A STUDY OF THE FACTORS THAT AFFECT LITHIUM ION BATTERY DEGRADATION

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by

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The undersigned, appointed by the dean of the Graduate School, have examined the thesis entitled

A STUDY OF THE FACTORS THAT AFFECT

LITHIUM ION BATTERY DEGRADATION

presented by Shihui Xiong,

a candidate for the degree of Master of Science,

and hereby certify that, in their opinion, it is worthy of acceptance.

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ABSTRACT

Secondary batteries have been applied in every aspect of our life, from cell phones, to laptops, medical devices, satellites, and renewable energy power stations. Li-ion batteries have shown superior advantages in their ability to store large amount of energy in compact spaces and their long battery life. However, battery capacity degradation, which causes battery failure, posts a serious concern to the economy and efficiency to individuals and industries. The degradation rate is affected by several factors including temperature, charge and discharge voltage, current, and the level at which the battery is charged or discharged. Understanding these factors can largely help to reduce the speed of battery failure and allow batteries to better serve their purpose. First, this thesis project did a review of existing literatures addressing how conditions including temperature, state of charge, depth of discharge, charge voltage, and C-rate affect Li-ion battery degradation rate and the conditions necessary to achieve optimal battery life. An experiment was done to study how battery chemistry, cycle frequency, and temperature affect battery degradation rate and observe how degradation affects battery performance. Results show that high and low temperature shorten battery life, cycle frequency is not consequential with Li-ion battery degradation rate, and INR batteries might have shorter battery life than IMR batteries. These findings will help consumers and companies better understand proper usage of Li-ion batteries.

Chapter One

Introduction

In the 21st century, due to the public's concern over generating grid electrical power by burning fossil fuels to avoid air pollution, energy imports, and global warming, the renewable energy industry has emerged and grown rapidly. Renewables have three main applications: renewable electricity, renewable heat, and biofuels in road transportation. According to the International Energy Agency, over the next five years, renewables in the electricity sector will be the fastest growing among these three applications, providing almost 30% of the power demand in 2023, up from 24% in 2017. During this period, 70% of global electricity generation growth is forecast to be met by renewable energies, with solar contributing the most, followed by wind, hydropower, and bioenergy [1].

Solar and wind energy are frequently used in grid-connected power stations to generate electricity and reduce the production of carbon. Through power electronic equipment, energy from sun and wind can be transformed into electricity and be fed into the power grid. One technology, the photovoltaic (PV) system, uses solar panels to collect light from the sun and to convert it to direct current (DC) electricity. Another one is concentrated solar power, which uses mirrors and lenses to collect heat from the sun and then use the heat to drive generator systems. Although both methods have their advantages and disadvantages, PV systems are far more popular than concentrators. Utility-scale solar can be achieved by large-scale PV systems which are designed to supply utility level power to the electric grid. Most solar parks are developed at a scale of at least 1 megawatt-peak (MW_P). Until 2018, the world’s largest PV power stations operated over 1 gigawatt [2].

Electricity generated by solar panels is fed into the power grid through solar inverters, a power conditioning unit, and grid connection equipment. Wind farms consist of many individual wind turbines, which are connected through capacitors, resistors or converters to the electric transmission network. Blades of a wind turbine capture the kinetic energy in wind, and rotate. The rotor passes the energy through a shaft to a generator, which turns the rotational energy into electricity. The capacitors, resistors, and converters connected to the wind turbines compensate the consumption of reactive power and control the speed of the wind turbine, which adjusts the voltage to match the grid level.

However, when energy from renewable resources are passed to the grid, it causes problems such as lower power quality, issues with voltage regulation, and many protection-related challenges, such as islanding. To be more specific, the traditional grid operates under one-way flow. When the electricity generated by the renewable power sources is injected into the grid, the voltage increases, sometimes over the acceptable range (5%). In addition, renewables like solar and wind are intermittent, which cause fluctuations in the generated energy. Voltage fluctuations in the grid require frequent adjusting by voltage regulators and can cause voltage flicker. Moreover, without proper storage, generated electricity can be wasted during the low energy demand time and might be unavailable when needed. Thus, technology is needed to improve the energy quality and efficiency of renewable power stations.

With the ability to improve the operating capacities of the electric gird through peak shaving and frequency control, battery energy storage systems (BESS) play an important role in integrating more variable renewable resources as well as enhancing the reliability of the power system. BESS consist of batteries, hybrid inverters, and battery management systems (BMS). In grid scale, hundreds and thousands of cells are connected in series and parallel to form battery modules for energy storage systems of megawatt level substations. The BESS are co-located with renewable energy plants, either to smooth the power supplied by the intermittent wind or solar output, or to shift the power output into other hours of the day when the renewable plant cannot produce power directly. These generation-plus-storage systems can either reduce the pressure on the grid when connecting renewable sources or be used to work off the grid.

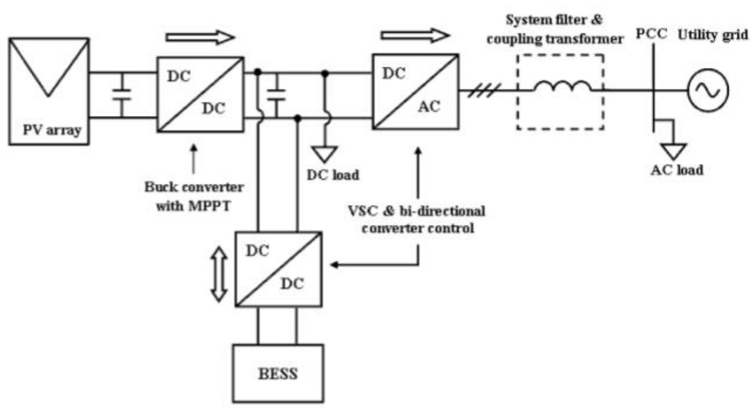

Figure 1.1 System configuration of grid-connected PV with BESS [30]

Figure 1.1 shows one system configuration of grid-connected PV with BESS [30]. The BESS is interfaced to a DC bus via a DC/DC buck/boost converter. The PV arrays is interfaced to the DC bus via a DC/DC buck converter with a maximum power point tracker (MPPT). DC/AC bi-directional converters with voltage source converters (VSC) are used for grid interfacing. The utility grid is ideally assumed to be an infinite AC system in this configuration.

BESS have gained increasing interest for various grid applications as they reduce intermittency of renewable energy, bring flexibility to power transmission and distribution, adjust power peaking, and restructure power markets. BESS is superior to most other energy storage techniques because of its fast response time, high efficiency, low self-discharge, and scaling feasibility. The capacity of BESS in stationary applications is projected to grow in the next decade from 11GWh in 2017 to between 100GWh and 167GWh in 2030 [3].

Among all the factors that can impact the efficiency and cost of the grid BESS, the battery type plays an important role. When choosing the most suitable batteries for an energy storage system, specifications including specific energy, or capacity that relates to runtime; specific power, or the ability to deliver high current; life-span reflecting cycle life and longevity; safety; performance at hot and cold temperatures; and cost all need to be considered. Other important factors are toxicity, fast-charge capabilities, self-discharge, and shelf life.

There are four main types of batteries for grid-connected renewable energy storage: lead-acid batteries, sodium-sulfur (NaS) batteries, vanadium redox (VRB) batteries, and lithium-ion batteries. Each of these has reached a certain level of maturity in stationary energy storage applications. Table 1.1 compares these batteries in terms of their electrical specifications, reliability, and cost.

Composition	NaS	VRB	Li-ion	Lead-acid
Shelf life/usable life	15 years, grid-scale battery storage 10 years of commercial operation.	20--30 years	2-3 years	10 years
Advantages	Long discharge time; Require minimal maintenance; High energy density; Environmentally friendly.	Store and release energy through a reversible electrochemical reaction.	High energy; Low self-discharging; High resiliency against deep and fast discharge; Low maintenance.	Reliable and cheap; Long discharge time.
Charge cycles	4500	>10,000	7000 before they experience loss.	200-300
Efficiency	89-92%	75-80%	90%	~80%
Drawbacks	Need to be operated above 300C temp; Material is metallic sodium, which is hazardous when in contact with water; Extra cost to prevent leakage.	Complicated system; Requirements of pumps, sensors, flow and power management.	Require protection from being over charged and discharged; Li-ion batteries age per charge or discharge.	Require high maintenance; Deep discharge significantly damages lead acid batteries; Short cycle life.
Temperature	>300 C	-5-50 C		
Cost (dollar/ kwhr)	500	300-500	average 209	186

Table 1.1 Comparison of VRB batteries, NaS batteries, Lithium-ion batteries and Lead-acid batteries

While each type of battery has its own advantages and disadvantages, the NaS battery is most suitable for peak shaving, transmission, and distribution network management and load-leveling; the VRB battery is best used in high capacity power systems with a range of 100kW to 10MW; and both the Li-ion battery and the lead acid battery are suitable in intermittent source power storage in renewable energy systems.

Thus, more comparisons can be made between the Li-ion battery and the lead acid battery. According to O’Connor [4], in 2016, lithium-ion batteries were just beginning to be used for large-scale solar power systems. Recently, lead-acid battery power grid energy storage systems are being replaced with Li-ion batteries. Li-ion batteries are superior to lead acid batteries for many reasons. First, Li-ion batteries have higher energy density, which enables manufacturers to store high levels of power in compact spaces. A typical lithium-ion battery can store 150 watt-hours of electricity in 1 kilogram of battery, while a lead-acid battery can store only 25 watt-hours per kilogram [4]. In addition, Li-ion batteries have superior resiliency that allows for deep and fast discharge without being damaged. Li-ion batteries can be discharged to about 80% State of Charge (SOC) and at a rate of C/2 (more on that in Chapter 2) without any long-term damage, while lead acid batteries lose potential cycles if they are discharged below 50% of their SOC or if discharged faster than C/8 [4]. What's more, when cycle life is considered, Li-ion batteries lower the cost in the long term as they require lower cost per cycle. According to Table 1.2 [4], which compares two types of lead acid batteries with one type of Li-ion battery, even though Li-ion batteries require a higher initial price, because of their superior cycle life, low maintenance, deep discharge and high energy efficiency, their price per cycle ($0.19) is lower than the price of most lead acid batteries per cycle ($0.71). Even though the flooded lead acid battery cost slightly less per cycle than the Li-ion battery, it requires regular maintenance; provides significantly less load power and specific energy; and takes four times longer to charge than the Li-ion batteries. Thus in conclusion, for the highest cost-saving and superior performance purposes, the Li-ion battery is most suitable for intermittent source power storage due to its long lifecycle, high energy density, low cost per cycle, and deep and fast discharge ability.

	Flooded Lead Acid	VRLA AGM	Lithium-Ion (NMC)
Initial Cost per Capacity ($/kWh)	131	221	530
Cost per Life Cycle ($/kWh)	$0.17	$0.71	$0.19
Specific Energy (Wh/kg)	30	40	150
Regular Maintenance	Yes	No	No
Number of Cycles to 80% SOH	200 – 1000	200 – 650	1000 – 4000
Typical State of Charge Window	50%	50%	80%
High Temperature Sensitivity	Degrades above 25°C	Degrades above 25°C	Degrades above 45°C
Available Power Constant Current	0.2C	0.3C	1C
Fast Charging Time (hrs)	8 – 16	4 – 8	2 – 4

Table 1.2 Cost comparison of flooded lead acid batteries, VRLA AGM batteries and Li-on batteries [4]

Li-ion batteries are extremely popular worldwide in renewable energy BESS application because of their superior characteristics. The 36 MW BESS of Younicos' 153 MW Notrees wind farm in Texas, which originally used lead-acid technology, replaced the lead acid batteries with Li-ion batteries in 2017. According to Froese [5], the new Li-ion battery system will increase the duration of discharge and have the capability to provide additional fast-responding services. Other Li-ion battery BESS examples include the 32 MWh BESS in the Tehachapi 4,500 MW Wind Energy Storage Project in California, US; The 32 MWh Ruien Energy storage project in Ruien, Belgium; The 4.3 MWh Alata project in Corsica, France; The 10 MWh Smarter Network Storage project in England, UK; The 8 MWh Laurel Mountain project in West Virginia, US; The 6.6 MWh Angamos project in Mejillones, Chile; The 2 MWh BESS in Johnson City, US; and the three National Wind and Solar Energy Storage and Transmission Demonstration Projects in Hebei, China, with capacities of 36 MWh, 16 MWh and 9 MWh.

Meanwhile, more cost-effective Li-ion battery technologies are starting to appear. A lot of companies, including Tesla, LG, Sonnen, Simpliphi Power, and Lithionics all have reliable products at reasonable prices. In 2018, Tesla's Model 3 battery pack costs $190 per kWh. General Motors' 2017 Chevrolet Bolt battery pack is estimated to cost about $205 per kWh [6]. Predictions indicate that the record for solar-plus-storage deployments in 2018 will be broken yet again in 2019, which is based on the forecast of falling solar and battery prices as well as a continuation of the federal Investment Tax Credit for solar that can include the cost of batteries as part of the installation [7]. In addition, Schmidt presents a model to estimate lifetime costs for 9 storage technologies in 12 applications from 2015 to 2050 [8], and concluded that Li-ion batteries will be the most competitive technology in the majority of applications in the coming decades.

