UNRAVELLING THE INTRICACIES OF LITHIUM-ION BATTERY AND ITS DEGRADATION DYNAMICS

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Article Info ABSTRACT

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In order to solve degradation-related difficulties, a thorough knowledge of Lithium-Ion Battery (LIB) behaviour is important given the rapid expansion of Electric vehicle (EV) and mobile devices. With LIBs driving EVs and influencing the direction of energy storage, the globe is embracing renewable energy. This study unravels the complex dynamics that affect LIB performance by exploring important topics including temperature affects, charging methodologies, and rapid charging. As a solution to longer charging periods, fast charging reveals trade-offs, such as increased deterioration and safety issues. Temperature turns out to be a critical component that affects lithium plating, ion diffusivity, and battery health in general. Sustainable LIB usage hinges on an efficient charging approach that takes health-related factors into account and minimizes temperature extremes, overcharging, and over discharging. An essential statistic that provides information on the degree of deterioration and its ripple effects on power, voltage, capacity, and internal resistance is the State of Health (SOH). This research uses a mathematical model that incorporates internal resistance and coulomb efficiency to capture the core of LIB behaviour during charging and discharging. The suggested approaches which include lower charging current, better charging, and thermal management show the way to longer battery life spans. Careful monitoring and management are essential when it comes to issues like charging inconsistencies, temperature extremes, and charge cycles. Essentially, this study explores the challenging landscape of LIBs, highlighting their weaknesses and suggesting ways to achieve highperformance, sustainable energy storage. The path to realizing the full potential of lithium-ion batteries requires ongoing research, creative thinking, and a dedication to reshaping the energy landscape to be more efficient and environmentally friendly.

Keywords: Lithium-ion battery, Battery degradation, Fast charging, Low temperature, State of health, Charging strategy, Simulation, Voltage model.

1. INTRODUCTION

The increase in operational duration of electric vehicles, mobile devices (Qu et al., 2019) and the upgrade in the functionalities of these devices make it necessary to consider factors that impact battery degradation and to put forward strategies to alleviate such functions. One of the paths towards transformation of energy systems addresses the mitigation of global warming and greenhouse gas, by a shift of fossil fuel to renewable energy. In electric vehicles, decarbonisation is achieved using lithium batteries in place of fossil fuel (Quinteros-Condoretty et al., 2021)**.** Lithium-ion battery is one of the most commonly used batteries in electric vehicles and mobile devices due to its characteristics of high energy density, high power density, low self-discharge rate among others **(**Han et al., 2019). Putting electric vehicles in view, there is the long charging time and the short driving time

problem which precipitates concern with users, and one way to address this issue by manufacturers was to introduce fast charging (Liu et al., 2021), and this has come with some disadvantages such as shortening the life span of the battery, reduced capacities of the battery and catastrophic failures, such as fire. The Lithium-Ion Battery (LIB) is a rechargeable battery that has a positive electrode (cathode), composed of metal oxide and a negative electrode (anode), composed of porous carbon (Galatro et al., 2020).Theoretically, during charge and discharge of the battery the ion exchange process should work endlessly, and the battery should always give 100% of its capacity, but this is not the case due to degradation, resulting in capacity fade and power fade (Galatro et al., 2020; Uddin et al., 2016).

