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Assessment of Round-Trip and Coulombic Efficiency in Lithium-Ion Batteries Using a Mathematical Modeling Approach under Variable Operating Conditions

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ABSTRACT

Accurate quantification of Coulombic efficiency and degradation is essential for evaluating the long-term performance of lithium-ion batteries used in electric vehicles and stationary energy-storage systems. However, existing battery-aging studies predominantly emphasize capacity fade and impedance growth, while the coupled evolution of Coulombic efficiency, capacity retention, and round-trip performance under aging and thermal conditions is less systematically quantified. This study develops an analytical framework for evaluating Coulombic efficiency and round-trip performance as functions of battery age and operating temperature. The framework is experimentally validated using a 3.6-V, 3-Ah lithium-ion cell under controlled charge–discharge conditions. Battery behavior is evaluated over 1500 cycles and across a temperature range of 0–

75 °C. The discharge capacity decreases from 2.704 to 1.783 Ah after 1500 cycles, corresponding to a capacity loss of approximately 34.1%, while Coulombic efficiency decreases from 90.1% to 59.43%. The proposed model is further evaluated against experimental measurements over the investigated temperature range, demonstrating close agreement. The results establish quantitative relationships between battery aging, thermal conditions, capacity retention, and Coulombic efficiency, providing a practical framework for battery-condition assessment and efficiency-aware battery-management strategies.

Keywords: Round-trip efficiency, Lithium-ion battery, coulombic efficiency, Capacity retention.

1. INTRODUCTION

In recent times, battery technological development has notably accelerated, due to the increased requirements for portable technology and the need to formulate eco-friendly energy storage technologies. Dry cell, nickel-metal hydride, lead-acid, lithium-polymer, and Li-ion batteries are the commonly used battery types for different applications. Batteries can be broadly categorized as primary and secondary based on their ability to be recharged. Once their capacity is fully depleted, primary batteries cannot be recharged and need to be disposed of instead of being reused, while secondary batteries, also known as rechargeable batteries, have gained significant popularity due to their ability to be reused multiple times [1].

Two prominent types of secondary batteries used in power applications are lead-acid and lithium-ion. Being the older technology, lead-acid batteries are comparatively big and bulky [2]. Lithium-ion batteries employ advanced chemistry that improves on lead-acid and other batteries that were previously prevalent in the market. The main constituent of a lithium-ion battery is the lithium-ion, which moves back and forth between the negative and positive electrodes throughout the process of charging and discharging [3]. Lithium-ion batteries are preferred for electric

vehicles and handheld appliances due to better energy density, environmental friendliness, a low self-discharge rate, and a longer cycle life than other secondary batteries. [3, 4]. Features include excellent cycle life, sealed cells and no maintenance required, wide temperature range to ensure reliable operation, low self-discharge rate, accelerated charging capability for faster recharging, delivering high discharge rate and high power demands, excellent energy and columbic efficiencies, high energy density, and specific energy properties, and they are free of memory effect [1], [2], [5].

Despite their numerous benefits, lithium-ion batteries are subject to degradation over the course of time. Battery degradation refers to the loss of capacity and performance that occurs as the lithium-ion battery ages and undergoes periodic charging and discharging cycles. Aging mechanisms are accountable for the degradation of battery performance, resulting in a decline in the battery's energy-storing capability and total power output [6]. Battery degradation is inevitable and has the chance to happen in both linear and non-linear forms [7]. Linear degradation occurs at a constant rate and can be predicted based on the count of charge and discharge cycles. Non-linear degradation occurs irregularly and is affected by various factors, including temperature, current, depth of discharge, etc., which are harder to predict [8]. Mechanical, chemical, electrochemical, electrochemical-mechanical, and thermal coupling are the five significant degradation forms associated with Li-ion batteries [4]. Battery degradation generally occurs through several mechanisms, including the development of solid electrolyte interphase (SEI) layers, structural decay of the positive electrode, and deterioration of negative electrode particles, which is noticeable at negative electrodes, while positive electrodes are affected by both fracturing of particles and breakdown of the positive electrode. The interaction between the five fundamental degradation mechanisms described earlier gives rise to a total of thirteen secondary degradation

pathways [4], [7]. Degradation effects can manifest in various forms, including capacity fade, power fade, impedance rise, and internal short. The degradation of commercial lithium-ion cells can be evaluated based on their discharge energy, capacity retention, and round-trip efficiency (RTE) [9]. Battery efficiency is intimately linked to degradation and is related to the battery's storage and delivery capacity. Also, battery performance and flexibility in various applications depend on battery efficiency. Battery efficiency can be classified into three categories: Coulombic efficiency (CE), voltage efficiency, and energy efficiency. The voltage efficiency is the ratio between the average discharge voltage and the average charging voltage [10]. All of these efficiencies, such as Coulombic, voltage, and energy efficiency, are round-trip efficiencies. Among them, Coulombic round-trip efficiency (CRTE) is especially important for different applications, particularly electric cars. A high CRTE level indicates that the battery can efficiently store and distribute energy and is an important aspect of electric cars to achieve accurate range estimates and range increase for driving on one charge [11]. The proliferation of electric vehicles (EVs) has led to an increase in the number of retired power batteries. These batteries still retain 80% of their primary energy, and it is anticipated that by 2028, there will be 120 GWh of retired batteries [12]. The increasing number of retired batteries produced by EVs is posing major challenges in proper disposal and management. These retired batteries can be repurposed for energy storage systems and renewable energy applications at scale, which helps both in keeping the batteries working longer and enhancing their remaining value. Compared with fresh batteries, second-life batteries can offer a more economical alternative to stationary energy storage. Despite the great potential of battery reutilization of batteries, the reliability of second-life batteries is a major issue. Performance degradation, capacity fade, and the risk of failure, as discussed in [12], can seriously inhibit safety and efficiency. However, it does not offer any solutions to this problem.

On the other hand, by employing CE monitoring, the attributes of retired power batteries can be examined and studied.

The majority of research is dedicated to capacity fading and impedance growth, but efficiency is rarely investigated [9]. Ignoring this factor causes difficulties and deteriorates battery performance. Efficiency must be assessed to detect issues in advance to be prepared. This underscores the urgent need to design an algorithm and model that could comprehensively evaluate the round-trip efficiency of batteries. It is challenging to make a lithium-ion battery last a long time, but even harder to prove that it will. The model developed can significantly contribute to assessing the lifetime (cycle life) that is required for energy storage and automotive applications, which is identified as the prime need for high-accuracy measurement of CE [13], [14]. Despite extensive research on lithium-ion battery degradation, significant gaps remain in quantitatively relating coulombic efficiency to capacity degradation and round-trip performance. Existing studies primarily emphasize capacity fade and impedance growth, while CE is generally considered a secondary indicator. Moreover, limited studies simultaneously evaluate CE, capacity retention, and round-trip performance under varying temperature and aging conditions. Therefore, an experimentally validated, computationally simple framework that establishes these relationships and can be readily integrated into real-time BMS applications is still required.

In this regard, in the present work, an analytical framework has been derived for computing round-trip efficiency. The developed model has undergone analysis across different operating conditions. The efficiency of the derived model has been studied under different charge and discharge C-rates, ambient temperatures, and retention rates. Further, the results have been validated experimentally.

The principal contributions of this study are as follows:

- I. A mathematical framework is developed to quantify Coulombic efficiency as a function of charge/discharge behavior.
- II. The relationship between battery aging, capacity retention and Coulombic efficiency is quantitatively investigated.
- III. The influence of ambient temperature on discharge capacity and Coulombic efficiency is systematically evaluated.
- IV. The proposed framework is experimentally validated under identical operating conditions.
- V. A degradation-oriented performance indicator based on capacity retention, CE and round-trip time is proposed for battery-condition assessment.

2. COULOMBIC EFFICIENCY AND ANALYTICAL FORMULATION

Coulombic efficiency (CE) is a measure of the effectiveness of electron movement within batteries during the charging and discharging processes. CE is calculated by comparing the total charge removed from the battery during discharge to the total charge input during charging. Lithium-ion batteries exhibit high CE ratings, reaching up to 99% at ordinary charging rates. In contrast, lead-acid batteries have lower CE, typically around 90% [15].