Because of the high popularity of Li-ion batteries among grid-connected BESS applications, I decided to focus my research on this spectacular battery. However, even with all those superior specifications mentioned above, Li-ion batteries still have a few drawbacks, such as self-discharging and aging, which shortens their lifespan. The purpose of my research is to study the factors that impact the Li-ion battery life, reasons behind them, and how to better prevent them in order to prolong Li-ion battery life and achieve better profits. My experiment is mainly focused on Li-ion battery degradation under deep discharge (>80%), extreme temperature, and the difference between two types of popular Li-ion chemistries.

In Chapter 2, an overview of the features of Li-ion batteries will be introduced, including different types of Li-ion batteries and their applications, battery charge and discharge mechanisms, and some terms and definitions related to batteries.

Chapter 3 will explain the Li-ion battery degradation mechanism and introduce factors that affect the degradation process.

In Chapter 4, an experiment with the purpose of observing the degradation pattern of a Li-ion battery under various conditions will be described. The experiment was done by repeating and recording data from charging and discharging several Samsung 2500mAh INR 18650 and LG 2500mAh IMR18650 Li-ion batteries under different temperatures and frequencies. Information regarding the lab equipment, experiment steps, recorded values and variables will be described in detail.

Chapter 5 contains the results of the experiment by plotting the cycle data of different sets of Li-ion batteries and discussing the analysis of the experimental data. Results show that cycling and aging cause Li-ion battery capacity degradation; high or low temperatures accelerate Li-ion battery degradation rate; cycle frequency does not affect battery life; the INR battery sometimes degrades faster than the IMR battery under the same cycling environment; and battery degradation shortens the battery discharge time and reduce the available energy and power.

Conclusions and suggestions for further study are provided in Chapter 6.

Chapter Two

Li-ion Batteries

2.1 Li-ion batteries and how they work

A Li-ion battery is a type of rechargeable battery that consists of a lithium compound cathode, a graphite (generally) anode, and electrolyte. Lithium ions move from the cathode to the anode when charging and move in the opposite way when discharging. Figure 2.1 is the demonstration of internal reactions and current change during battery charge and discharge [31]. While charging, lithium compounds break into lithium ions, electrons, and other lithium compounds. Electrons go from the cathode to the anode through external conductors, lithium ions move from cathode to anode through the electrolyte, and current goes from the anode to the cathode.

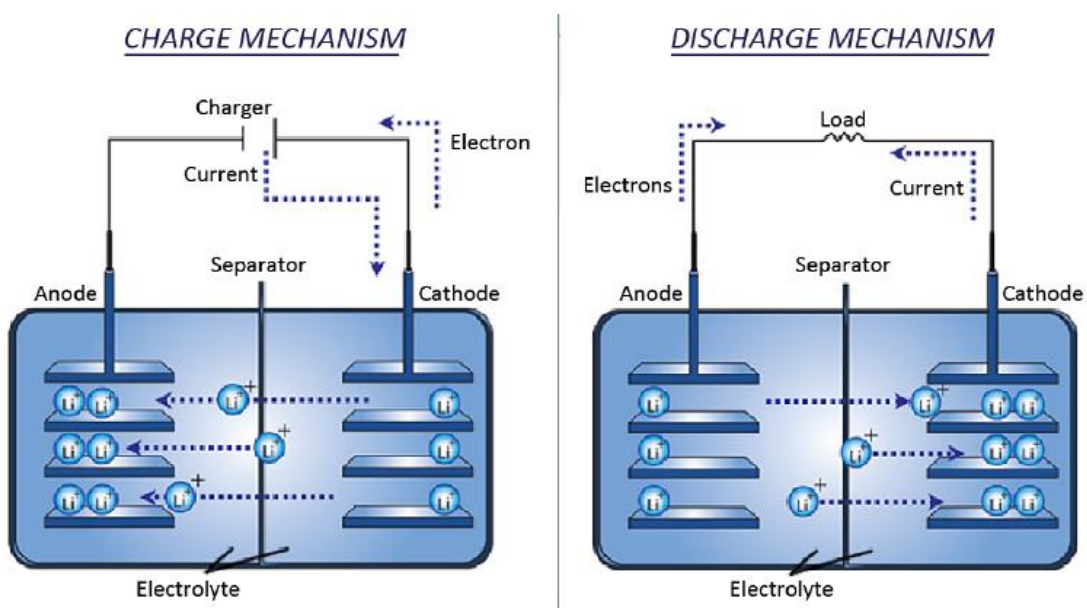

Figure 2.1 Charge and discharge mechanism of li-ion batteries [31]

Graphite is used in most Li-ion batteries as the anode because it has an intercalated structure to hold the lithium ions and increase battery capacity. The lithium ions and electrons react with carbon on the anode and form a carbon lithium compound. Equation 2.1 shows the chemical reactions inside Li-ion batteries when being charged. The process is reversed during discharge.

Cathode/ Positive: $LiXXO2 \rightarrow Li_{1-x}XXO_2 + Li^+ + xe^-$

Anode/ Negative: $C + xLi^+ + xe^- \rightarrow Li_xC$

Overall: $LiXXO_2 + C \rightarrow Li_xC + Li_{1-x}XXO_2$

XX means various combining elements of the battery cathode material.

Equation 2.1 Chemical reactions during charging li-ion batteries

2.2 Terms and definitions of Li-ion batteries

Below are definitions of the vocabulary used to describe the battery conditions, including C-rate, state of charge (SOC), depth of discharge (DOD), terminal voltage and open-circuit voltage; as well as the battery specifications, including cut-off voltage, capacity, cycle life, specific energy, energy density, internal resistance, charge voltage, and charge current.

2.2.1 Battery conditions

1) C-rate

A C-rate is a measure of the normalization of the discharge current of a battery against its maximum capacity. One C rate means that the discharge current will discharge the entire battery in 1 hour. The discharge current equals the C-rate times the maximum capacity of the battery. For example, for a battery with a capacity of 100 Ah, 1C rate means the discharge current is 100 Amps. A 5C rate for the same battery would be 500A and discharge the entire battery in 0.2 hour. The higher the C-rate, the shorter the discharge time. A C/2 rate would be 50A discharge current and the discharge time would be 2 hours.

2) State of charge (SOC)

SOC (%) is the percentage of the present battery capacity over the maximum capacity.

3) Depth of discharge (DOD)

DOD (%) is the percentage of battery capacity that has been discharged over the maximum capacity. 80% DOD or more is considered a deep discharge.

4) Terminal voltage (V)

The voltage between the battery terminals when connected to load. Terminal voltage changes with battery SOC and charge/discharge current.

5) Open-circuit voltage (V)

The voltage between the battery terminals when no load is connected. The open-circuit voltage of the battery depends on SOC [9].

6) Charge retention

The remaining battery capacity that is available after the battery has been stored or used for a given amount of time.

2.2.2 Battery specifications

1) Cut-off voltage (V)

Cut-off voltage is the lowest allowable voltage, at which the battery is considered "empty". Some electronic devices powered by Li-ion batteries, such as cell phones and laptops, will automatically shut down when the cut-off voltage (3V/cell) has been reached.

2) Capacity (Ah)

The battery capacity, also known as the coulometric capacity, is the total Amp-hours (Ah) available when the battery is discharged at a certain C-rate from 100 percent SOC (full) to the cut-off voltage (empty). Capacity can be calculated by multiplying the discharge current by the discharge time to estimate the battery's status. Capacity is used as a threshold for retiring batteries. Manufacturers suggest replacement of batteries when battery depth of charge drops to 80% of their maximum capacity.

3) Cycle life

Cycle life is the number of discharge and charge cycles that the battery can experience before it fails to meet specific performance criteria. The actual operating life of a battery is affected by several factors, including C-rate, DOD, temperature, load size, and so on (more on that in Chapter 4).

4) Specific energy (Wh/kg)

Specific energy, also known as the gravimetric energy density, is the nominal battery energy per unit mass. Along with energy consumption in different applications, it determines the weight of the battery required to achieve a certain total energy.

5) Energy density (Wh/L)

Energy density, also known as the volumetric energy density, is the nominal battery energy per unit volume. Along with energy consumption of different applications, it determines the size of the battery required to achieve a certain total energy.

6) Internal resistance (IR) (Ω)

The resistance within the battery. It is usually different when charging and discharging, and it depends on the battery SOC. The higher the internal resistance, the lower the battery efficiency.

7) Charge current (A)

The constant current that charges the battery and increases the voltage (to about 70% SOC) before transitioning into constant voltage charging [9].

8) Charge voltage (V)

The voltage the battery is charged to when full capacity is reached. The charge voltage is generally reached when the battery is charged to about 70% SOC by the charge current, and then becomes stable until the charge process ends.

2.3 Charge and discharge of Li-ion batteries

2.3.1 Charge process of Li-ion batteries

Figure 2.2 shows the voltage, current and capacity change during charge of Li-ion batteries [10]. In the beginning of the charge, the charge current is constant while the battery voltage increases until reaching a peak voltage. Then the battery enters saturation charge, during which the voltage stays the same while the current starts decreasing until the charge is terminated when the current reaches 3% of rated current. Then the charge process ends, and the battery is considered fully charged. Some low-consumer users stop the charging as soon as the battery voltage reaches cut-off (constant) voltage to save time. The charged battery reaches about 85% SOC. Otherwise the capacity keeps increasing until the termination.

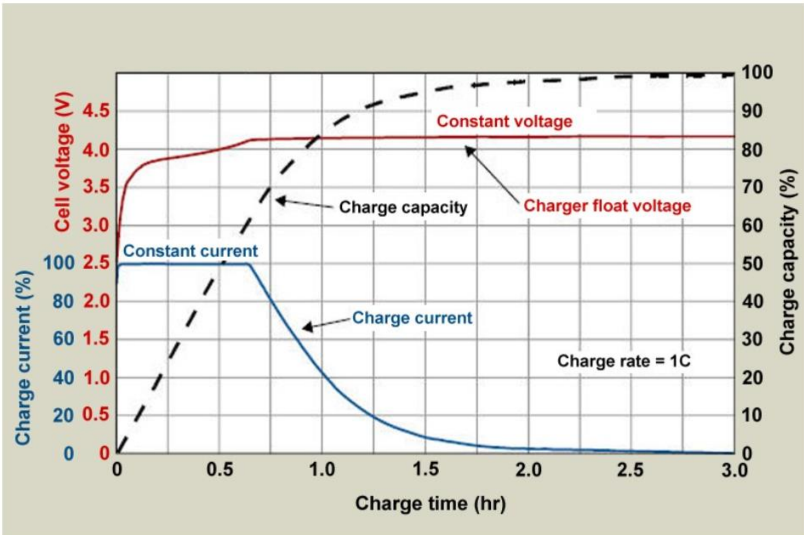

Figure 2.2 Voltage/capacity/current vs. time when charging Li-ion batteries [10]

The charging process is shown with more details in Figure 2.3. Stage 1 is the constant current charge stage; Stage 2 is the saturation charge, at the end of which the battery finishes charging. During Stage 3, which is after the charge ends, the battery voltage begins to drop because the battery tends to release its stress. A Li-ion battery that has been charged longer in saturation stage can keep the high voltage for a longer period of time than one that has not. The open circuit voltage of a Li-ion battery will eventually settle to between 3.70V and 3.90V [10].

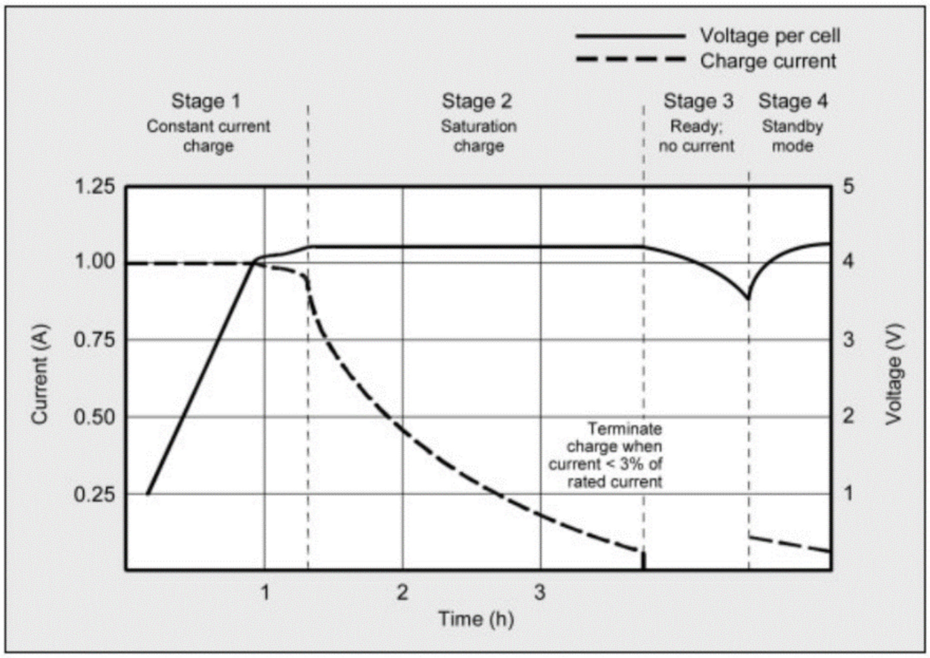

Figure 2.3 Charge stages of lithium-ion [10]

A higher charge current doesn't necessarily fasten the charging process because even though it accelerates the voltage increase to the peak voltage, it slows down the saturation charge process. Higher charge rate can quickly fill a battery to about 70 percent. Extremely fast charge can cause serious damage to the battery, cause capacity loss, and lead to safety issues. The advised charge rate of an Energy Cell is between 0.5C and 1C. Battery manufactures recommend a charge rate of 0.8C or below to prolong battery life [10].