A well-designed charging strategy can protect batteries from degradation, and this can be done by considering health related elements into the charging process (Liu et al., 2019). Battery aging is accelerated with fast charging at temperatures below $25\degree C$ (Koleti et al., 2019) because at such temperatures, more metallic deposits of lithium are produced, which can lead to mechanical deformation within the cell. Low temperature is one factor that causes poor performance of LIB, as it results in a slowdown of specie transfer, that is, when temperature decrease from 20 $^{\circ}$ C to -40° C, the ion diffusivity in anode suffers a significant decrease, and cell's internal resistance increases, thereby reducing the capacity of the cell; it is easy to see, from these, how the combination of fast charging and low temperature can be disastrous for LIB. At $-40\degree C$, the limited transport kinetics, during charging, causes lithium deposit on the anode surface, which brings about lithium plating (Koleti et al., 2019). Some way to keep the battery's temperature at required range is therefore necessary, before and after use. Lithium plating, beside occurring at charging at low temperature, is a side reaction that goes with fast charging. This is a process where ionic lithium is converted to metallic lithium to cover the anode electrode. When this happens, there will be less ionic lithium in circulation and this will degrade the battery (Liu et al., 2021). Another disadvantage of this is that the metallic dendrites have the possibility to penetrate the separator, leading to a short circuit that lead to thermal runaway and explosions (Liu et al., 2021; Liu et al., 2019). Studies shows that other key parameters that can have effect on battery's degradation are anode and cathode active material thickness, porosity, particles size, cell size, cell shape. The overall performance is of a battery is measured by the state of health of a battery. The state of health of a battery at a point in time tells how much the battery has degraded. A declined in the state of health also results in a decline in battery capacity (the amount of energy the battery can store), the voltage (the electrical potential it can produce), power (the rate at which the battery can deliver energy), and increase in internal resistance. When the state of health of a battery has declined drastically, the battery becomes susceptible to overheating. At such, it is not safe for use.

There are several factors that contribute to batteries degradation in state of health. They include:

i. Charge cycle: The number of times a battery is charged and drained causes chemistry within the battery to degrade. This process is known as the charge cycle. Internal friction occurs between the ions and the electrolyte when they move from the anode to the cathode and vice versa. A portion of the kinetic energy of the ions is transformed into heat energy during this process. Friction and speed have an inverse relationship in physics. This implies

that friction decreases with increasing speed. Speed increases translate into more kinetic energy being stored, less kinetic energy being lost, and less heat being produced. This suggests that rapid charging will lessen the deterioration that would otherwise occur from the charge cycle. In this instance, temperature becomes a crucial component. Fast charging is necessary to lessen the battery's deterioration during charge cycles if the influence of temperature drags back the kinetics of ions in the electrolyte. If not, less friction should arise from the kinetic energy lost to heat accelerating the motion of ions in the electrolyte (internal resistance).

ii. Temperature extremes: To maintain a battery in a safe functioning range, it is critical to regulate the surrounding air temperature. This is due to the fact that both high and low temperatures can generate chemical instability and electrochemical reaction obstruction, respectively.

iii. Overcharging and Over discharging: these actions might put the battery under undue stress and harm the electrodes. Recharging a battery is advised before it loses more than 20% of its capacity.

2. RELATED WORKS

Lander et al. (2021) showed that battery lifetime extension through effective thermal management significantly decreases the battery life cycle cost and carbon foot print. Gao et al. (2020) proposed a novel health aware multi-objective optimal charging strategy to simultaneously shorten charging time and relieve battery degradation. Gao et al. (2017) suggested that battery charging current and cut off voltage should be reduced to retard battery degradation. They came to this inference through an established experimental model that quantitatively describes the relationship. Farzin et al. (2016) proposed a model for estimating battery life degradation based on utilization pattern. Recent progress on fast charging in terms of material chemistry, thermal issues and charging optimization were reviewed by Xie et al. (2020). Winslow et al. (2018) discussed the available literature on end-of-life lithium-ion batteries (LIBs) from a waste management standpoint. Wei et al. (2022) proposed a knowledge-based, multi-physics-constrained fast charging strategy for lithium-ion battery (LIB), with a consciousness of the thermal safety and degradation. Wang et al. (2016) made a study on thermal effect on lithium batteries in terms of thermal runaway, and response under cold temperature. They discussed heat generation methods with the aim of performing accurate battery thermal analysis. Lin et al. (2021) provided a snapshot of recent advances in lithium plating research in terms of mechanism, detection, and mitigation. Qu et al. (2019) proposed pulse self-heating strategy for quick and safe warming of lithium-ion battery. Koleti et al. (2019) developed two novel charging strategies for lithium-ion batteries, designed to prevent the onset of lithium plating when the cells are charged at low ambient temperatures. (Han et al., 2019)presented a comparative review on key issues on battery degradation during the whole life cycle. Liu et al., (2019) proposed a constrained multi-objective optimization framework to achieve economy-conscious battery charging management.

3. METHOD

Generic reaction of lithium during discharging and charging.