CE is widely utilized as a primary metric to assess internal processes that impact the lifespan of batteries. CE for an n th cycle is defined as the measured discharge capacity of that cycle, $C_{D(n)}$, over the previously measured charge capacity, $C_{C(n)}$ [16,17].

$$CE = \frac{C_D(n)}{C_C(n)} \quad (1)$$

CE is crucial for determining the state of charge (SOC) of a battery and is most commonly evaluated using the coulomb counting method [18]. CE is essential for estimating the range and energy

consumption of electric vehicles (EVs). The CE and SOC must be determined for EVs because a high CE depicts a longer battery lifespan, and EV range is based on the overall battery performance.

A higher Coulombic efficiency means a longer battery cycle life. Lower charge acceptance rates, self-discharge during charging, battery temperature, and the speed of battery aging are all possible factors lowering efficiency. The growing range of applications for energy storage systems illustrates the importance of battery efficiency. Not accounting for it will result in poor performance and shortened battery life, which will hamper the development and progress of battery technology. Important factors to consider in battery efficiency assessment are that reporting energy efficiency measurement results leads to an accurate view of the practical viability of a new material or electrode configuration. Battery performance assessment clarifies the understanding of battery degradation as well as the comparison of the performance of two cells with identical capacity but produced by companies producing different batteries. Evaluation of battery efficiency also aids in the estimation of battery life in a relatively shorter duration [19], [20], and it plays a decisive role in monitoring the battery's condition since it constitutes one of many measures of the battery's state of health (SOH).

The coulombic efficiency, which is widely used as a metric, can be computed as follows [4, 21]:

$$CE = \frac{Q_D}{Q_C} \quad (2)$$

Here, Q_D is the discharge capacity and Q_C is the charge capacity of the cell in the same cycle. Ah is commonly used as a representative of cell capacity.

$$\text{Coulombic Efficiency (\%)} = \frac{\text{Discharge Ah}}{\text{Charge Ah}} \times 100$$

The Ah counting technique necessitates the full integration of the current $I(t)$, which will be either the charging or discharging current at a given time t [9],[14]. The constant 3600 is used for converting the units of time.

$$\text{Discharge Ah} = \frac{\int I_D dt}{3600 \times \eta_{\text{discharge}}} \quad (3)$$

$$\text{Charge Ah} = \frac{\int I_c dt}{3600 \times \eta_{\text{charge}}} \quad (4)$$

Substituting (3) and (4) into the CE formula, the coulombic efficiency can be expressed as

$$CE = \frac{\frac{\int I_D dt}{3600 \times \eta_{\text{discharge}}}}{\frac{\int I_c dt}{3600 \times \eta_{\text{charge}}}}$$

In many cases, it is ideal for the discharge efficiency ($\eta_{\text{Discharge}}$) to be equal to the charge efficiency (η_{Charge}), and this is often expected due to the linear degradation of the battery.

$$\eta_{CE} = \frac{\int I_D dt}{\int I_C dt} \times 100 \% \quad (5)$$

Where: I_D = Discharge Current, and I_C = Charge Current.

A battery's coulombic efficiency should come with a few big ideas. However, knowledge of the terms is going to be useful in analyzing the efficiency and performance of the batteries because their best-known features lie in the accurate and effective conversion of electrical charge accurately and effectively. Efficiency loss is the percent loss of efficiency from a maximum value (i.e., 100%). It provides information on losses of efficiency (η_L) for the battery under various operating conditions as (6).

$$\eta_L = 100\% - \eta_{CE} \quad (6)$$

Capacity retention indicates the battery's proficiency in storing energy over a long-term open-circuit rest time. Retained capacity (CR_n) is influenced by the duration of rest and temperature of the cell during the rest, and past operating behavior of the battery. This relationship is formulated as follows (7).

$$CR_n = \frac{\eta_{cn}}{\eta_{c0}} \times 100 \% \quad (7)$$

The capacity retention measures how long a battery can retain stored energy during a large open-circuit rest period. Retained capacity is based on the duration of the entire rest time. The temperature of the battery during the rest period and the previous operational history of the battery are expressed as below.

$$DDR = \frac{C_{DI} - C_{DF}}{C_{DI}} \times 100 \% \quad (8)$$

Where C_{DI} depicts the initial discharge capacity in ampere-hour (Ah), and C_{DF} is the final discharge capacity in ampere-hour (Ah).

Round Trip Time (RTT) is the time taken for the battery to complete one cycle of charge/discharge; it depicts the storage capacity of the battery, and it is expressed as follows,

$$RTT = t_c + t_d \quad (9)$$

Where t_c and t_d depict the battery charging and discharging time in seconds.

Actual capacity and theoretical capacity are two important terms that are related to each other. The actual capacity denotes the quantity of charge (measured in Coulombs) that a battery can deliver during discharge. The theoretical capacity of a battery is the maximum charge it can carry based on its chemical composition and design. It is computed using Faraday's law. Similar to this is the term known as Coulombic efficiency, or charge efficiency. It measures how efficiently a battery can convert electrical energy during the charging process. Discharge efficiency is the

performance of a battery in delivering electrical energy during the discharge process. It's closely associated with Coulombic efficiency.

2. EFFICIENCY MEASUREMENT SYSTEM AND MODELLING

As shown in (5), the efficiency of a battery is measured through charge and discharge capacities. Two modes for collecting these measurements are put into place: charge mode and discharge mode. In the starting state, the battery is loaded into charge mode and charged from 0% SOC to 100% SOC. Then, the battery is switched to discharge mode, whereby it is discharged from 100% SOC to 0% SOC. It is important to note that only one mode is active at any given time, and the switching logic controls the transition between the modes.

During both charge and discharge modes, dedicated circuits are used to measure the respective charge and discharge currents. These currents are then input into an efficiency computing circuit. To determine the charge and discharge capacities in Ah, the measured currents are integrated over time. Using (5), the coulombic efficiency is calculated and displayed on a screen or display device. Furthermore, a stop logic is implemented to halt the simulation after completing the desired number of cycles. This ensures that the evaluation process is conducted for the specified duration.

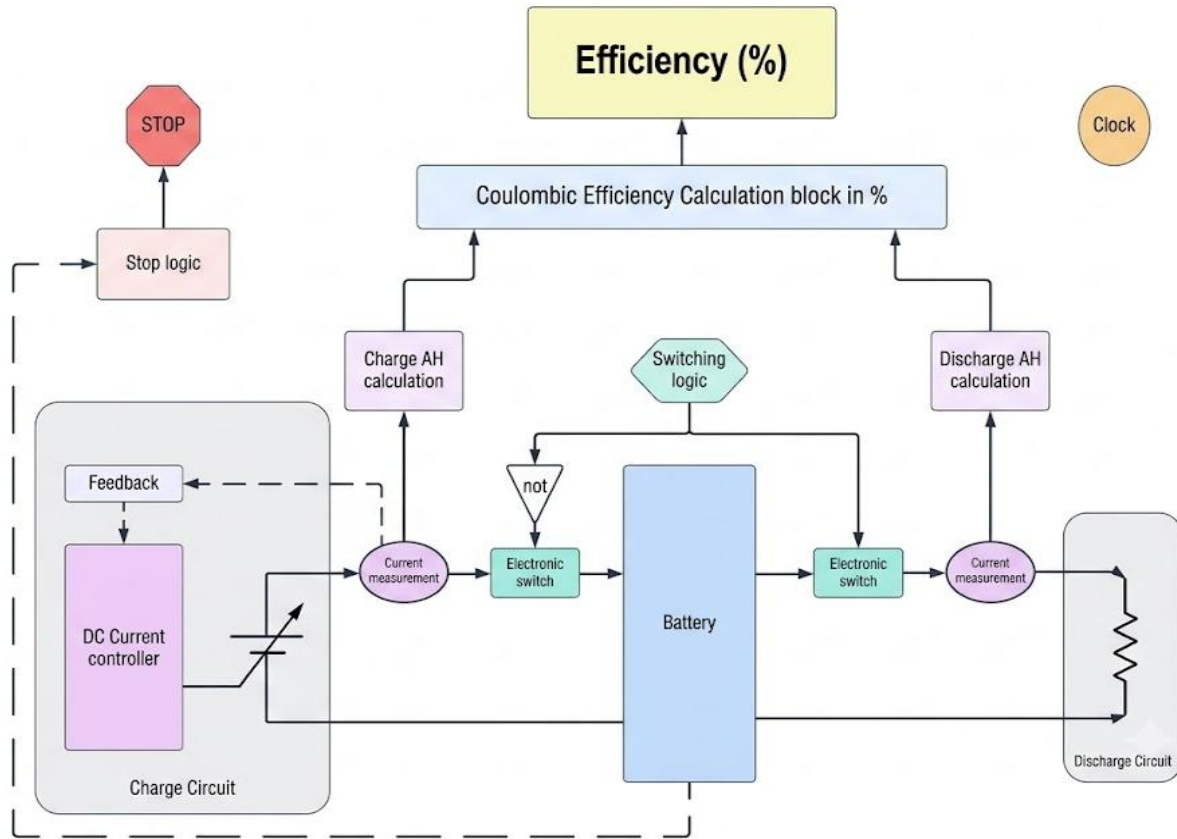


Fig 1. Schematic of the proposed model

The proposed system's different modes of operation have been described below.

