any random combination of SOC swing and SR and not only the 11 cases discussed earlier. However, the following considerations were taken into account for the simulation:

- The initial SOC level value at instant time k+1 must be higher than or equal to the final SOC level value at instant time k.
- There is always a discharge in every cycle.
- Each realization is finished after 800 cycles.

TABLE 2. Escalating values for two commercial batteries.

SR	ICR18650-22P	CGR18650
100-0	0.9992869	0.9995538
100-25	0.9992899	0.9995565
75-0	0.9993109	0.9995724
100-50	0.9992759	0.9995458
75-25	0.9993059	0.9995690
50-0	0.9993239	0.9995825
100-75	0.9993139	0.9995753
75-50	0.9992979	0.9995626
62.5-37.5	0.9992949	0.9995600
50-25	0.9993299	0.9995873
25-0	0.9993409	0.9995956

For the Monte Carlo simulations, we calculated the amount of total cycles after the normalized capacity reaches the threshold value of 70% since at this point the battery is considered fully degraded. The bar diagram presented in Fig. 5 shows the estimated total number of cycles until it reaches its EoL. In this case, it can be observed that the majority of the cases reach its EoL after 517 cycles (used at different/irregular SOC swing values).

Fig. 6 shows the obtained degradation curve for the following cases: the constant value of eta, the maximum and minimum value of eta, and one realization of the Monte Carlo. It is possible to see that the case of constant eta reaches the 70% threshold at 500 cycles, which is the value expected observed in the datasheet. In the case of the Monte Carlo simulation, the battery lifespan is 3.2 - 3.6% higher in terms of extra cycles (with respect to calculation with a constant eta). Furthermore, Fig. 7 shows a zoom-in of the threshold area.

By looking at Fig. 7, we can observe that the Monte Carlo results place the battery lifespan within the minimum and maximum degradation. Also, the EoL obtained through the Monte Carlo simulations can be considered the closest to the real one (or closer than that obtained through a constant eta).

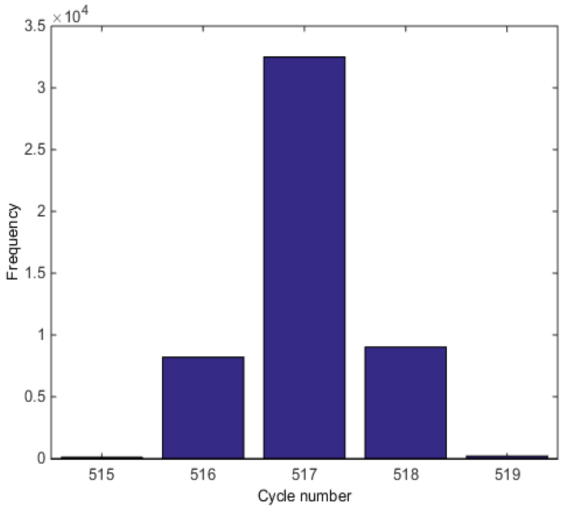

Fig. 5. Bar diagram of the estimated total number of cycles

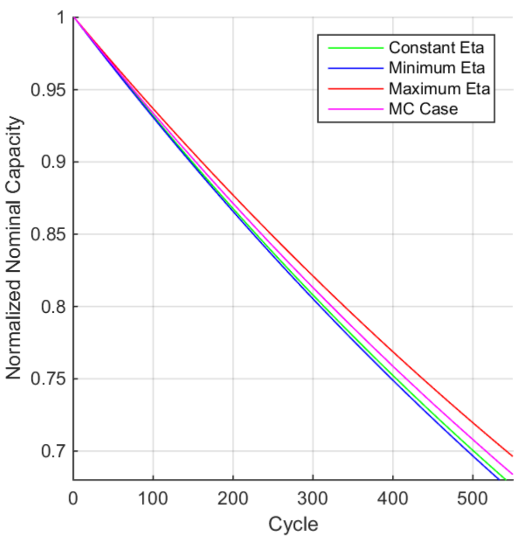

Fig. 6. Simulated degradation process of the Samsung ICR18650-22 when operated under different conditions.

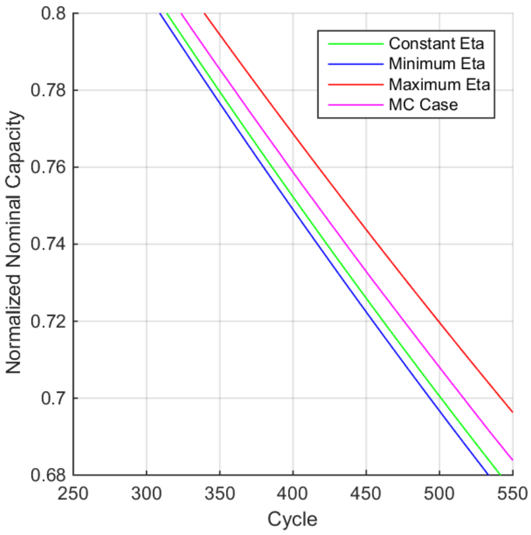

Fig. 7. Zoom in over the 70% threshold area

Conclusions

This paper presents a methodology that can model the degradation of lithium-ion batteries when these are charged and discharged erratically. The proposed methodology can do model degradation of a lithium-ion battery type subject to erratic charge/discharge cycles where degradation data under symmetrical charge/discharge cycles (namely, under a standard protocol) has been provided by the manufacturer. To do so we use the concepts of (i) SOC swing, (ii) average swing range and (iii) Coulombic efficiency to model degradation in a simple manner through interpolation techniques. We use both deterministic and Monte Carlo simulations to obtain capacity degradation as a function of the number of cycles.

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