Li-ion batteries with cathode materials combining cobalt, manganese, nickel and aluminum typically can be charged to 4.20V/cell with a tolerance of +/- 50mV/cell. Some nickel-based Li-ion batteries can only be charged to 4.10V/cell while some high capacity ones may go to 4.3V/cell or higher [10]. Overcharge Li-ion batteries can cause overheat, extreme damage, or even catch on fire. Protection circuits are designed in battery packs to protect the cells from being overcharged. Charging a non-cobalt battery such as Lithium iron phosphate requires special charger for battery protection.

2.3.2 Discharge process of Li-ion batteries

The discharge characteristics of Li-ion batteries differ based on their capacity and loading. Li-ion batteries can be divided into two groups: the power cell and the energy cell. The power cell generally has a moderate capacity but high load capabilities, which works well in heavy load current applications such as power tools. The energy cell, on the other hand, is designed with maximum capacity to prolong runtime, which is widely applied in portable electronic devices such as laptops and cellphones. Battery capacity and loading are determined by particle size on the electrodes. The larger the particles, the larger the electrode surface area for more capacity. Finer electrode particles achieve higher battery power.

The 18650 Li-ion battery is a popular cell that has been used in power tools, medical devices, e-bikes, and electric vehicles (EV). “18650” stands for diameter 18 mm by length 65 mm, and “0” means that the shape of this type of battery is cylindrical. Figure 2.4 shows the voltage, current and capacity change over time during discharge of a 2500 mAh 18650 Li-ion battery.

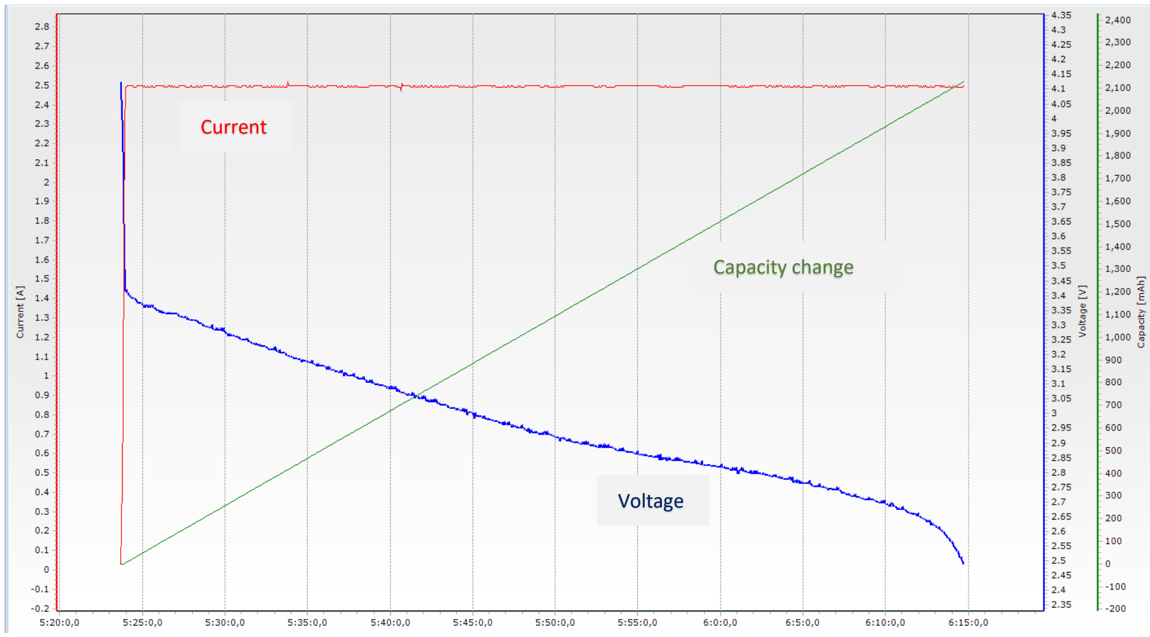

Figure 2.4 Voltage/current/capacity vs time during discharge

During discharge, the voltage of Li-ion batteries is a smooth curve when the power is extracted constantly. The capacity discharged is linear with time and the current is constant. Li-ion batteries discharge faster with increasing discharge current, which provides more power.

However, the energy cell has low endurance and less capacity when discharged at high C-rate. Figure 2.5 shows the discharge process of the 3200mAh 18650 Li-ion battery at 0.2C, 0.5C, 1.0C, 2.0C. The cut-off voltage at the end of discharge is 3.0V. At the discharge cut-off voltage of 3.0V, the cell discharged under 2.0 C only produced 2300 mAh instead of the specified 3200 mAh. It is also shown in Figure 2.5 that the lower the C-rate, the more capacity is produced at the end of discharge.

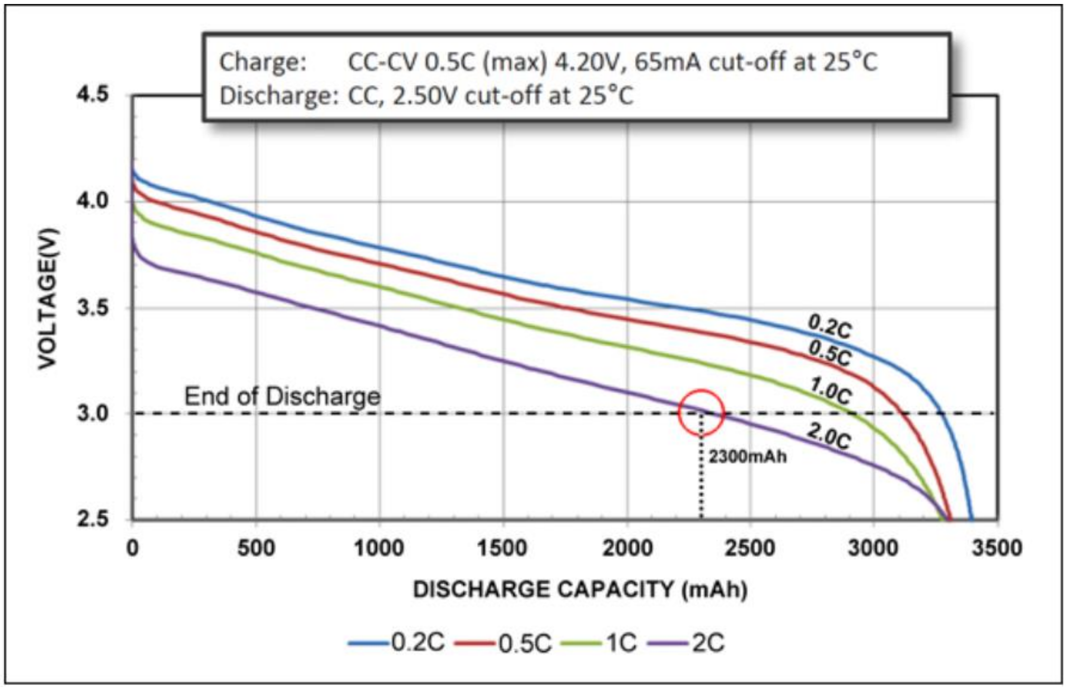

Figure 2.5 Discharge characteristics of NCR 18650B Energy Cell by Panasonic [32].

In large energy storage systems, the energy cells are usually connected in parallel and series to achieve large capacity with high power load. One such example is electric vehicles (EV). The higher the loading requirement, the heavier and more expansive the system becomes.

The power cell, on the other hand, has lower capacity but much higher power. Figure 2.6 shows the discharge process of UR18650 power cells under 0.2C, 0.5C, 1C, 2C and 5C (10A). The cells all managed to produce 2000 mAh at the end of discharge even under stressful discharging with high current.

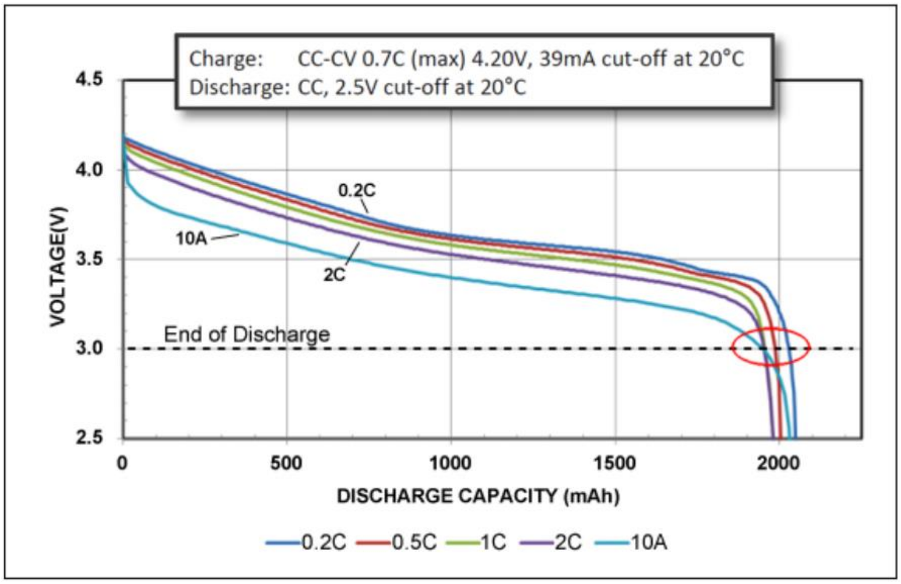

Figure 2.6 Discharge characteristics of UR18650RX Power Cell by Panasonic [32].

However, even though the high discharge current will not reduce the discharge capacity of power cells, the stress created by the fast discharge accelerates battery degradation and shortens battery life. This also applies to the energy cell. Currents beyond specified charge and discharge current of the battery are not recommended. Chapter 3 talks more about battery degradation and lifespan.

2.4 Li-ion battery chemistries classification

Li-ion batteries are made in all shapes and sizes with different chemistries, but the compositions of Li-ion batteries are the same: the cathode, the anode, and the electrolyte. In most cases, the anode of Li-ion batteries is made of carbon/ silicon and graphite. However, the cathode of Li-ion batteries is made of different Lithium compounds, which gives each battery unique characteristics such as capacity, power density, cycle life, and safety. Table 2.1 shows the five most common commercial Li-ion battery chemistries.

Battery types	Advantages	Disadvantages	Applications
Lithium cobalt oxide $LiCoO_2$ (ICR)	High specific energy (capacity), which prolongs battery runtime	Unstable; Low specific power; Relatively short lifespan; Low thermal stability; Require built-in protective circuitry; Expensive	Energy cell; Digital portable devices such as mobile phones and laptop.
Lithium manganese oxide $LiMn_2O_4$ (IMR)	High specific power (load capability); Safe, high thermal stability; Low IR	Limited cycle and calendar life; Relatively low capacity (roughly one-third lower than Li-cobalt);	Electric vehicles; Power tools; Medical devices; Hybrid and electric vehicles; Uninterruptible power supply (UPS).
Nickle-manganese-cobalt $LiNiMnCoO_2$ (INR)	High specific power; Safe, high thermal stability; Improved specific energy; Relatively large capacity; Long cycle life		
Lithium nickel cobalt aluminum oxide $LiNiCoAlO_2$ (NCA)	Stable; Long cycle life; Large capacity; High energy density	Low specific power	Electric power train; Grid storage
Lithium iron phosphate $LiFePO_4$ (LFP)	High thermal stability; Long cycle life; High capacity; High power; Safe, tolerate to abuse		Renewable energy storage [11]

Table 2.1 Pros/Cons/Application of five popular Li-ion batteries

Different chemistry plays a different role in the performance of the Li-ion battery. Cobalt gives the battery high specific energy, but it is very unstable; Manganese improves battery safety by allowing batteries to discharge at a high current while maintaining low temperatures; Nickel provides batteries high energy; Aluminum provides the battery with stability, large capacity, and long cycle life.

Table 2.1 shows the many disadvantages of lithium cobalt oxide (ICR) and Lithium manganese oxide (IMR) batteries. Newer systems combine these two chemistries along with other chemistries such as nickel, aluminum, iron, and phosphate to improve longevity, loading capabilities, safety, and lower cost. Lithium manganese nickel (INR) battery chemistries include manganese, nickel, and cobalt. The combination of these chemistries provides the benefits of all these elements, including a relatively high capacity, high loading capacity, and cost saving as the battery does not require extensive built-in circuits. Research is being conducted on innovating highly efficient Li-ion batteries by adjusting the ratio of manganese, nickel, and cobalt. Lithium nickel cobalt aluminum oxide (NCA) is used by Tesla in their electric car batteries. However, without manganese, NCA batteries can only tolerate lower discharge currents.

2.5 Li-ion battery degradation

Even though Li-ion batteries have grown in popularity in a large number of applications, including EV, grid, portable devices, power tools, and so on, the battery degradation, which consists of capacity degradation, increase of IR, and self-discharging, is still causing the short lifespan of Li-ion batteries and the large amount of cost from battery consumers._Methods of slowing down self-discharging and prolonging battery lifespan are being continuously studied in the research and industrial fields. The Li-ion battery degradation mechanisms, factors affecting the process, and how to achieve maximum battery life are described in the next chapter.