Mode I: This mode of operation is the charge mode. Here, the battery is connected to a charging circuit. The initial circuit consists of a direct current (DC) voltage source connected in series with a DC controller. The key purpose of the DC controller is to sustain constant current characteristics. The DC controller controls the input DC voltage based on feedback from a current measurement sensor unit, attaining a stable output current. The charging method used in the simulation is constant current and the tool to achieve it is the DC controller. Mode II: Discharge mode requires connecting the battery to a discharge circuit which consists of a simple resistance block that allows for nearly constant discharge current, as shown in Figure 1. By varying the resistance value, one can obtain the desired discharge C-rate. The discharge C-rate of a lithium-ion battery is the

discharge rate with respect to its capacity. A desired discharge C-rate is obtained by tuning the available resistance value.

3. PROPOSED TECHNIQUE

The proposed simulation scheme involves many important phases that allow the simulation to mimic real-world conditions in a controlled virtual environment. When these proposed steps are implemented in a systematic and precise manner, the simulation results will be very accurate and reliable. This section describes the main steps in the simulation algorithm. A detailed description of the steps involved in the simulation process is usually given by

- a) Initialization: At the start of the flow chart, the model parameters are initialized. This includes the cell parameters, ambient temperature, cycle start and end SOC, constant current charging value, discharge load value, simulation time based on the cycle estimated time, and max charge voltage.
- b) Activate the charge circuit and deactivate the discharge circuit: The subsequent step involves turning on the charge circuit and turning off the discharge circuit.
- c) Update charge voltage: The charge voltage is tuned to retain a constant charging current for a reliable lithium-ion battery charging process. If there is a change in the charge current, the charging voltage circuitry is updated to ensure the preservation of a steady current during the charging process.
- d) Activating and deactivating the charge/discharge circuit: This step involves simultaneously tuning and ON/OFF on the charge/discharge circuitry as per the operating condition.
- e) Adjust the charge voltage: Following the activation of the charge circuit, the charge voltage is modified or updated. So that the charge current is maintained constant. If the charge current is changed, then the charge voltage is updated again to ensure a constant current value in charging.

- f) Calculate charge coulombs: While the charging process is continuing, the charge coulombs are calculated at each time by integrating the charge current over time. This calculated value is stored for further use.
- g) Deactivate the charge circuit and activate the discharge circuit: Upon reaching 100% State of Charge (SOC), the charge circuit is turned off, and the discharge circuit is turned on.
- h) Calculate discharge coulombs: The discharge coulombs are calculated by integrating the discharge current over discharge time.
- i) Evaluate efficiency: When the cell SOC reaches 0%, the efficiency is evaluated by dividing discharge coulombs by the charge coulombs.
- j) Stop simulation: After the efficiency is evaluated, the simulation stops.

Based on the above steps, the flow chart of the efficiency computing process is obtained, and it is shown in Figure 2.

3.1 BATTERY MODELING

Battery modeling plays a significant role in examining, estimating, or forecasting the real-time functioning of a battery. A more user-friendly and enhanced dynamic battery model, which builds upon Shepherd's model, has been developed and validated in [22]. The generic model developed is modelled as a voltage source under control, with its output being determined by the current state of charge (SOC) of the battery. One notable characteristic of this model is the ease with which a dynamic model can be obtained from battery datasheets. The model includes different tasks to account for the voltage dependency within various operating modes of the lithium-ion battery, as detailed in Figure 3.