3.1. Discharging (release of energy)

Cathode (positive electrode) $LiCoO₂ \rightarrow Li + CoO₂ + e^{-}$

Overall reaction during discharging

 $LiCoO₂ + LiC₆ \rightarrow Li₂CoO₂ + C₆$ (3)

3.2. Charging (Absorption of energy)

Cathode (positive electrode)
\n
$$
Li^{+} + CoO_{2} + e^{-} \rightarrow LiCoO_{2}
$$
\n(4)

Lithium ion moves back from the anode to the cathode during charging.

Cobalt oxide, $CoO₂$ gains an electron to form lithium cobalt oxide, $LiCoO₂$.

Anode (negative electrode)

$$
Li^{+} + e^{-} + C_{6} \rightarrow LiC_{6} \tag{5}
$$

Lithium ions are de-intercalated from the anode material, and the anode material gains an electron.

Overall reaction during charging

 $Li_2CoO_2 + C_6 \rightarrow LiCoO_2 + LiC_6$ (6)

3.2.1 Understanding Reaction Mechanisms

Equation (1) describes the release of energy during discharging as lithium ions move from the cathode to the anode, producing cobalt oxide and an electron. Equation (2) represents the intercalation of lithium ions into the anode material, releasing an electron during the process. Equation (3) gives overall reaction during discharging, combining the cathode and anode reactions.

3.2.2. Capacity and Energy Efficiency

Equation (6) illustrates the process during charging where lithium ions move back from the anode to the cathode, recombining.

3.2.3. Cycle Life and Degradation

Equation (4) describes the absorption of energy during charging as lithium ions move back to the cathode, forming and gaining an electron. Equation (5) represents the de-intercalation of lithium ions from the anode material gaining an electron. Equation (6) overall reaction during charging, combining the cathode and anode reactions.

3.2.4. Material Selection and Composition

Equation (1) describes the release of energy during discharging as lithium ions move from the cathode to the anode. Equation (2) represents the intercalation of lithium ions into the anode material releasing an electron. Equation (3) overall reaction during discharging, combining the cathode and anode reactions. Equation (4) describes the absorption of energy during charging as lithium ions move back to the cathode.

Figure 1 illustrates the safe working region of each battery based on its specific features. When a single cell in a line of lithium-ion batteries outside its safe working range, the battery will experience a thermal runaway, which causes internal heating and damage. As a result, the battery's internal resistance increases to the point where internal power loss is too great

V (Voltage) Over Voltage(OV) $4.2v$ V max Over Temperature(OT) Under Safe Operating Area(SOA) Temperature(UT) $2.5v$ V mir Under Voltage (UV) T (Temperature) Tmax
55°C Tmin
-20°C

and the temperature rises to a point where the battery melts. If this doesn't occur, the battery's lifespan may be shortened by an internal short circuit or lithium plating.

3.3. Voltage Model and Rationale

Figure 2 gives a Voltage time graph of a discharge Lithium-Ion Battery, from which a mathematical model is derived.

Figure 2: Voltage time graph of a discharge Lithium-Ion Battery

3.3.1. Mathematical Modeling of Lithium Battery

The mathematical model in this work is derived from Figure 2. In this model, the cell voltage is considered to be constant and equal to the open circuit voltage (OCV) on the following assumptions:

- I. Voltage is not a function of current.
- II. Voltage is not a function of past usage.
- III. Voltage is constant.

Therefore,

$$
v(t) = OCV \tag{7}
$$

Further, when a battery is fully charged, the voltage is higher than when the battery is fully discharged. This means that the State of Charge (SOC) $y(t)$ affects the battery voltage. $y(t) = 100\%$ when the battery is fully charged.

Total capacity q (mAh) of a battery is defined as the total amount of charge taken from the battery during discharge from $y(t) = 100\%$ to $y(t) = 0\%$..

$$
\dot{y}(t) = -i(t)/q \tag{8}
$$

$$
\dot{y}(t) = y(t_0) - 1/q \int_{t_0}^t i(\tau) d\tau
$$
\n(9)

When the sign of input current is positive, the cell is being discharged and vice versa. The input current is normalized by dividing it by the total capacity of the cell so that when they are equal, the SOC is one, which means 100%.