2.6 Other features of Li-ion batteries

2.6.1 Self-discharge

- Definition

Self-discharge means the battery experiences energy loss even when it is inactive. It is a battery characteristic that happens due to chemical reactions inside the battery without connections between the electrodes. It can also be caused by improper handling during manufacturing. Because of self-discharge, Li-ion batteries initially have less than a full charge in their first cycle. As shown in Figure 2.7, after a battery is fully charged, it starts to self-discharge. Self-discharge is fastest right after the charging process, which decreases the battery charge for 10%. Then the process slows down and levels off, which lowers the battery charge to 80% in 30 days even when it is inactive [11].

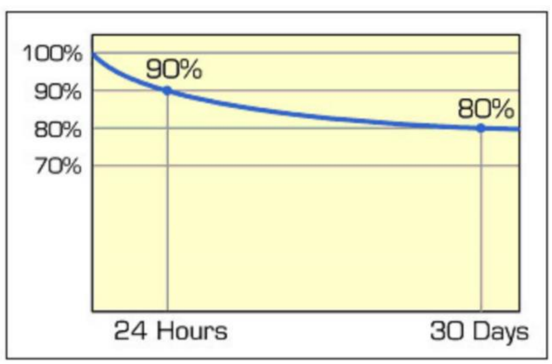

Figure 2.7 A nickel-based battery self-discharge as a function of time [11]

Self-discharge rate varies with battery type and chemistry and increases with battery age and cycling. Under recommended circumstances, Li-ion batteries self-discharge about 5% in the first 24 hours and then lose 1%-2% per month, along with the 3% per month consumed by the protection circuit [11]. Storage and cycling environment including temperature, SOC and DOD can also affect the self-discharge rate. The higher the battery self-discharge rate, the more capacity is lost. This also means the battery degrades as it has less available energy with the same amount of input. Unusually high self-discharge rate can be indicated as the failure of a battery.

Self-discharge mechanisms are essential for battery manufacturers to recognize as they vary in different forms and cause different capacity loss in individual batteries. In a battery system that consists of thousands of cells, the self-discharge rate of each cell needs to be examined to eliminate battery failure. Moreover, it is important to keep batteries at the proper temperature and SOC under storage to avoid elevated self-discharge.

- Factors that affect the speed of battery self-discharge

Self-discharge increases with age, cycling and elevated temperature.

1) Temperature

Self-discharge accelerates under high temperatures, and the discharge rate typically doubles with every 10°C increased [11]. Table 3.1 shows the amount of Li-ion batteries' capacity loss in a month under different temperatures and SOCs. The capacity loss accelerated with the increasing of temperature. The storage under 0°C shows the least elf-discharge.

State-of-charge	0°C (32°F)	25°C (77°F)	60°C (140°F)
Full charge	6%	20%	35%
40–60% charge	2%	4%	15%

Table 2.2 Li-ion batteries self-discharge per month at different temperatures and SOC [11]

2) SOC

As shown in Table 2.2, high SOC significantly accelerates Li-ion battery self-discharge. The fully charged Li-ion batteries degraded more than twice as fast as those with 40%-60% charge.

3) DOD

Deep discharge also increases battery self-discharge rate. Figure 2.8 compares the self-discharge of a new Li-ion battery with a battery that was deep discharged to beyond 2.5V and one that was discharged to 0V, which is shown in the green line marked as "14 Day Short Condition" [11]. The deep discharge battery shows slightly faster self-discharge (8mV/day) of 1mV/day more than the new battery (7mV/day), while the 0V battery self-discharged three times faster (24mV/day) than the new battery.

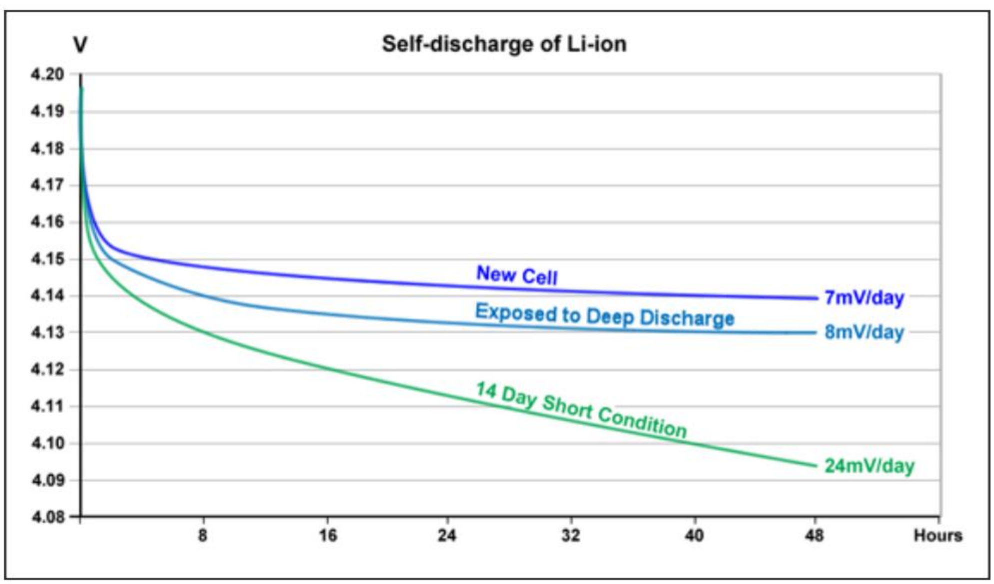

Figure 2.8 Self-discharge of new and deep discharged Li-ion batteries [11]

Li-ion batteries should avoid discharge to below 2.5V/cell as this can cause significant capacity loss. When the Li-ion battery stays in a low-voltage state for longer than a week, copper dendrites grow on the anode, which results in elevated self-discharge and a possible safety issue. It is recommended to store Li-ion batteries around 40%-50% SOC [12].

In conclusion, in order to minimize Li-ion battery self-discharge, the battery temperature should be kept close to 0 ℃ as an increase in temperature accelerates this process. The SOC of Li-ion batteries should be kept around 40%-60% to avoid damage from deep discharge and full charge.

2.6.2 Recovery effect

When discharge current is interrupted for an extended period, the voltage may recover and slightly increase. By alternating discharge and inactive periods, instead of constant discharge, the recovery effect can extend battery life. The amount of recovery life depends on the battery load, recovery time and DOD. However, this effect is mainly observed in lead-acid batteries applications, and is not significant in Li-ion batteries [13].

Chapter Three

Lithium Ion Battery Degradation

Battery life is one of the main factors to be considered when it comes to economic efficiency of Li-ion battery applications.

3.1 Definition of battery life

Battery life is expressed in two terms: cycle life and calendar life. One of the main features of battery life loss/degradation is capacity fade, which occurs when the battery's ability to store energy decreases over time. A battery's capacity fade is magnified by usage. In this thesis, capacity loss is used to show battery degradation and is measured by percentage of the initial capacity of the battery. For example, a battery degraded by 20% capacity means this battery can only be charged and discharged with 80% of its initial capacity.

Cycle life is the number of complete cycles a battery can be charged and discharged before its capacity degrades to 80% of its initial capacity. A discharge/charge cycle is commonly understood as the full discharge of a charged battery that is followed by a recharge, but multiple partial discharges and charges can also form a cycle as well. Calendar life is the time for which a battery can be stored as inactive until its capacity degrades to 80% of its initial capacity. Calendar-life loss starts immediately after Li-ion batteries are made and increases over time. Cycle-life loss increases with the usage of batteries. The typical estimated life of a Lithium-ion battery is about two to three years or 300 to 500 charge cycles, whichever occurs first, depending on different environments and cycle situations [14].

Cycle life and calendar life are closely related. An increase in battery cycles decreases the remaining calendar life, and a battery that was stored for a long time provides fewer cycles. Cycling conditions such as charge/discharge current, DOD, and temperature can affect the speed of the degradation process.

3.2 Li-ion batteries capacity degradation/loss

3.2.1 Capacity loss overview

Li-ion batteries capacity changes are dominated by different mechanisms during each phase in their lifetime. Figure 3.1 is a graph based on a life prediction model for Li-ion batteries, which shows that there are three phases of battery total capacity change over their lifetime. The X axis represents the timeline of battery life, typically months or years, and the Y axis is the percentage of remaining capacity over the initial capacity. The curve marked with circles is the plot of Li-ion battery remaining capacity as a function of time.

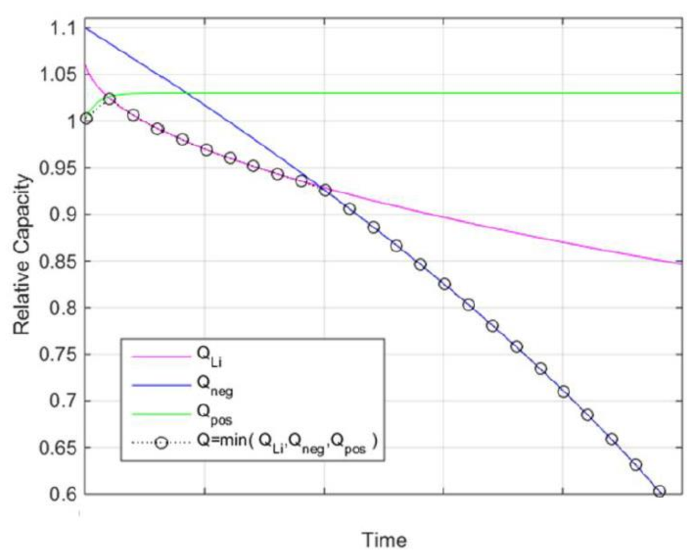

Figure 3.1 Battery capacity as the minimum of three limiting mechanisms [15]

Phase 1: Slight capacity increase at initial cycles

Electrolyte wetting in porous electrodes is increased during the initial cycles, which increases the contact between electrolyte and positive electrode sites. This slightly increases the Li-ion battery capacity. Temperature is the main factor that affects this process and thus controls battery capacity at beginning-of-life. The higher the temperature, the larger the initial capacity.

Phase 2: Moderate capacity loss during early cycles

Capacity loss at early cycles occurs mainly because of solid electrolyte interface (SEI) growth, which is a lithium compound layer that grows on the anode that consumes cyclable lithium ions (more in 3.2.2).

Phase 3: Severe capacity loss after large number of cycles

Large numbers of cycles lead to loss of negative electrode sites (which store cyclable lithium ions) due to electrode mechanical damage during cycling.

Eleven 1500 mAh Li-polymer batteries, which are pouch cells for mobile phones, were tested on a Cadex C7400 battery analyzer. These batteries were cycled between 3.0 V/cell and 4.2V/cell at a current of 1.5 A for 250 cycles and the capacity degradation is shown in Figure 3.2 [16]. All eleven batteries had a capacity of 88% to 94% at the beginning of cycling, which decreased to 73% to 84% after 250 full discharge cycles.

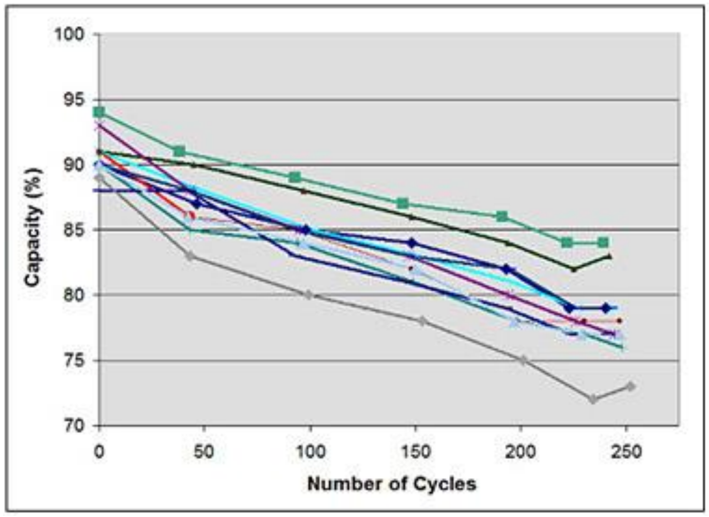

Figure 3.2 Capacity loss of 11 new Li-ion batteries as part of cycling over 250 cycles [16]

3.2.2 Li-ion battery capacity degradation mechanisms

Li-ion battery degradation is mainly caused by several chemical exothermic reactions which happen inside the battery, including chemical reduction of the electrolyte and solid electrolyte interphase (SEI) growth on the anode; chemical oxidation of the electrolyte on the cathode; thermal decomposition of the electrolyte, the cathode, and the anode; and internal short circuit due to charge effects. Further discussion of the first two mechanisms follows.

- Solid electrolyte interphase (SEI) growth

During Li-ion battery charge, lithium ions move to the anode and the battery voltage increases. Due to electrochemical decomposition of the electrolyte on the anode, a layer called solid electrolyte interphase (SEI), which is composed of lithium oxide and lithium carbonate, grows on the surface of the anode. This formation happens at the initial cycles, as shown in Figure 3.3 [33], which consumes recyclable lithium ions.