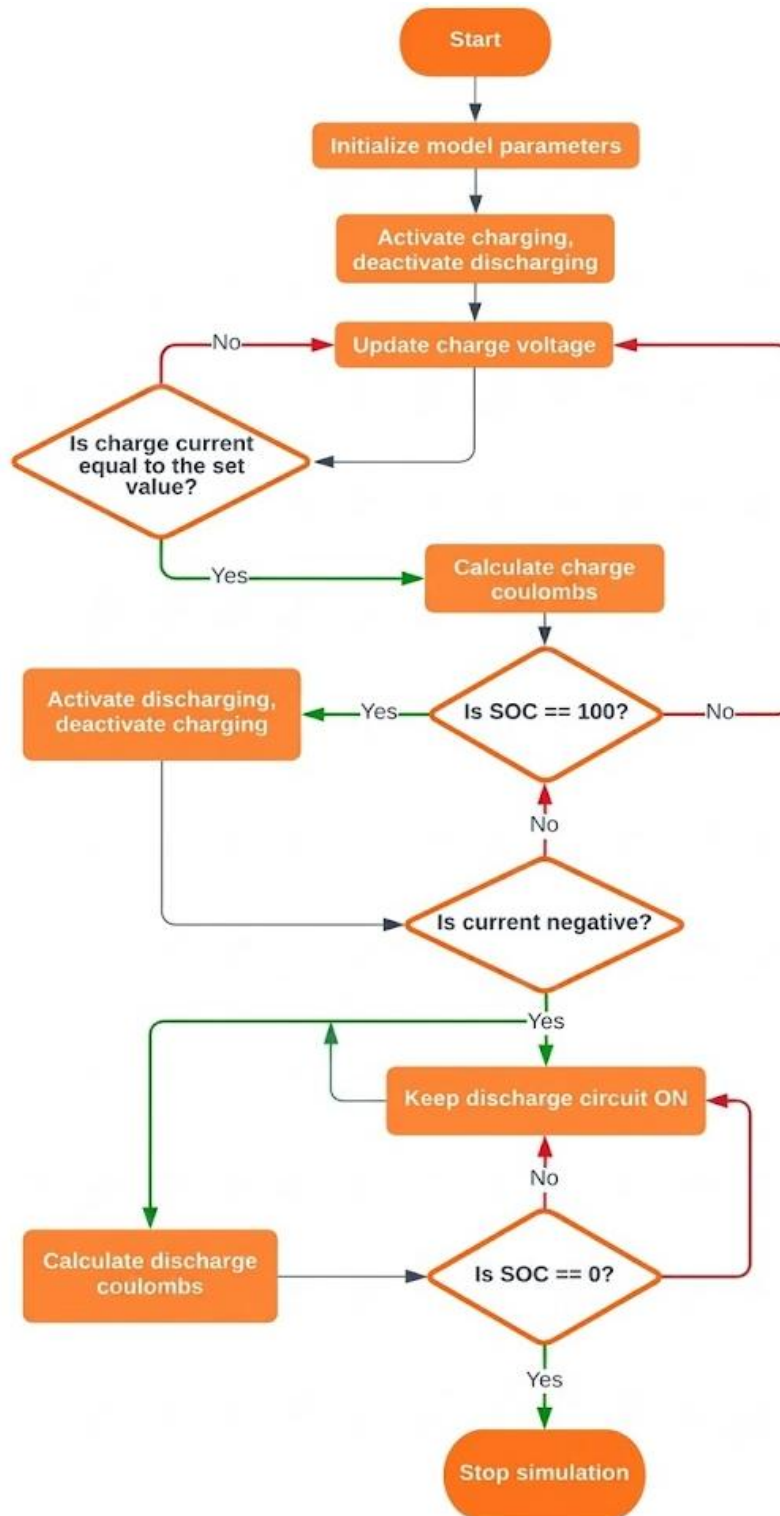


Fig 2. Flow chart for efficiency computing process

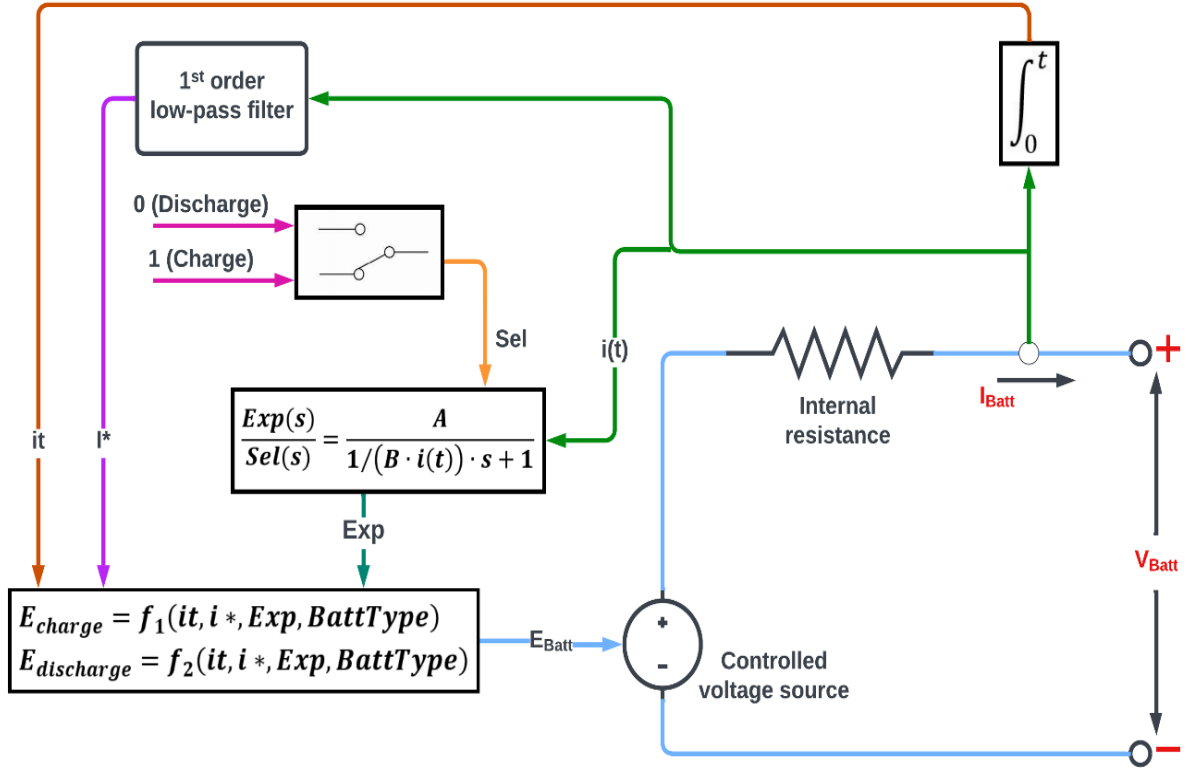


Fig 3. The battery model - Equivalent circuit

The discharge curve of a lithium-ion battery reveals non-linear dynamic behaviour. This behaviour is mathematically defined by (10) based on the Shepherd model [23].

Discharge model ($i^* > 0$);

$$f_1(i_t, i^*, i) = E_0 - K \frac{Q}{Q - i_t} (i^* + i_t) + A \exp(-B i_t) \quad (10)$$

In the given context, where: E_0 represents the constant voltage (V), K stands for the polarization constant or resistance (Ω), i^* denotes the low-frequency current dynamics (A), i represents the battery current (A), q is the extracted capacity (Ah), Q signifies the maximum battery capacity (Ah), A represents the exponential voltage (V), and B represents the exponential capacity (Ah⁻¹). The charge curve of a lithium-ion battery is characterized by an inverse shape compared to the discharge curve. Equation (11) depicts the characteristics of the charge curve [23].

The Charge model ($i^* < 0$);

$$f_2(i_t, i^*, i) = E_0 - K \frac{Q}{i_t + 0.1Q} i^* - K \frac{Q}{Q - i_t} i_t + A \exp(-Bi_t) \quad (11)$$

The battery parameters utilised in the model have been detailed in Table 1.

Table 1: Parameters of the Lithium -ion battery

PARAMETER	NAME/VALUE	UNITS
Cell Type	Lithium-Ion	--
Nominal voltage	3.7	V
Rated capacity	3	Ah
Cut-off Voltage	3.0	V
Fully charged voltage	4.2	V
Nominal discharge current	3	A
Internal resistance	0.012333	Ohms
Capacity at nominal voltage	2.713	Ah
Initial cell temperature	20	deg. C
Ambient temperature T1	-20	deg. C
Ambient temperature T2	55	deg. C
Capacity at EOL (End of Life)	1.8	Ah

3.2 MODELING OF CHARGE-DISCHARGE CIRCUIT

To verify the columbic efficiency of the battery under different operating conditions, it is necessary to calculate the charge and discharge capacity of the lithium-ion battery. This necessitates the use of specific circuits for charging and discharging the lithium-ion battery. The charge circuit is designed with a DC voltage source in series with a DC controller. The current characteristics are always fixed while charging. The input DC voltage is varied with the DC controller block so that the output current is constant. During the charging process, the charging current is measured and provided as input to the efficiency computing circuit. This circuit calculates the charge capacity, which is then used to determine the columbic efficiency of the battery. Moving on to the discharge circuit, it is constructed with a simple resistance block, as shown in Fig. 1. This configuration is nearly constant in its discharge current. During the discharge process, the discharge current is measured and provided as

input to the efficiency computing circuit. This circuit measures the discharge capacity, which is used to calculate the columbic efficiency of the battery. The charge and discharge circuits are modeled with almost constant charge and discharge current, respectively. This can be done to measure the capacities of the battery, which is a very important factor in calculating the Coulomb efficiency. Due to the steady current characteristics of the charge circuit, controlled charging is available, maintaining a controlled and measured level of charge to the battery. This facilitates accurate estimations of charge capacity, or the amount of charge the battery can store. On the other hand, the discharge circuit has the advantage of almost constant discharge current that enables it to release energy from the battery with a great degree of control. Then the discharge current is measured to calculate the discharge capacity, which is basically the charge that the battery is able to deliver. Charging and discharging are tightly controlled by these specialized charge and discharge circuits, which allow for the accurate determination of the battery's capacities. These readings are necessary to determine the Coulombic efficiency, which gives the effect of the battery on electrical energy during the charging and discharging process. Fig. 4 depicts the charging and discharging current profile over a single cycle.

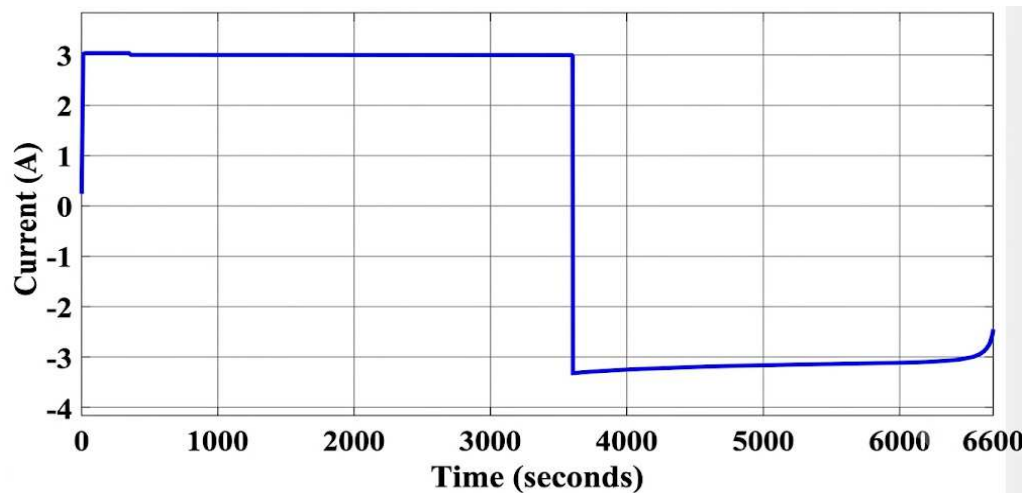


Fig 4. Current profile over a single charge-discharge cycle

3.3 CIRCUIT SWITCHING LOGIC

In accordance with the circuit operation, the battery commences with an initial State of Charge (SOC) of 0%. Following that, it undergoes the charging process until it attains 100% State of Charge (SOC). Subsequently, the battery undergoes discharge until it returns to a 0% State of Charge (SOC). To alternate between the charge and discharge circuits, a switching logic is necessary. Figure 5 represents the triggering pulses for MOSFETs in the charge and discharge circuits.