In discreet time, on the assumption that current is constant over sampling interval Δt .

$$
v(t) = OCV(y(t))
$$

\n
$$
\dot{y}(t) = -i(t)\eta(t)/q
$$
\n(10)

The assumption behind equations (10) is that not all the charge that goes into the battery during charging raises up the SOC of the battery. Some of the charges are consumed by the internal resistance of the battery and other side effects by the chemical reactions in the battery. For this reason, the coulomb efficiency (η) of the battery cell is introduced into the model. If the battery is perfectly efficient $\eta = 1$. That is in an ideal scenario. In reality the value of η is less than 1 and Coulomb efficiency = charge out/charge in.

When the internal resistance R_0 of the battery cell in included in the model, the mathematical expression for cell voltage becomes

$$
v(t) = OCV(y(t)) - i(t)R_0
$$
\n(11)

The power dissipated by internal resistance goes as heat and that impacts the energy efficiency of the battery negatively.

The $i(t)R_0$ model instantaneous response to a change in input current while in practice there is a dynamic response to a current step. That is, when a battery stops discharging, the battery does not rise to its open circuit voltage immediately but it's a time to gradually get to that level. This occurs due to the slow internal diffusion of lithium from a part of the battery to the other. In this way, concentration that was built up while the cell was being discharged gets back to equilibrium. The diffusion voltage in the cell, no matter how small, was added to the model get a Thevenin model.

$$
v(t) = OCV(y(t)) - v_{c1}(t) - i(t)R_0
$$
\n(12)

Where $v(t)$ is voltage at a time t, and $y(t)$ is state of charge at a time t This can also be seen as

$$
v(t) = OCV(y(t)) - R_1 i_{R1} - i(t)R_0
$$
\n(13)

This is illustrated in Figure 3 where $RA = R_1$ and $RB = R_0$ and $CA = C_1$ $i(t) = i_{\text{pa}} + C_4 \dot{v}_{\text{pa}}(t)$ $r_1(t)$ (14)

Since
$$
v_{c1}(t) = R_1 i_{R_1}(t)
$$
,

$$
i(t) = i_{R1} + R_1 C_1 \frac{di_{R_1}}{dt}(t)
$$
\n(15)

$$
\frac{di_{R_1}}{dt}(t) = -\frac{1}{R_1c_1}i_{R_1}(t) + \frac{1}{R_1c_1}i(t) \tag{16}
$$

Figure 4 is a graph of state of health of lithium-ion battery generated using computer models that mimic the behaviour of lithium-ion batteries. The state of health (SOH) of lithium-ion batteries is displayed on the graph at various operating temperatures, and discharge depths. A battery's capacity in relation to its initial capacity is measured by its SOH. The graph indicates that SOH decreases with increasing operating temperature, and discharge depth.

Figure 4: State of Health (SOH) of Lithium-Ion Batteries at Different Operating Temperatures and Discharge Depths

4. CONCLUSION

The utilization of electric vehicles (EVs) and mobile devices is growing as a result of technology advancements and the demand for renewable energy sources. This demonstrates how crucial it is to identify and address the factors influencing battery degeneration. There are several challenges with switching from non-renewable to renewable energy sources, particularly when it comes to lithium-ion batteries (LIBs) in electric vehicles (EVs). These include battery lifetime, charging methods, and overall performance. The drawbacks of fast

charging include less battery capacity, faster battery degeneration, and potential safety risks such catastrophic failures. It was created to ease concerns over protracted charging times. Temperature is significant because low temperatures can produce reduced ion diffusivity and high temperatures can cause chemical instability and lithium plating. It becomes imperative to have an effective charging strategy that considers factors linked to health as well as mitigating factors such as extremes in temperature, overcharging, and over discharging. The state of health (SOH) of a battery is an important metric that affects internal resistance, voltage, power, and capacity as well as indicating the extent of degradation. Several studies recommend strategies including temperature regulation, optimal charging, and reduced charging current to extend battery life. Extreme temperatures, improper charging, and charge cycles are some of the things that lead to battery degeneration. Careful administration and control are therefore necessary. The presented mathematical model fits the battery's behaviour both while charging and discharging and takes into account the internal resistance and coulomb efficiency of the battery.

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