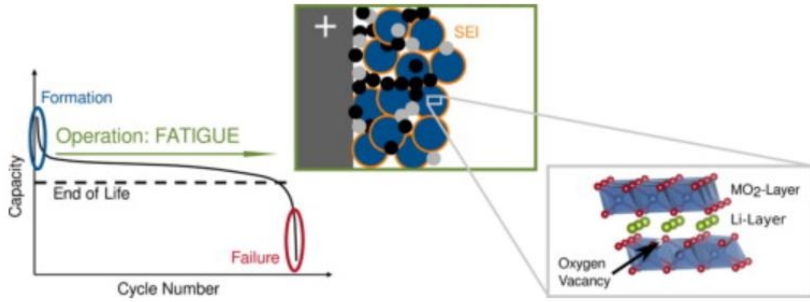

Figure 3.3 Formation of SEI [33]

During discharge, due to the formation of the SEI layer, not all lithium ions move back to the cathode and the battery capacity degrades. After the initial cycles, the SEI layer continues to thicken over cycling, which eventually blocks the interaction between graphite and electrolyte and leads to battery failure.

The SEI has an impact on Li-ion batteries' initial capacity loss, self-discharge characteristics, rate capability, and safety. It is essential to the long-term performance of Li-ion batteries. By using suitable solid-state electrolytes and Li-containing anodes, further consumption of lithium ions and capacity loss can be overcome [17]; thus, the electrode, the cycle performance, and service life can be improved. Formation and growth of the SEI layer are affected by many factors from within the battery, including the type of graphite, electrolyte composition, and electrochemical conditions. External factors, such as high temperature and high SOC, also accelerate the SEI growth and shorten the battery life.

- Electrolyte oxidation

Electrolyte oxidation is the process of forming a layer in the cathode during cycling due to high battery voltage (above 4.1V/cell) and elevated temperature, which is similar to the growth of the SEI layer. The longer the battery holds the high voltage, the faster it degrades. This reaction can cause larger capacity loss in batteries than cycling effects. Electrolyte oxidation of the cathode also partially causes battery self-discharge. The speed of battery capacity degradation depends strongly on its operating conditions, including temperature, charge and discharge rate, DOD, and charge voltage during cycles. High temperatures, deep discharge, high SOCs, and high cycle rates all cause stress on the battery and accelerate the capacity loss.

NASA discovered that Li-ion batteries with voltage of above 4.1 V/cell tend to decompose due to electrolyte oxidation on the cathode, while those with lower voltages degrade due to the SEI layer growth on the anode [12].

- Lithium plating

Lithium plating is the formation of metallic lithium around the anode of a Li-ion battery during charging, in which lithium ions from the cathode are inserted into compounds with layered structures in the anode, which is called intercalation. When the speed of moving lithium ions is larger than the speed of intercalation, the lithium ions accumulate and form metallic lithium. This process occurs mainly when Li-ion batteries are overcharging (above 4.2V/cell), charging at low temperatures (below 15°C), and charging under high currents [18].

3.3 Factors that affect Li-ion battery lifespan

Knowing what the factors are and how they affect battery capacity loss is essential for minimization of battery capacity loss and achieving optimal battery efficiency. Conditions including battery age, temperature, SOC, and DOD all have different effects on a Li-ion battery's lifespan as the result of battery calendar-life loss and cycle-life loss. How environmental factors during battery storage, as well as cycling conditions during usage, affect battery life are discussed in this section.

3.3.1 During storage

1) Temperature

Temperature is the dominant cause of battery capacity loss during storage. High temperatures cause thermal decomposition of the electrodes and electrolyte. Decomposition of the electrolyte increases the SEI film thickness on the anode, which consumes lithium ions, increases the cell IR, and reduces battery capacity. In addition, gases are formed during the decomposition, which increases the internal pressure in the cell and poses safety issues. Table 3.1 shows percentage of Li-ion batteries' capacity lost in one year when stored in different temperatures [16]. The Li-ion batteries were stored under the same SOC (40%). The higher the temperature, the more the batteries degrade. In addition, Table 3.1 also shows that extreme temperature significantly accelerates the capacity loss. The 25 degree increase from 0°C to 25°C only caused 2% more capacity loss, while the 20 degree increase from 40°C to 60°C caused 10% more capacity loss.

Temperature	40% charge	100% charge
0°C	98% (after 1 year)	94% (after 1 year)
25°C	96% (after 1 year)	80% (after 1 year)
40°C	85% (after 1 year)	65% (after 1 year)
60°C	75% (after 1 year)	60% (after 3 months)

Table 3.1 Estimated recoverable capacity when storing Li-ion batteries at various temperatures and SOC [16]

For Lithium-ion batteries, temperatures above 30°C are considered stressful environments and can cause significant battery calendar-life loss [16]. It is recommended to store Li-ion batteries at temperatures between 5°C and 20°C to prolong battery life [14].

2) State of Charge (SOC)

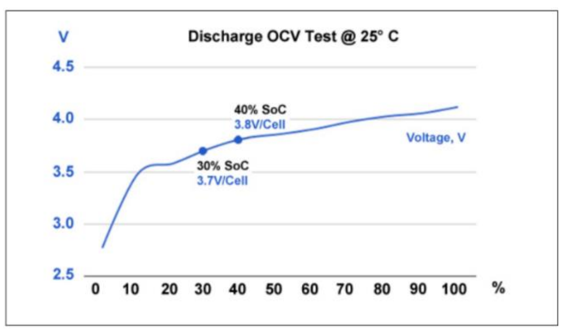

Figure 3.4 Discharge voltage as a function of SOC [16]

For Li-ion batteries, open circuit voltage (OCV) increases with SOC, as shown in Figure 3.4. During storage, the higher battery SOC, the higher the battery OCV. However, high OCV can increase SEI growth and initiate electrolyte oxidation inside Li-ion batteries, which causes capacity loss and increase of IR. Figure 3.5 shows different Li-ion battery degradation rates at various SOCs during ten years of storage. The remaining capacity of Li-ion batteries decreases faster as the SOC level increases [19].

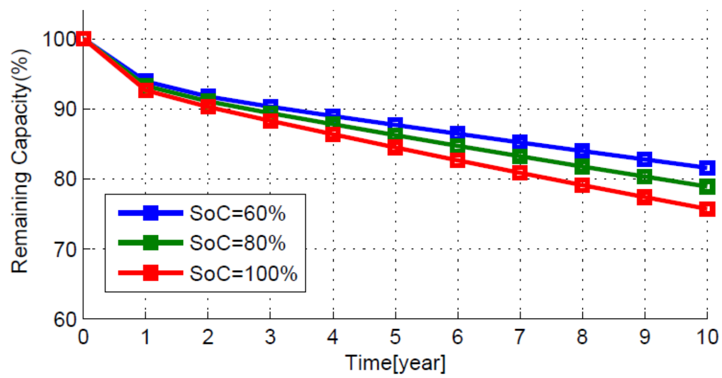

Figure 3.5 Calendar aging with varying SoC at 25 Celsius [19]

Table 3.1 also includes SOC as a variable, which shows that the Li-ion batteries that were stored at 100% SOC retained significantly less capacity than the ones stored at 40% SOC. However, a SOC lower than a certain level increases the battery IR and capacity fading [20]. Extremely low OCV (< 2V/cell) results in the slow degradation of LiCoO2 and LiMn2O4 batteries' cathode, the release of oxygen, and irreversible capacity loss [21].

Thus, maintaining Li-ion batteries at an intermediate SOC level can reduce battery degradation and prolong battery life. It is recommended to charge or discharge Li-ion batteries to approximately 50% SOC before storage [14].

3.3.2 During cycling

1) Temperature

Increased temperature during battery operation can improve battery performance. For example, warming a dying battery in a mobile phone in one's pocket might provide additional runtime due to improved electrochemical reaction. Manufacturers specify batteries' nominal temperature at 27 °C to prolong battery runtime. However, prolonged cycling under high temperature shortens battery life. A battery operated at 30°C has a reduced cycle life by 20%. At 45°C, the battery only has half of its optimal lifetime, which can be achieved when operating at 20°C [22].

Extremely low temperatures increase the battery IR and decrease significant amount of discharge capacity. A battery that provides 100 percent capacity at 27°C (80°F) will typically deliver only 50 percent capacity at -18°C (0°F) [22]. Figure 3.6 shows the variations of the discharge capacity of a lithium polymer cell when discharged from 4.2 V to 3.0 V at different temperatures [23]. The batteries' capacity at low temperatures (0°C, -10°C, -20°C) are lower than the ones at higher temperature (25°C, 40°C, 60°C). In addition, charging Li-ion batteries at low temperatures (below 15°C) leads to lithium plating due to the slow-down of the intercalation of lithium ions. This process accelerates Li-ion battery degradation by increasing battery IR and decreasing battery discharge capacity [18].

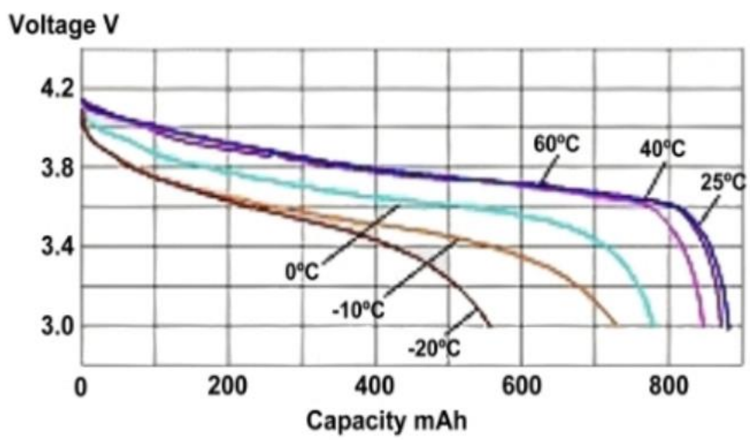

Figure 3.6 Battery discharge capacity at various temperatures [23]

Thus, moderate operating temperatures are recommended to improve Li-ion battery performance and lifespan. A temperature of 20°C or slightly below is recommended for Li-ion batteries to achieve optimum service life. A temperature of 27°C, however, is recommended by manufacturers for maximum battery runtime [22].

2) Depth of discharge (DOD)

DOD has a dominant effect on the cycle life of Li-ion batteries. Deep discharges cause pressure in Li-ion cells and damage negative electrode cites, which accelerates capacity loss and possible cell damage. As shown in Figure 3.7, the higher the cycling DOD, the shorter the battery cycle life.

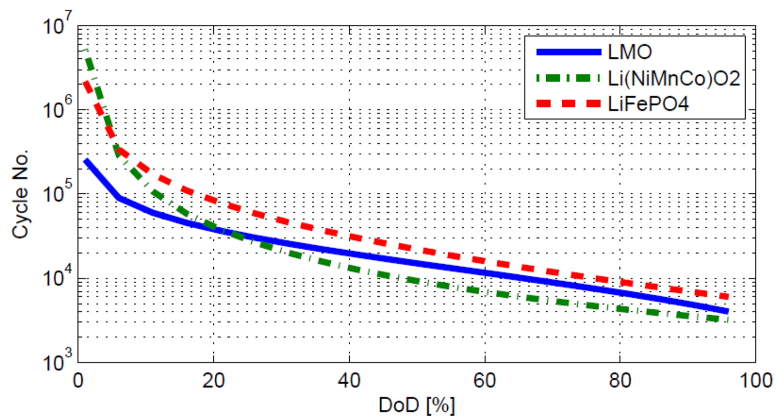

Figure 3.7 Li-ion battery cycle number vs. DoD [19]

DODs above 50% are considered deep discharge. When a Li-ion battery is discharged from 4.2V to 3.0 V, roughly 95% of its energy is spent, and continued cycling will result in the shortest battery life. Full discharge should be avoided during Li-ion battery cycling to reduce capacity loss. Partially discharging and charging Li-ion batteries is recommended to prolong battery life.

Manufacturers often use the 80% DOD formula to rate a battery, which means only 80% of the input energy is delivered during battery use and another 20% is reserved to achieve longer battery service life. However, even though decreasing DOD can prolong Li-ion battery cycle life, too low a DOD can lead to insufficient battery runtime and the inability to finish certain tasks. Around 50% DOD is recommended during usage of Li-ion batteries to achieve maximum lifespan, as well as to provide optimal battery service time.

3) Charge voltage

High charge voltage gives Li-ion batteries high capacity and enables prolonged battery runtime. However, it is not recommended to fully charge Li-ion batteries. Charging Li-ion batteries above 4.1V/cell leads to lithium plating, which increases the loss of lithium ions as they form metallic lithium on the anode. This process not only decrease the battery capacity, but also might lead to internal short circuiting and cause fires. Figure 3.8 shows Li-ion batteries capacity degradation under high charge voltages (> 4.2 V/cell). The higher the charge voltage, the faster the capacity degrades and the shorter the cycle life.

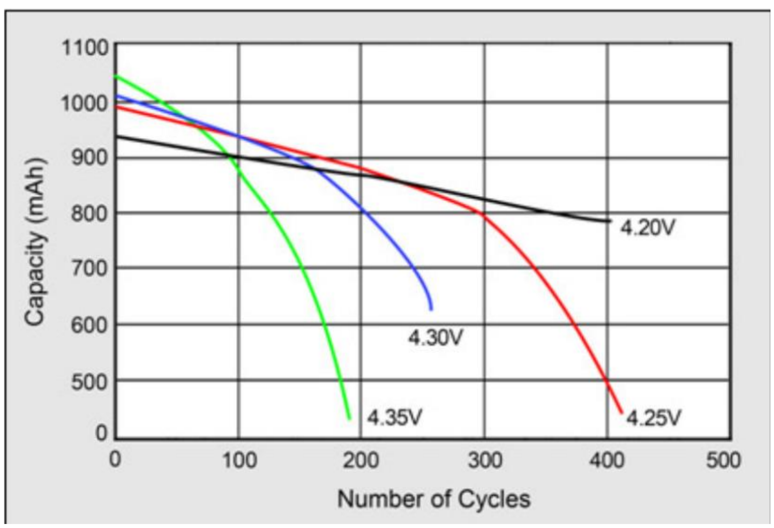

Figure 3.8 Effects on cycle life at elevated charge voltages [24]

Table 3.2 shows that among charge levels from 3.70V- 4.30V, 4.20 V is the charge voltage level at which batteries gain the most capacity (100%) under Li-ion battery safety specifications. Every 70mV reduction in the charge voltage lowers the overall capacity by about 10% [16]. Table 3.2 also shows the shortened cycle life because of the high charge voltage. Cycle life at the charge voltage of 3.90 V is the longest (2400-4000) among charge levels from 3.90V- 4.30V, and it is reduced to half with every increase of 0.10V in charge voltage.