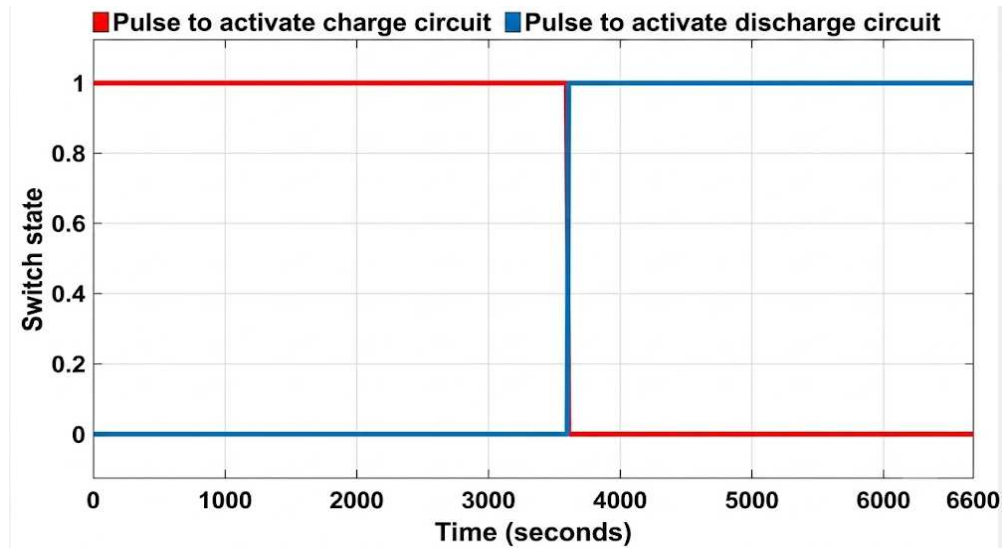


Fig 5. Triggering pulses for MOSFETs in charge and discharge circuits

In the switching logic, the battery is initially linked to the charge circuit. Once the battery attains full charge, it necessitates transitioning to the discharge phase. Therefore, if either the Charge of the battery reaches 100% or the current direction is reversed, the switching logic comes into play. It operates by connecting the battery to the discharge circuit; the equivalent model for circuit switching logic is shown in Figure 6.

The purpose of incorporating the NOT logic is to ensure that only one circuit, either the discharge or the charge circuit, is connected to the battery at any given time. This logic ensures appropriate functionality of the charging/discharging circuitry and further prevents the system from abnormal operations.

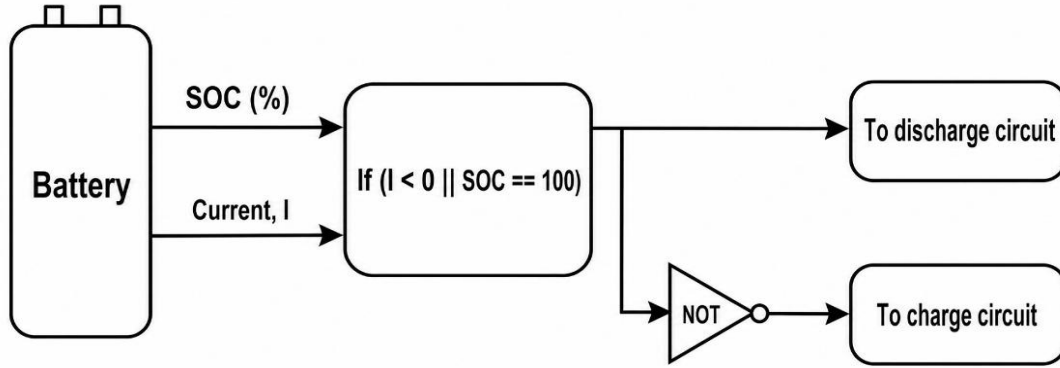


Fig 6. Equivalent model for circuit switching logic

3.4 MODELING OF THE EFFICIENCY OF THE COMPUTING CIRCUIT

This step is of paramount importance for computing the columbic efficiency of the lithium-ion battery. As shown in Figure 1, the circuit involves two inputs – charge and discharge currents – which are obtained from the charge and discharge circuits. The charge current is collected from the charging process and the discharge current is obtained during the discharging process. These currents are then subjected to an integrator block with respect to time, hence arriving at the charge and discharge capacities. Then, the charge and discharge capacities can be used in determining the columbic efficiency based on (5). This efficiency measure gives the ratio of the actual charge or discharge capacity to the theoretical capacity. Considering the columbic efficiency, the performance and effectiveness of the battery have been tested. Further, the computed performance indices are displayed for interpretation of lithium - ion battery performance under varying real-time operating conditions. This allows the visualization of the efficiency values for further analysis and interpretation of lithium - ion battery performance under varying operating conditions. The accurate identification of the columbic efficiency provides important insights for lithium - ion battery researchers and engineers. Such knowledge is essential from a battery performance, lifespan, efficient energy storage system, and applicability-based perspective for electric vehicles, integrating renewable energy, and portable electronics.

3.5 SIMULATION STOP LOGIC

To calculate the efficiency for the n th cycle, it is necessary to stop the simulation after the n th discharge is completed. This requires the implementation of a stop logic. The stop logic is activated when the battery is connected to the discharge circuit and its State of Charge (SOC) is equal to 0%. The switching logic indicates the battery's connection to the discharge circuit when it is in a HIGH output condition. Therefore, if the switching logic is in a HIGH output condition and the SOC of the battery is at 0%, the stop logic is triggered, and the simulation will be halted. Figure 7 shows the simulation stop logic equivalent model. This framework ensures that the results conclude after the desired number of charge-discharge cycles and permits the accurate computation of the efficiency of a lithium-ion battery for the specific cycle of interest.

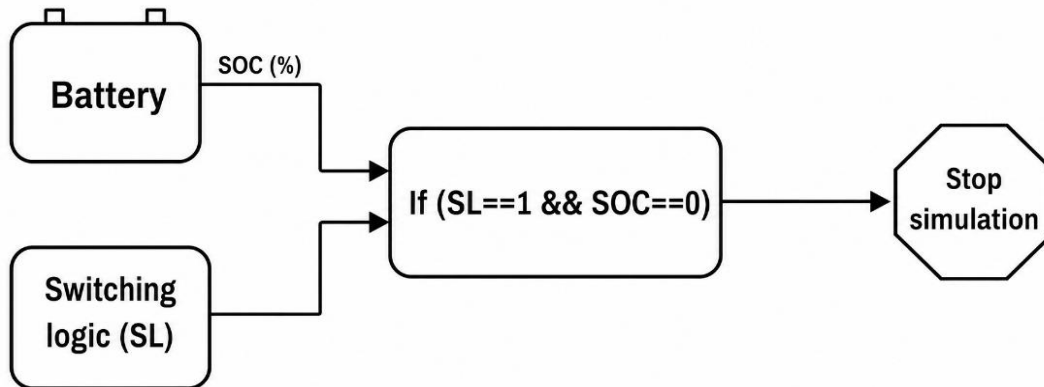


Fig 7. Equivalent model for simulation stop logic

4. EXPERIMENTAL SETUP FOR DATA ACQUISITION

A hardware prototype that implements the efficiency computing model has been designed and implemented. The prototype features the algorithm mentioned above and exhibits similar features to the simulation model in the way that it operates. Nevertheless, it is distinguished from the simulation model, as when a semi-charged part of the cell goes into the circuit, the prototype starts the discharge process that will result in zero SOC of the cell before commencing the calculation

process, as shown in Fig. 2. The main elements for this proposed prototype consist of a lithium-ion battery, a charging circuit, a discharging circuit, and a microcontroller.

4.1 LITHIUM-ION BATTERY

An 18650 Li-ion cell with a nominal voltage of 3.6V and rated capacity of 3000mAh has been used in this experiment. This specific lithium-ion battery has a higher cutoff voltage of 4.2V on open circuit, and 4.4V when connected to a charger, indicating a fully charged state. Similarly, a lower cutoff voltage of 2.5V means an empty state for this battery. Also, for charging, the operating temperature range of the battery is between 0°C and 50°C, while in discharging, -20°C to 75°C.

4.2 CHARGING CIRCUIT

To fulfil the requirements of the algorithm, the initial charging process involves raising the cell's State of Charge (SOC) from 0% to 100%. This task necessitates the utilization of a charging circuit, which consists of a power source capable of delivering a constant current output and a current-sensing module connected in series with a switch. In the experimental prototype, a linear DC power supply is employed as the constant current power source, offering a maximum power output of 180W. After ensuring the cell is at 0% SOC, the relay module connected in the charge circuit closes and connects the cell to a constant current source through the ACS712 module. This module

continuously sends the charging current data to the microcontroller, where the mathematical computations will be performed. The battery is charged at a 0.5C rate until it reaches 100% SOC.

4.3 DISCHARGING CIRCUIT

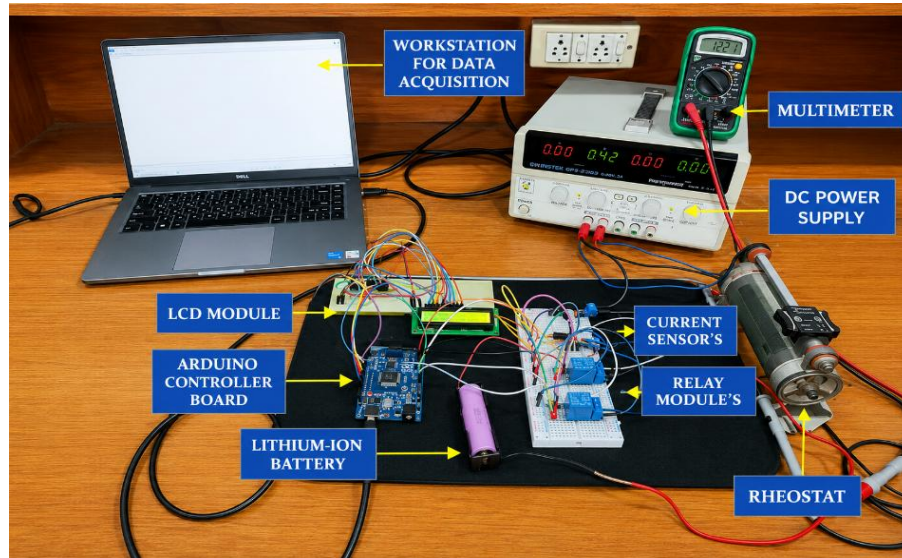


Fig 8. Experimental Setup

After charging the cell to 100% SOC, the next step in the algorithm is to discharge the cell back to 0% SOC. In order to accomplish this, a discharge circuit is made of a load and a current-sensing module connected in series with a switch. The rheostat of 15Ω and 3.2A is used for the cell discharging, and once the battery is fully charged, the relay modules switch from the charging circuit to the discharging circuit by the microcontroller. This is done so that the cell is discharged back to 0% SOC with a 0.2C discharge rate, thanks to the resistive load. The ACS712 module in the discharge circuit continuously updates the microcontroller with discharge current data, which is then used by the microcontroller to compute the coulombic efficiency. Table 2 displays the overall experimental setup specifications.

Table 2 Experimental setup Specifications

Components	Specifications
Battery	3000mAh, 3.6V 18650 Li-ion cell
Linear DC power supply	GW Instek GPS-2303: 0-30Vdc, 0-3A, 180W
Micro controller	Arduino Mega 2560 microcontroller board– Atmega2560
Load	Wire-wound rheostat, 15 Ohms, 3.2A
Current measurement	ACS712 module, 30A
Switching	1 CH 5V Relay Module
Display	16x2 Liquid Crystal Display
Multimeter	MAS830-L Digital multimeter

4.4 MICRO-CONTROLLER

The Arduino Mega microcontroller board is used in this prototype for the implementation of the algorithm. Arduino Mega is built around the ATmega2560 microcontroller, which runs at a clock speed of 16MHz. The Arduino Mega has a vast set of digital and analog input/output pins. Arduino Mega is programmed using Arduino Integrated Development Environment (IDE) software, which is easy to use. The code of the CE computing algorithm has been uploaded and stored on the board for execution. To display real-time information, the microcontroller board is connected to a Liquid Crystal Display (LCD) to provide current cell voltage, circuit current, total Coulombs counted and Coulombic efficiency. In the CE computing process, the voltage of the cell is continuously monitored by the microcontroller's built-in ADC (Analog-to-Digital Converter). The microcontroller starts with a fully discharged cell at 2.5V. The charging circuit relay is turned on, and the cell starts charging at 1.5A. When the cell is at 4.2V, the microcontroller turns off the charging circuit relay. After a short wait, the microcontroller switches on the relay of the discharging circuit. The cell is then discharged through a Rheostat until its voltage reaches 2.5V. At this point, the microcontroller stops the process of discharging and gives the final Coulombic efficiency of the end process. During the charging process, the microcontroller calculates the charge Coulombs by taking the current value of the charge circuit sensor. The discharge of Coulombs is

also measured and recorded. Finally, we evaluate the Coulombic efficiency using the charge and discharge Coulombic values. This efficiency value is then displayed on a 16x2 LCD screen.

5. RESULTS ANALYSIS AND DISCUSSION

In this section, battery performance under different operating conditions has been described. To verify that the lithium-ion battery model is accurate, a comparison has been carried out between simulated terminal voltage response and the measured voltage profile. The experimental and simulated voltage profiles are shown in Figure 9 for charging and discharging. It has been observed that the simulated charging profile is similar to the experimentally measured voltage profile, and the voltage is still gradually increasing with the charging state to the fully charged condition. In the discharge case, the simulated voltage profile also shows the characteristic nonlinear voltage variation and the rapid voltage drop near the end of the discharge. The close agreement between the experimental and simulated profiles shows that the battery model developed can accurately reflect the terminal voltage characteristics of LIB cells. Therefore, the validated battery model can later be considered to investigate the influence of battery aging and operating circumstances on discharge capacity, Coulombic efficiency, and round-trip performance.

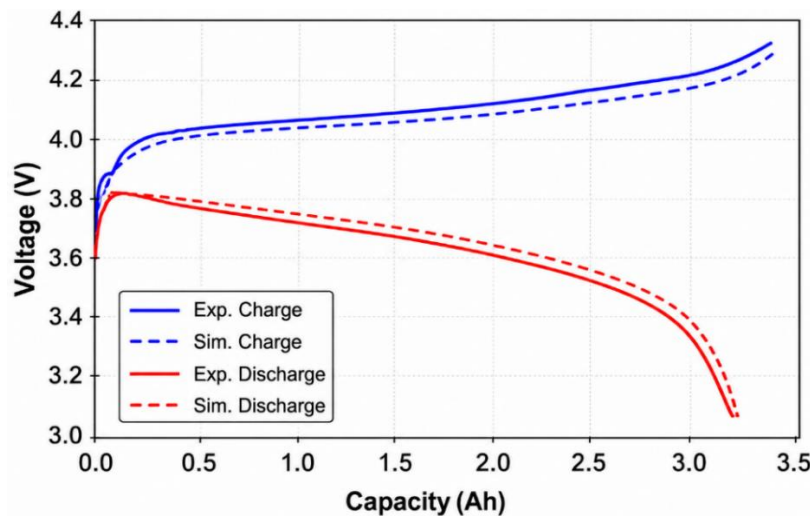


Figure 9 Experimental and simulated voltage profile

In this regard, the relationship among discharge capacity, state of health (SOH) and cycle number of the lithium-ion is of utmost importance to explore the performance of the battery. Figure. 10 shows the evolution in discharge capacity and state of health (SOH) of the lithium-ion cell as a function of cycle number. The cell shows a progressive degradation as the cycle number increases. The discharge capacity decreases from 2.704 Ah at the beginning of the cycle to 1.783 Ah after 1500 cycles. This corresponds to a capacity loss of about 34.03%, which indicates the cell's storage capacity is significantly reduced during long cycling. The corresponding SOH decreases as the cycle number increases from 100% at the start of the test to 65.96% at the end of the cycle. The close relationship between the capacity fade and SOH reduction suggests that the discharge capacity is the biggest indicator of battery aging. The nearly monotonic decrease in both conditions indicates that in time, charge-discharge operation leads to a deterioration of the cell's electrochemical performance. The degradation trend in Fig. 10 is consistent with the capacity retention results, in which the cell retains about 65.96% of its former capacity after 1500 cycles. Therefore, the results show that long cycling significantly reduces the battery's energy storage capacity. Such capacity degradation is especially important for EV applications since it decreases the achievable driving range and the overall energy efficiency of the battery system.