Charge level (V/cell)	Discharge cycles	Available stored energy
[4.30]	[150–250]	[110–115%]
4.25	200–350	105–110%
4.20	**300–500**	**100%**
4.15	400–700	90–95%
4.10	600–1,000	85–90%
4.05	850–1,500	80–85%
4.00	1,200–2,000	70–75%
3.90	2,400–4,000	60–65%
3.80	See note	35–40%
3.70	See note	30% and less

Table 3.2 Discharge cycles and capacity as a function of charge voltage limit [16]

For most Li-ion batteries, a voltage above 4.10V is considered as high voltage and significantly accelerates battery degradation. Lower charge voltage prolongs battery life but provides less runtime for the user. Moreover, Li-ion batteries should avoid discharge below 2.5V/cell. Optimal charge voltage is 3.92V, which allows the batteries to achieve longest cycle life [16].

Electronic products such as laptops and cellphones usually have a high voltage threshold to achieve maximum battery runtime. Large energy storage systems for more expensive applications such as EV or satellites, on the other hand, set the voltage threshold lower to prolong battery life. In both cases, however, it is important not to overcharge Li-ion batteries, which will damage them, significantly shorten battery life, and potentially cause fires or explosions.

4) Cycle bandwidth/ ΔSOC

Cycle bandwidth is the range of a battery being discharged expressed in SOC. For example, in Figure 3.9 [25], '100-25@20C' means discharge the battery from 100% SOC to 25% SOC at 20 C-rate and the bandwidth is '100-25'. Figure 3.9 shows the battery capacity degradation under different cycle bandwidths. The X axis is cycle number and the Y axis is remaining capacity. The cycle bandwidths are in the legend on the bottom right. The cycle current is 20 C. DOD can be calculated by subtracting the two numbers in bandwidth. For example, DOD of '100-25' bandwidth is 75%.

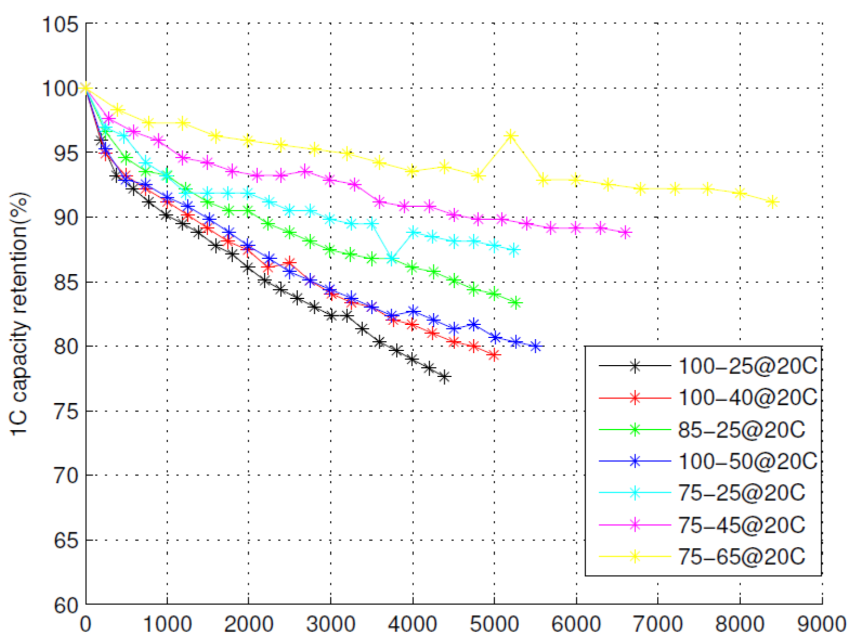

Figure 3.9 Capacity loss as a function of charge and discharge bandwidth [25]

From Figure 3.9, comparison of the slopes of the black (100-25), red (100-40) and dark blue (100-50) curves, which represent SOCs of 75%, 60% and 50% respectively, shows that when discharging a battery from 100% SOC, the higher the DOD, the faster the degradation. Of the three, the black curve decreases fastest and the red curve decreases the slowest. The same conclusion can be drawn from the light blue (75-25), purple (75-45) and yellow (75-65) curves as the light blue decreases the fastest while the yellow decreases the slowest. Moreover, Figure 3.9 also shows that with the same DOD, the higher the maximum SOC, the faster the degradation. Take the red curve (100-40) and the green curve (85-25) as an example, which both have a DOD of 60%, but has a maximum SOC of 100% and 85% respectively. The red curve shows faster degradation than the green one. This can also be seen in the dark blue (100-50) and light blue curve (75%-25%).

In conclusion, in order to prolong battery life but also maximize use of the battery capacity, batteries should be cycled in mid-state-of-charge. Industrial devices such as electric vehicles typically limit the charge bandwidth from 25% to 85% to gain longest battery life [16].

5) Charge current/ C-rate

High C-rates cause increasing IR, loss of available energy, safety issues, and irreversible capacity loss. First, high C-rates causes lithium plating. When the Li-ion battery is charged with a high current, this forces the lithium ions to move at a faster rate while access to the anode surface is limited [18]. Thus, lithium ions accumulate on the surface of the anode and form metallic lithium. This process is accelerated when the battery fast charging at low temperatures and high SOC. Also, the lithium layer might form in a dendritic format due to gravity effect, which might elevate battery self-discharge. In extreme cases, it can cause battery inner short circuiting and potentially lead to fires. Moreover, high charge and discharge current also cause more energy loss as part of the energy is transferred to heat because of battery IR. When the C-rates exceed a certain level, the elevated temperature inside the battery can also cause stress, damage the battery, and accelerate capacity loss.

Figure 3.10 shows the discharge capacity degradation process of Li-ion batteries cycled under 1C, 2C, and 3C [24], which shows a severe acceleration of Li-ion battery capacity degradation with the increase of C-rate. The higher the C-rate, the faster Li-ion batteries degrade. A C-rate of 0.8C or below is recommended for energy cells to prolong battery life and ensure safety. Power cells can be charged and discharged with higher current.

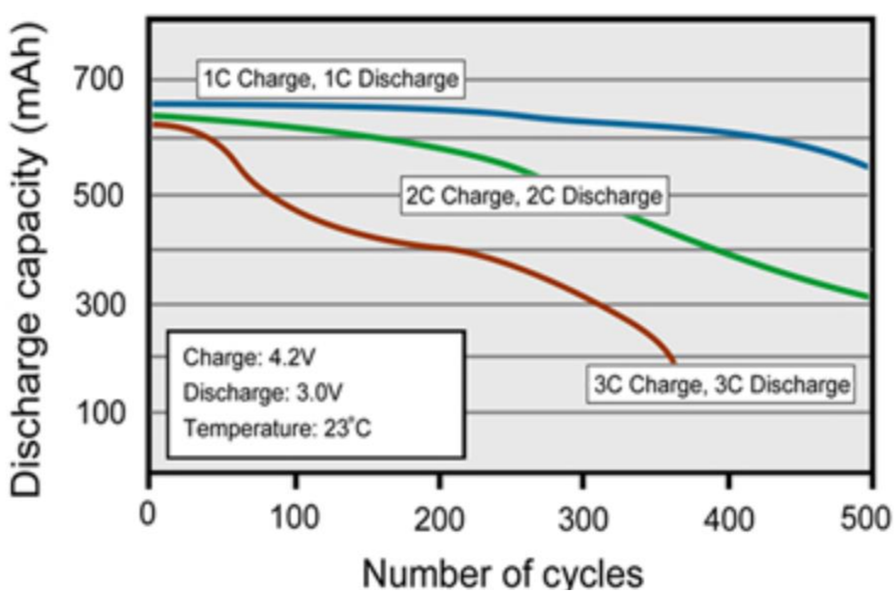

Figure 3.10 Cycle performance of Li-ion with 1C, 2C and 3C cycling [24]

6) Cycle frequency

A large number of cycles increases the SEI layer growth and causes mechanical stress to Li-ion batteries, especially when the cycling is frequent (e.g. 4 cycles or more per day). During cycling, the Li-ion batteries lose both positive and negative Li reaction sites in electrodes and the active surface area decreases, which decreases the battery capacity in turn [15]. In addition, the SEI build up during cycling increases the battery IR, thus lowering the electronic conductivity and reducing loading ability. The thickening of SEI layer and decreasing of Li sites along with some other chemical changes inside the Li-ion battery leads to capacity loss and eventually battery failure.

Even though no published information was found addressing this issue, the assumption was made that one of the reasons high cycle frequency accelerates battery degradation is the high temperatures it causes. Frequent cycles without time for batteries to cool down can cause chemical stress that leads to decomposition of electrolyte and electrodes. Experiments were done to verify this assumption, which are described in Chapter 5.

3.4 Methods to prolong the Li-ion battery lifespan

3.4.1 Cycle and storage environment

As mentioned in Section 3.3, factors including calendar time, cycle number, temperature, SOC, DOD, C-rate, ΔSOC, and charge and discharge voltage can all affect the lifespan of Li-ion batteries whether they are in storage or in usage. The optimal cycle or storage environments for maximum Li-ion battery longevity are listed in Table 3.3.

	Temperature		SOC	C-rate		Voltage	DOD
In storage	5-20 Celsius		Around 50%				
Cycling	Longevity	20℃	25%-85%	Power cell	Specified	High: 3.92V Low: 3V	Around 50%
	Performance (maximum runtime)	25℃		Energy cell	<=0.8C		

Table 3.3 Environments that best prolong battery life

According to battery-testing firm Cadex Electronics, a fully charged lithium-ion battery will lose about 20 percent of its capacity after a year of typical storage. When the temperature is high, the degradation gets faster. The best way to maintain a long-term battery storage is to run the charge down to 50 percent, remove the battery from the device, and keep it cool. But even under ideal storage conditions, the battery could die without being used after three or four years.

3.4.2 Adding additives

By using suitable solid-state electrolytes and Li-containing anodes, further consumption of lithium ions in SEI growth can be overcome [17]. Thus, the rate of capacity loss can be decreased.

Chapter Four

Experiment Design

4.1 Overview

The purpose of this project was to verify theories about Li-ion battery characteristics, the Li-ion battery degradation process, the factors that impact the battery life, and to compare Li-ion INR and IMR chemistries. Factors studied include degradation rate comparison between INR and IMR Li-ion batteries; and high and low temperature effects on Li-ion battery degradation. Also, the effect of cycle frequency on battery degradation was studied because few studies have addressed this topic.

In this project, several 18650 Li-ion batteries, which include Samsung 2500mAh INR 18650-25R Li-ion batteries and LG 2500mAh IMR 18650-HE2 Li-ion batteries, were cycled using direct current under different temperatures and rest times using a smart battery charger, the iCharger 1010B+. All the equipment is described in the next section. Since capacity loss is the main phenomenon of battery degradation, the battery discharge capacity during charge and discharge were recorded by the cycling equipment and used as the indication of battery degradation. Other than discharge capacity loss, battery IR increase can also be used to indicate battery degradation. The battery voltage, current, temperature, and IR were also recorded to observe the Li-ion battery degradation processes. Calculations were done to analyze the measured data and verify the properties of the battery.

4.2 Equipment

4.2.1 INR18650-25R and IMR 18650-HE2 Lithium ion rechargeable cells

Figure 4.1 The INR18650-25R Li-ion cell

Figure 4.2 The IMR 18650-HE2 Li-ion cell

Figures 4.1 and 4.2 show the INR-25R and IMR-HE2 Li-ion batteries tested in the experiment. As mentioned in Chapter 2, the number 18650 means the length of the cell is 65 mm and its diameter is 18 mm. “0” means the shape of the cell is cylindrical. INR stands for lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$) and IMR stands for lithium manganese oxide ($LiMn_2O_4$). Both the INR-25R and the IMR-HE2 are power cells, have an initial capacity of 2500 mAh, and can discharge at the maximum current of 20A.

The standard charge for these two batteries means that at 25℃, one charges the cells with a constant current of 1.25A (0.5C) until the voltage increases to 4.2V. Then the current decreases and one cuts off the charge when it decreases to 100mA. As shown in Table 4.1, it takes 180 mins to fully charge the battery under a standard charge.

The standard discharge is to discharge the cells with a constant current of 0.5A down to cut-off voltage of 2.5V. The maximum discharge current is 20A. As shown in

Table 4.1, the battery has a standard discharge capacity of 2500mAh under 0.5A discharge current (0.2C). The charged 25R cell has a rated discharge capacity of 2450mAh under the discharge current of 10A (4C). The higher the current, the less the discharge capacity. The maximum charge current is 4A. Moreover, charging the battery to above 4.2V or discharging it to below 2.5V should be avoided, as overcharge and over-discharge cause irreversible damage to INR-25R and IMR-HE2 batteries [26].