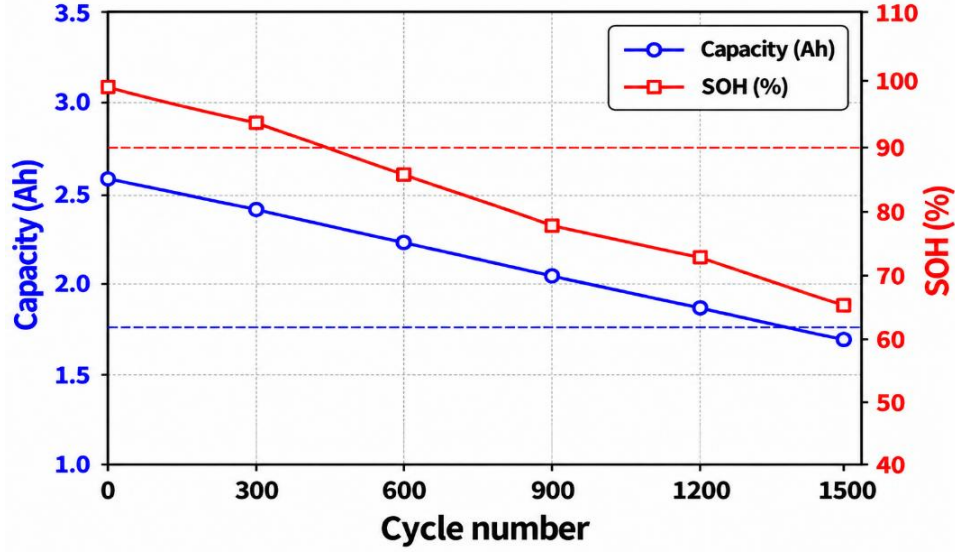


Figure 10 Evolution of discharge capacity and state of health of the lithium-ion cell

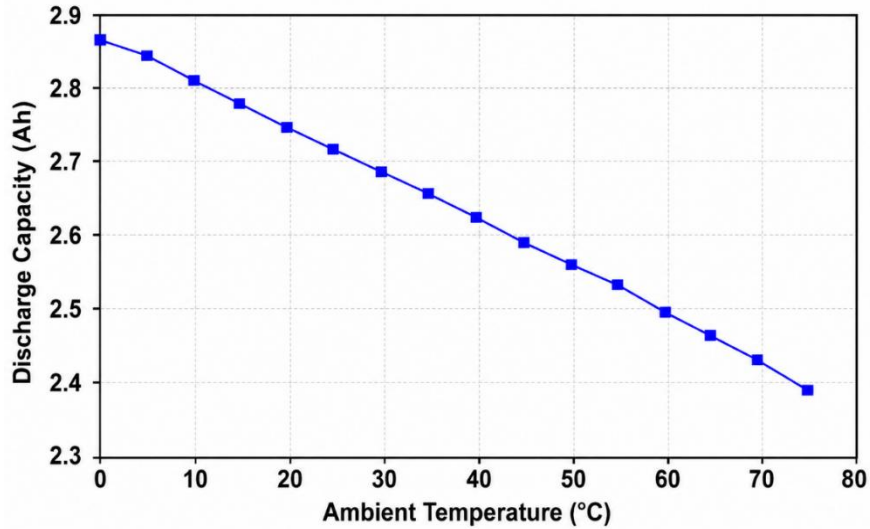


Fig 11. Ambient temperature vs. discharge capacity

Figure 11 shows the effect of ambient temperature on the discharge capacity of the battery. The results are obtained by varying the ambient temperature from 0 °C to 75 °C. It can be observed that the discharge capacity decreases progressively with an increase in ambient temperature. The discharge capacity decreases from approximately 2.86 Ah at 0 °C to approximately 2.39 Ah at 75 °C. Using Equation (8), the overall reduction in discharge capacity over the investigated temperature range is calculated as 17.13%. This reduction demonstrates that elevated ambient temperature adversely affects the available discharge capacity of the battery. Therefore, ambient

temperature is an important factor that should be considered when evaluating battery performance and designing battery-management strategies.

Figure 12 and Table 3 illustrate the variation of battery coulombic efficiency with cycle number at an ambient temperature of 25 °C, a charging current of 3 A, and a discharge load of 1.25 Ω . The developed model was used to evaluate the battery performance over 1500 charge–discharge cycles. A continuous reduction in coulombic efficiency is observed with increasing battery age. At the beginning of life, the coulombic efficiency is approximately 90.1%, whereas it decreases to 59.43% after 1500 cycles. This represents a reduction of approximately 30.67 percentage points, demonstrating the progressive deterioration of the battery's charge-retention performance with repeated cycling. The corresponding efficiency-loss values presented in Table 5 exhibit the opposite trend. The efficiency loss increases from 9.90% at the initial cycle to 40.57% after 1500 cycles. This indicates that an increasingly larger fraction of the charge supplied to the battery is not recovered during the subsequent discharge process as the battery ages. The simultaneous decrease in coulombic efficiency and increase in efficiency loss therefore provide complementary indicators of the progressive degradation of the battery. In addition, the capacity-retention values decrease continuously from 100% at the beginning of life to 65.96% after 1500 cycles. The simultaneous reduction in coulombic efficiency and capacity retention indicates that battery aging adversely affects both the charge-transfer performance and the available capacity of the cell. The results demonstrate a strong degradation trend with increasing cycle number, with the aged battery exhibiting substantially lower efficiency and capacity-retention capability than the fresh battery. Overall, the results demonstrate that battery age has a significant influence on coulombic efficiency and capacity retention. The progressive increase in efficiency loss, together with the reduction in capacity retention, confirms the degradation of battery performance during prolonged cycling.

These results are particularly relevant for battery-management applications, where monitoring efficiency and capacity-related indicators can provide useful information for assessing the operating condition and degradation state of an aging lithium-ion battery.

Table 3 Variation of coulombic efficiency, efficiency loss, and capacity retention with battery cycle number

Battery age in Cycles	Efficiency (%)	Efficiency loss (%)	Capacity Retention (%)	Battery age in Cycles
1	90.1	9.9	100.00	1
120	87.67	12.33	97.30	120
240	85.21	14.79	94.57	240
360	82.76	17.24	91.85	360
480	80.3	19.7	89.12	480
600	77.85	22.15	86.40	600
720	75.39	24.61	83.67	720
840	72.94	27.06	80.95	840
960	70.48	29.52	78.22	960
1080	68.03	31.97	75.50	1080
1200	65.57	34.43	72.77	1200
1320	63.12	36.88	70.06	1320
1440	60.66	39.34	67.33	1440
1500	59.43	40.57	65.96	1500

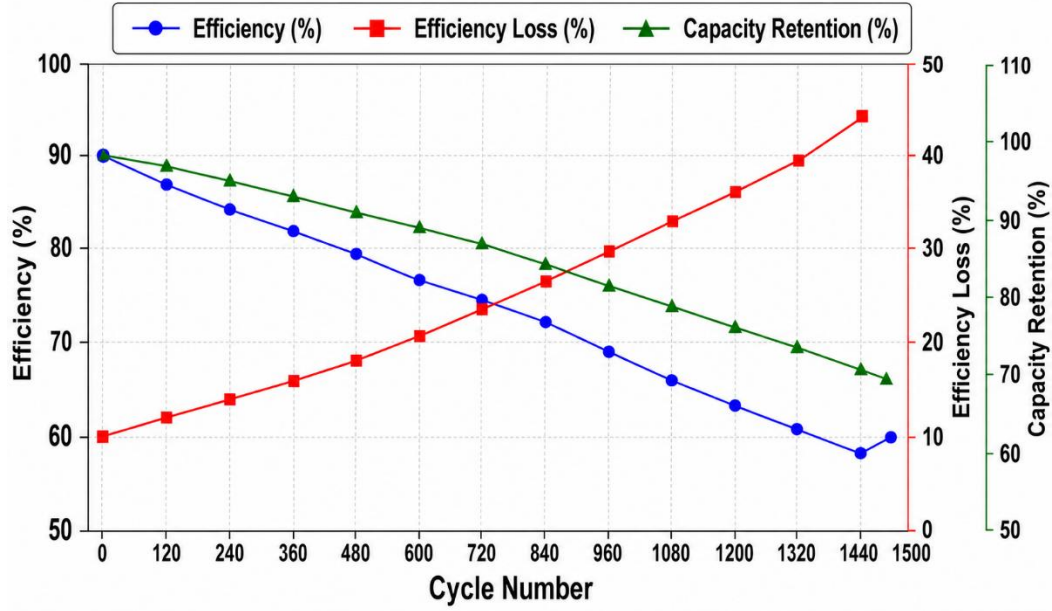


Figure 12. Variation of coulombic efficiency, efficiency loss, and capacity retention with battery cycle number

The effect of ambient temperature on the battery's Coulombic efficiency is shown in Figure 13 and Table 6. The results are obtained from the developed simulation model with a charge current of 3A, a discharge load of 1.25Ω , and this analysis is done for the 1st cycle of the battery, i.e., the battery being used for the simulation was new and had zero life initially. The simulation test analysis is done from 0°C to 70°C in steps of 5°C (i.e., the number of simulation samples performed is 15 samples). It can be observed that the battery's coulombic efficiency is decreasing with an increase in ambient temperature from Figure 13 and Table 6. The coulombic efficiency at 0°C is 95.6%, and the coulombic efficiency at 70°C is 80.2%. The proposed model was validated by comparing the simulated coulombic efficiency with the experimentally measured efficiency under the same operating conditions (charging current of 3 A, discharge load of 1.25Ω , and the same ambient temperatures). This resulted in a close match to the experimental measurements over the entire temperature range, as observed in Table 6 and Figure 13. The maximum deviation of the simulation compared to the experimental results is within an acceptable limit, corroborating the accuracy and dependability of the developed model that predicts the performance of the battery under various thermal conditions.

Table 4 Ambient temperature vs Efficiency

Ambient Temperature (°C)	Simulation Efficiency (%)	Experimental Efficiency (%)	Absolute Error (%)
0	95.6	95.1	0.5
5	94.5	94.0	0.5
10	93.4	93.0	0.4
15	92.3	91.9	0.4
20	91.2	90.8	0.4
25	90.1	89.8	0.3
30	89.0	88.7	0.3
35	87.9	87.6	0.3
40	86.8	86.5	0.3
45	85.7	85.4	0.3
50	84.6	84.3	0.3
55	83.5	83.2	0.3

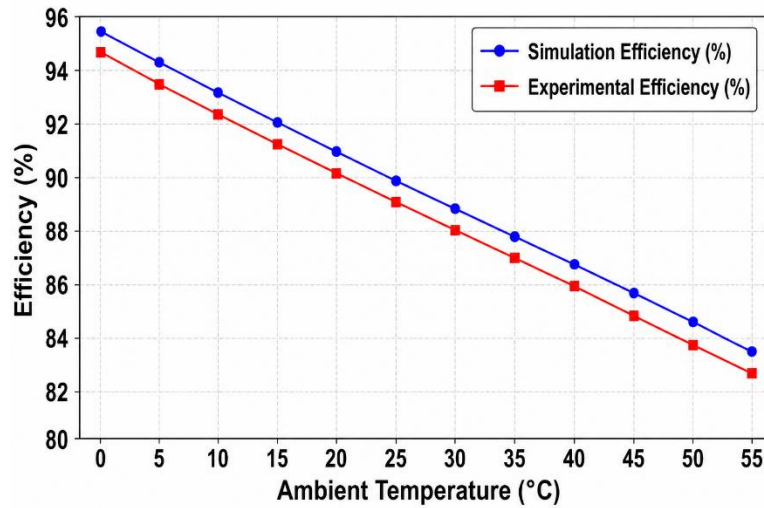


Fig 13. Ambient temperature vs Coulombic efficiency

Table 5 shows the variation of the round-trip time (RTT) with battery age, and the trend is also shown in Fig. 14. The RTT is decreasing with the number of cycles of the battery. The RTT is 6689 s during the first cycle and gradually decreases to 5609 s after 1500 cycles. This corresponds to a reduction of 1080 s, representing an overall decrease of approximately 16.14% over the aging period. The reduction in RTT is nearly monotonic, with no significant variations during the cycling time. The RTT drops from 6689 s at the

beginning of the test to 6538 s at 210 cycles, 6278 s at 570 cycles, 6019 s at 930 cycles, and 5760 s at 1290 cycles, and then to 5609 s at 1500 cycles. The nearly linear decrease in RTT is a clear indication that aging is associated with battery aging. The decrease in RTT could be explained by the loss of the available charge storage capacity of the battery as it ages. As the battery undergoes charge-discharge cycles, degradation, i.e., loss of active lithium, growth of solid electrolyte interphase (SEI), and loss of electrochemically active material, progressively reduces the available capacity. The total charge that can be stored and then delivered during a complete charge-discharge process is therefore reduced. As RTT is calculated from the time spent on charging and discharging the battery, a lower available capacity will correspond to a shorter round-trip time under the expected operating conditions. Qualitatively, the average rate of RTT reduction over the available range is 0.72 s per cycle, but this is an average and it should not be considered as a uniform degradation rate, because RTT also depends on the current, charging/discharging process, temperature, and battery operation. So the aging of the battery has a significant impact on RTT, and the observed reduction in RTT can be another marker of capacity degradation. But the decrease in RTT should not be interpreted as a sign of better battery performance. It is simply a reflection of the less energy the aging battery can hold and deliver, because, as the batteries age, the battery is less able to charge. Hence, the combined analysis of capacity retention, coulombic efficiency, and RTT provides a more comprehensive assessment of battery aging and degradation. From this analysis, it can be concluded that the storage capacity of the battery will be reduced with the increase in the battery's age.

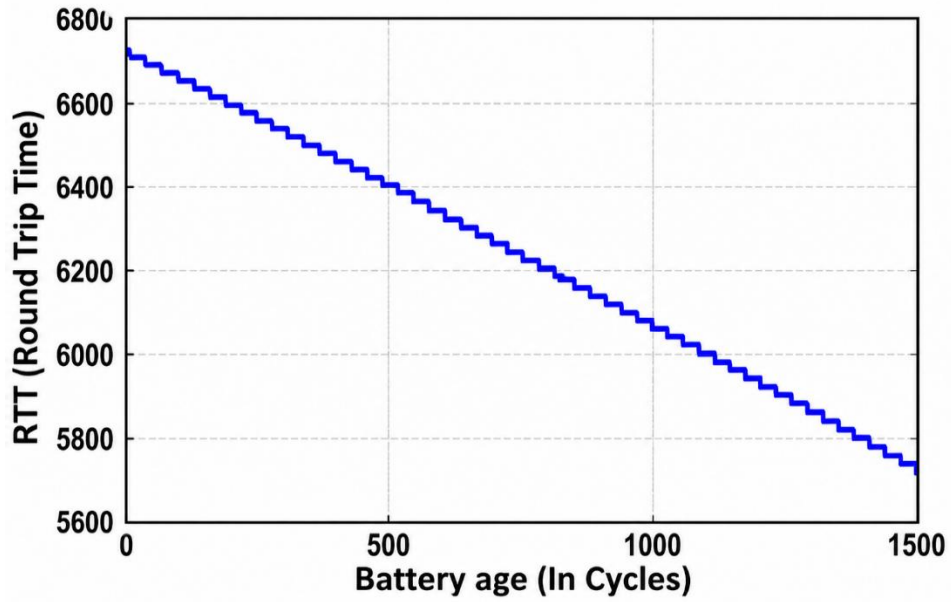


Fig 14. Round-trip time versus Battery's age

Table 5 Battery's age v/s RTT

Battery age in cycles	RTT(Round Trip Time)
1	6689
90	6624
210	6538
330	6451
450	6365
570	6278
690	6192
810	6105
930	6019
1050	5933
1170	5846
1290	5760
1410	5674
1500	5609

6. CONCLUSION

This study described a mathematical modeling framework for investigating the round-trip and coulombic efficiency of lithium-ion batteries by determining the operating effects, including the ones related to aging and temperature, through different operating conditions. The adopted model successfully summarized the critical performance metrics such as discharge capacity, coulombic efficiency, efficiency loss, capacity retention, and round-trip time. The results showed that the aging of batteries has a significant negative impact on overall performance. After 1500 charge-discharge cycles, the discharge capacity decreased by 34.07% (from 2.704 Ah to 1.783 Ah) and the coulombic efficiency diminished from 90.1% to 59.43%, respectively, which was closely associated with a surge in efficiency loss rates from 9.9% to 40.57%. Battery capacity retention decreased to 65.96% and round-trip time shortened from 6689 s to 5609 s, which revealed that the battery's ability to provide energy storage and also delivery was drastically reduced. Moreover, by raising the ambient temperature from 0 °C to 75 °C, the discharge capacity of the battery was decreased by 17.13%, indicating the significant influence of operating conditions on the battery. As a whole, this model serves the same role as a well-established conceptual framework used in estimating lithium-ion battery performance and degradation, with important results in predicting battery performance, life cycle assessment and formulation of a practical battery management solution for electric vehicles.

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