Type		Spec.
Chemistry		NCA
Dimension (mm)	Diameter	18.33 ± 0.07
	Height	64.85 ± 0.15
Weight (g)		Max. 45.0
Initial IR (mΩ AC 1kHz)		≤ 18
Initial IR (mΩ DC (10A-1A))		≤ 30
Nominal Voltage (V)		3.6
Charge Method (100mA cut-off)		CC-CV (4.2±0.05V)
Charge Time	Standard (min), 0.5C	180min
	Rapid (min), 4A	60min
Charge Current	Standard current (A)	1.25
	Max. current (A)	4.0
Discharge	End voltage (V)	2.5
	Max. cont. current (A)	20
	Max. momentary pulse (A, <1sec)	100
Rated discharge Capacity	Standard (mAh) (0.2C)	2,500
	rated (mAh) (10A)	2,450

Table 4.1 Specifications of INR18650-25R Lithium-ion battery [26]

Figure 4.3 shows the INR-25R battery degradation during 250 continuous cycles at 23℃. The test method of these cycles is charging the battery with 4A charge current to 4.2V cut-off voltage, resting the battery for 10 mins, discharging the battery with 20A discharge current to 2.5V cut-off voltage, resting the battery for 30 mins, and repeating the process [26]. The blue line in Figure 4.3 represents the battery energy, which decreases from below 8.5Wh to about 5.5Wh; the red line represents the battery discharge capacity, which decreases from below 2.6Ah to below 1.8Ah. Obvious degradation is shown throughout the 250 cycles.

The manufacturer estimates that with standard charge and maximum continuous discharge at 25℃, after 250 cycles, the remaining capacity of INR18650-25R Li-ion batteries should be at least 1500mAh, which is 60% of the nominal capacity [26].

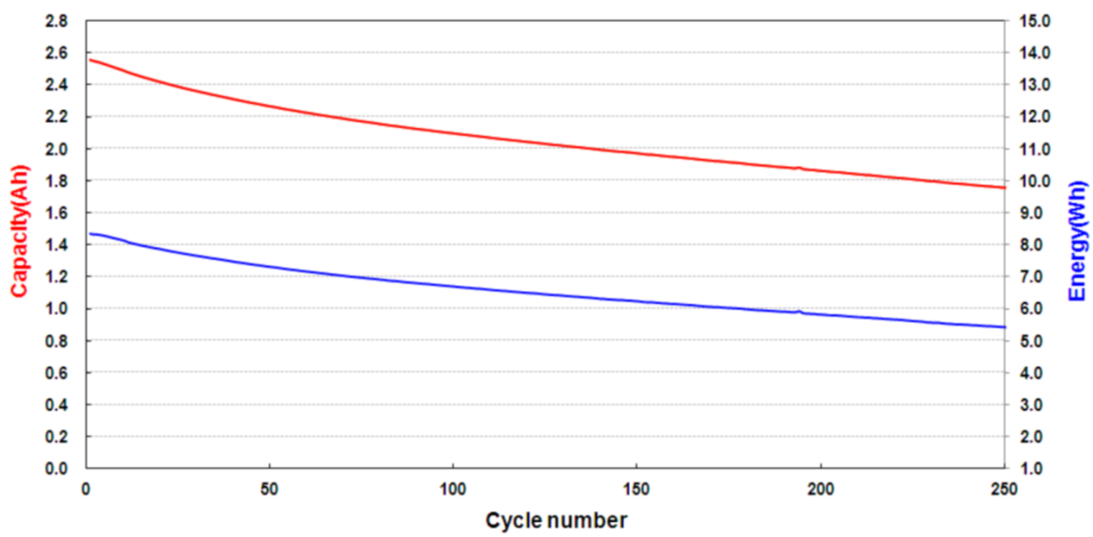

Figure 4.3 20A discharge cycle life of INR-25R battery at 23℃ [26]

4.2.2 Synchronous Balance Charger/Discharger iCharger 1010B+

Figure 4.4 iCharger 1010B+ External controls and connections [27]

Figure 4.4 shows the external controls and connections of the iCharger 1010B+. The iCharger requires an input DC voltage of 10V to 18V. The maximum charge current is 10A and the maximum discharge current is 7A. Up to ten Li-ion batteries can be connected in series and be charged or discharged at the same time using this charger. iCharger specifications are given in Table 4.2.

Specifications	**1010B+**
Input voltage range:	10.0 – 18.0VDC
Charge current range:	0.05 – 10.0A
Discharge current range:	0.05 – 7.0A
Maximum charge power capacity:	300W @ input voltage > 13.5V
Maximum discharge power capacity:	30W
Maximum regenerative discharge power capacity:	300W
Maximum extern discharge power capacity:	280W @ 40V/7A
Current drain for balancing:	<300mA
Balance accuracy:	<10mV
Lithium (LiPo/LiIo/LiFe) battery cell count:	1 – 10 series (In non-balance mode, expand LiFe to 12s)
NiCd/NiMH battery cell count:	1 – 25 series
Pb battery cell count:	1 – 18 series (2 –36V)
Battery setup memories:	10
Intelligent temperature control:	Yes
PC Connect:	USB port
Weight:	410g
Dimensions (L X W X D):	143X97X26mm 5.63"X3.82"X1.02"

Table 4.2 Specifications of 1010B+ iCharger [27]

The iCharger1010B+ has built-in protection for reversed polarity (input or output), low input voltage, high battery temperature, high charging capacity, and time overrun. Moreover, the charger can charge and discharge Li-ion batteries in different modes, including Discharge, Balance Charge, Cycle, and so on, with customized voltage and current. The Cycle Mode was used in this project, which ensures the continuity of decreasing battery life during cycling. The iCharger 1010 B+ screen during batteries cycles is shown in Figure 4.5 [27].

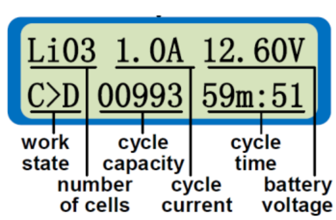

Figure 4.5 Screen of iCharger 1010B+ during Li-ion batteries cycle mode [27]

4.2.3 LogView Software

LogView is a menu-based application software used in the tasks of monitoring, data collection, configuration, and so on. It was used in this experiment, connected to the iCharger to measure the battery specification, and to record, display, and plot the cycling data. The data were then collected and analyzed to determine battery performance. Figure 4.6 shows the text and graphic views of the LogView software [28].

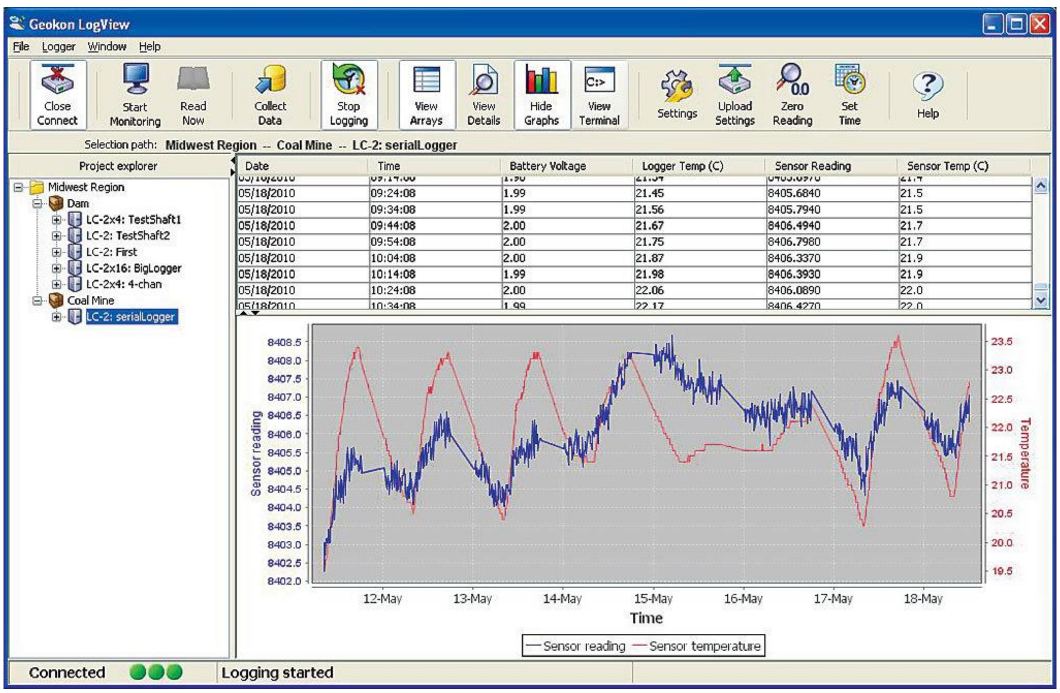

Figure 4.6 LogView Text and Graphic Views for static and dynamic display of data [28]

4.3 Experimental procedures

In this section, the experimental procedures are described for using cycles with the settings of 4.2V-2.5V cut-off voltage, full charge and discharge, and 2.5A charge/discharge current (1C).

Step 1: Set up iCharger 1010B+

Connect the iCharger to the power supply. Set the battery type to “Lilo”, which means Li-ion batteries; the charger mode to ‘CYCLE’, which allows the charger to charge and discharge the battery more than one time without manual control. Set the voltage range to “4.20V-2.50V”, the charge/discharge current to “2.5A”, which is 1C for the 2500mAh batteries used in this experiment. Set the cycle number to “8”, and the rest time to “20 mins” for cool down between cycles. The iCharger view after set-up is shown in Figure 4.7.

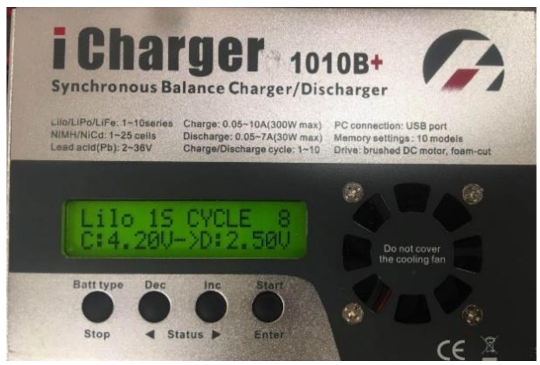

Figure 4.7 iCharger 1010B+ view after set-up

Step 2: Connect Li-ion batteries

The battery is connected to the iCharger through wires connected to the battery case, as shown in Figure 4.8.

Figure 4.8 iCharger connected with one Li-ion cell

Step 3: Set up LogView

Connect the iCharger to a computer through a USB port. Download the LogView, create a file, start a new data collection, set the machine type to "iCharger1010B+," and choose the corresponding channel. The created data collection in the menu bar is shown in Figure 4.9.

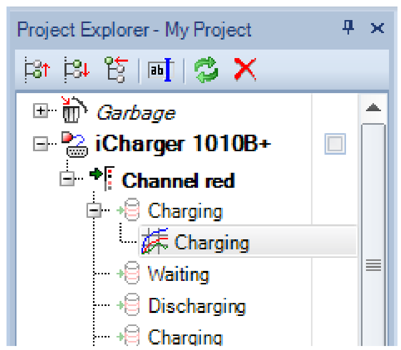

Figure 4.9 Menu bar

Step 4: Start the cycling

Long press (for three seconds) the "Start/Enter" button on the iCharger to start the cycle process, which is the farthest right button on the machine. The iCharger view during charging is shown in Figure 4.10. The symbols from top left to bottom right on the screen have the following meanings: "Li01" means one Li-ion battery is being cycled; "1.8A" means the charge current is 1.8A at the moment; "4.20V" means that the voltage of the battery is 4.2V at the moment; "C > D" means the iCharger is in CYCLE mode and if the "C" is blinking, the battery is charging, or if the "D" is blinking, the battery is discharging. "00343" means the battery capacity has changed 343 mAh at the moment. And, "10m:02" means the charging process has started for 10 mins and 2 secs.

Figure 4.10 iCharger view during charging in CYCLE mode

Step 5: Export data from LogView

During the cycles, data including voltage, current, power, capacity, temperature, and IR are recorded in plots and tables by LogView and can be exported in .jpg files. Figures 4.11 and 4.12 show the current, voltage, and capacity change as a function of time during charge/discharge of one INR-25R Li-ion cell. The blue line shows the battery output voltage, the green line shows the battery capacity change, and the red line shows the battery current change. The figures show that the charge and discharge capacity are about 2150 mAh, the charge voltage is 4.2V, the charge current is 2.5A, and the discharge process took less than 1 hour but the charge process took close to 2 hours.

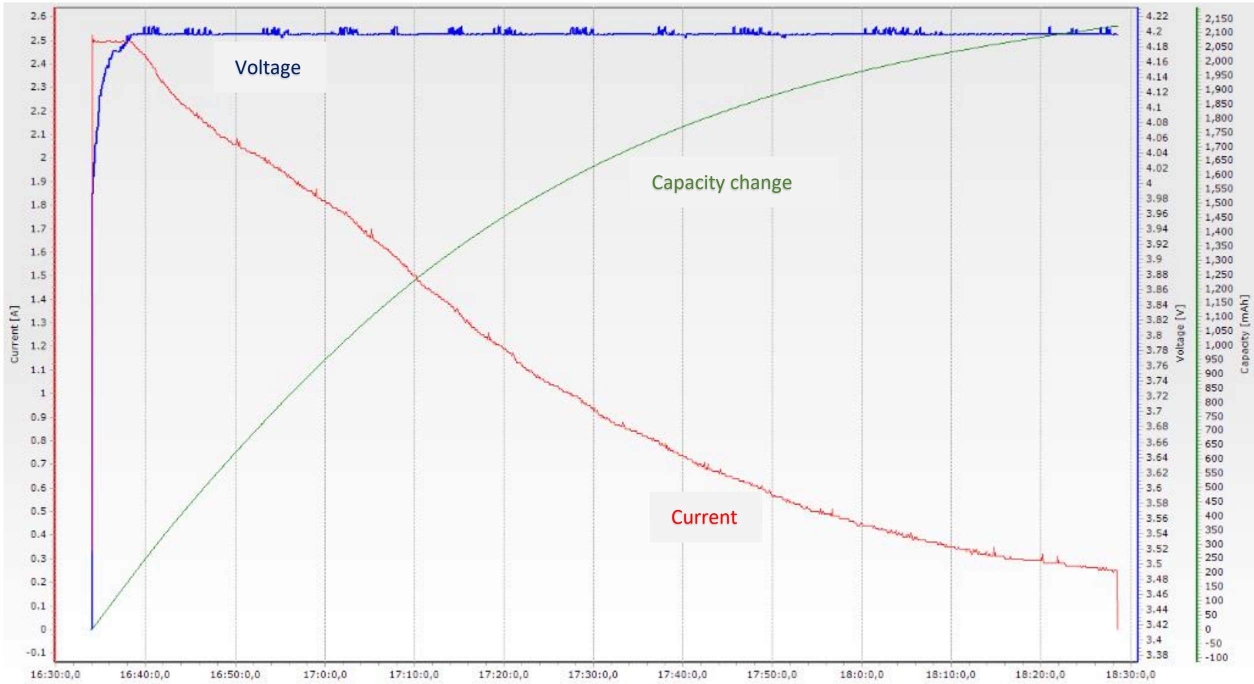

Figure 4.11 Current, voltage, capacity change during charging INR 18650 Li-ion battery

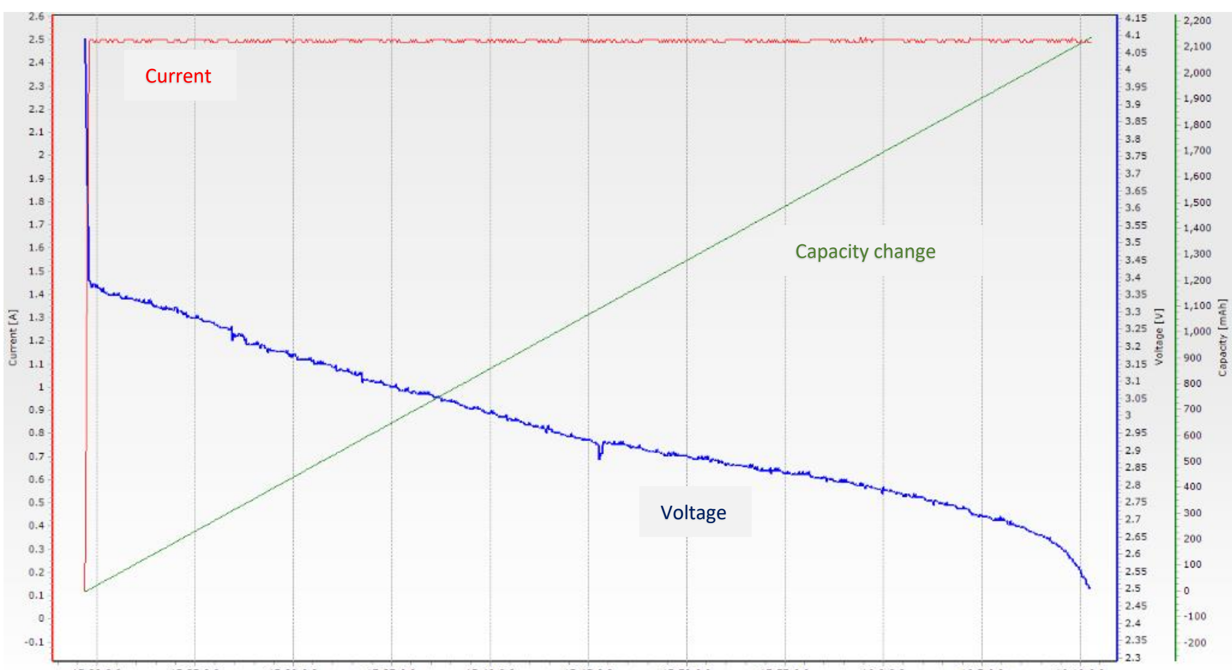

Figure 4.12 Current, voltage, capacity change during discharging INR 18650 Li-ion battery

4.4 Variables and parameters design

In this project, the battery capacity loss and its decreasing rate were used to determine battery degradation and battery life loss. Full discharge capacity of Li-ion batteries needs to be measured and should show a decreasing trend during usage. Battery voltage is commonly used to estimate battery capacity for most batteries. However, it is hard to determine Li-ion battery capacity simply based on battery voltage because of the way the voltage changes along with the battery capacity and SOC. As shown in Figure 4.13, which is a plot of the discharge voltage as a function of SOC, the actual voltage range during the SOC change from 10% to 90%, is only 0.5V, which is from 3.5V to 4.0V. For example, at 25℃, IMR batteries have 3.8V at 40% SOC, and have 3.7V at 30% SOC. The 0.1V gap can cause a 10% capacity difference in the battery. Thus, it is difficult to pin every percent of SOC to a certain voltage. In addition, the reading is affected by temperature and previous charge and discharge activities [16].

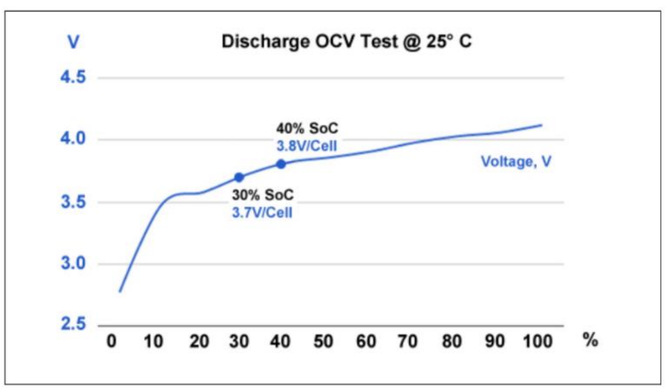

Figure 4.13 Discharge voltage as a function of SOC [16]

Because of the difficulty of estimating capacity using voltage, the traditional charge/discharge cycle method was used to measure Li-ion battery capacity. The full charge and discharge (100% DOD) method was used for the experiment in studying the effects of temperature, battery chemistry, and cycle frequency on capacity degradation rate, as it is easier for the observation of capacity loss.

To study battery chemistry, one IMR battery and one INR battery that have the same specifications were cycled under the same DOD, temperature, current, and cycle frequency for 250 cycles. For the cycle frequency study, two IMR batteries were cycled under the same DOD, temperature, and current, but with different frequency, which allowed 2 mins and 20 mins of rest between each charge and discharge, respectively. To examine temperature, four INR batteries were cycled under the same frequency, DOD, and current, but with temperatures of 5℃, 27℃, 27℃ and 50℃ respectively.

The battery degradation rate can be shown by the decrease of discharge capacity during cycling, and the effects of various conditions are shown by the difference in the degradation rate. The conditions that accelerate the degradation shorten Li-ion battery life. Data including battery capacity change, voltage, current, temperature, power, and time are recorded and analyzed in Chapter 5 to determine the environmental and cycling effects on battery life. Moreover, the effect of battery degradation on battery performance are also observed and discussed in Chapter 5.

Chapter Five

Results and Analysis

In this chapter, data from testing the Li-ion batteries are presented. Analysis of the battery degradation related to the battery cycling environment and aging, as well as the observation of the impacts of battery degradation on battery performance, are discussed.

5.1 Degradation during cycling and storage

5.1.1 Degradation due to cycling effect

In this experiment, battery degradation is shown by the decrease of battery discharge capacity during cycling. One INR-25R Li-ion cell was cycled with 4.2V-2.5V cut-off voltage, 2.5A charge/discharge current, at 27˚C, for 250 cycles. The voltage range should allow the battery to fully charge and discharge (100% DOD). The discharge capacity of the battery was recorded, which ideally represents the remaining energy available when the battery is fully charged. As shown in Figure 5.1, the discharge capacity decreased gradually throughout the cycles from 2318 mAh to 2110 mAh. A total of 208 mAh of capacity were lost during these 250 cycles, which indicates battery degradation.

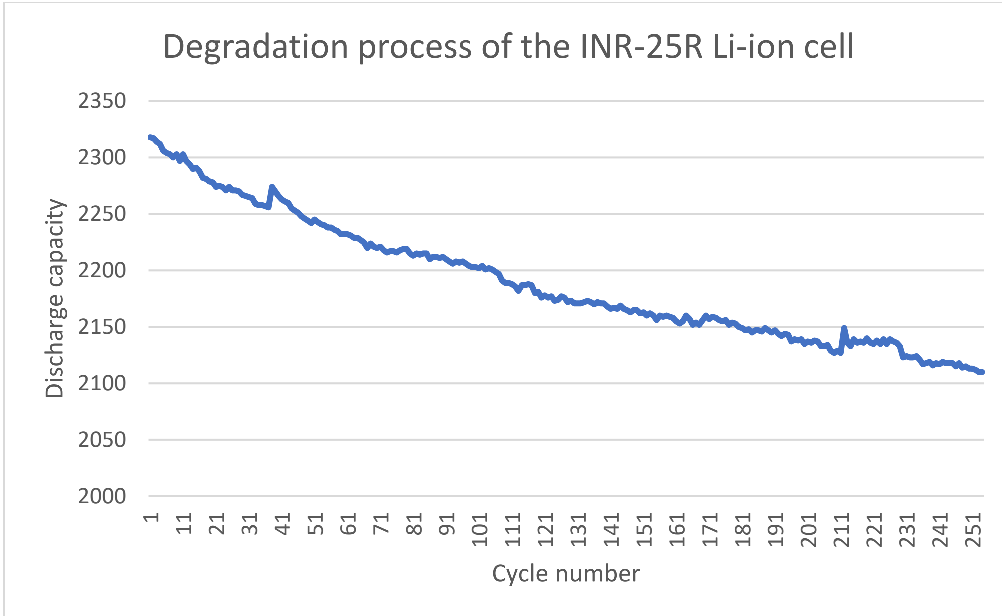

Figure 5.1 Degradation process of one INR-25R Li-ion cell at 27 ˚C under 4.2V-2.5V, 2.5A over 250 cycles

The battery's IR was also recorded several times to observe the change of IR during Li-ion battery degradation. Result are shown in Table 5.1. They show that the IR of the INR-25R battery fluctuated but changed insignificantly over 250 cycles.

Cycle number	1	37	61	72	89	142	171	244
IR(Ω)	279	279	279	285	279	291	289	286

Table 5.1 Recorded IR of the Li-ion battery after various cycles

5.1.2 Degradation due to aging effect

In order to verify the impact of time on Li-ion battery degradation, one INR-25R battery that was purchased two years prior was cycled once to obtain initial data. The charge/discharge current was 2.5A, the charge/discharge voltage was 4.2V-2.5V. It had been in storage and remained inactive during these two years. It was charged and fully discharged once again with the same current and voltage to measure the same data after these two years of storage. The measured data are discharge capacity and discharge time as the other data are very similar. As shown in Table 5.2, the discharge capacity of the battery after two years of storage is 2142 mAh, which is significantly less than the initial discharge capacity of 2409 mAh. The discharge time was 51mins, which is slightly shorter than the initial discharge time of 57mins.

Timeline	Discharge capacity	Discharge time
2 years ago	2409mAh	57mins
2 years later	2142mAh	51mins

Table 5.2 Discharge capacity and time comparison of a INR-25R battery before and after two years of storage

Thus, it is verified that Li-ion batteries experience significant capacity loss even without being used. About 267mAh of capacity were lost during the two years of storage, which is higher than the capacity loss during 250 cycles (208mAh) in section 5.1.1. This shows that battery aging is the main factor that causes battery degradation and shortens battery lifespan.

5.2 Factors that affect degradation rate

5.2.1 Degradation at different temperatures

INR batteries have high load capacity and thermal stability. Thus, INR-25R batteries should ideally be able to stand extreme temperatures without dramatic capacity change. In addition, as mentioned in Chapter 3, Li-ion batteries function best at room temperature (27˚C) and achieve optimal battery life at 20˚C. Higher or lower environmental temperatures can accelerate the battery capacity degradation. Four INR-25R batteries were cycled under controlled temperatures to observe the temperature effects on battery life.

Two batteries were cycled at 27 ˚C and 5 ˚C with 4.2V-2.5V voltage range, 2.5A current, and a 2-minute rest gap between charge and discharge. The capacity degradation of these two batteries over 73 cycles are shown in Figure 5.2. The battery cycled at 5 ˚C shows obviously faster capacity loss than the one cycled at 27 ˚C, which shows that low temperatures accelerate battery degradation and shorten battery life.

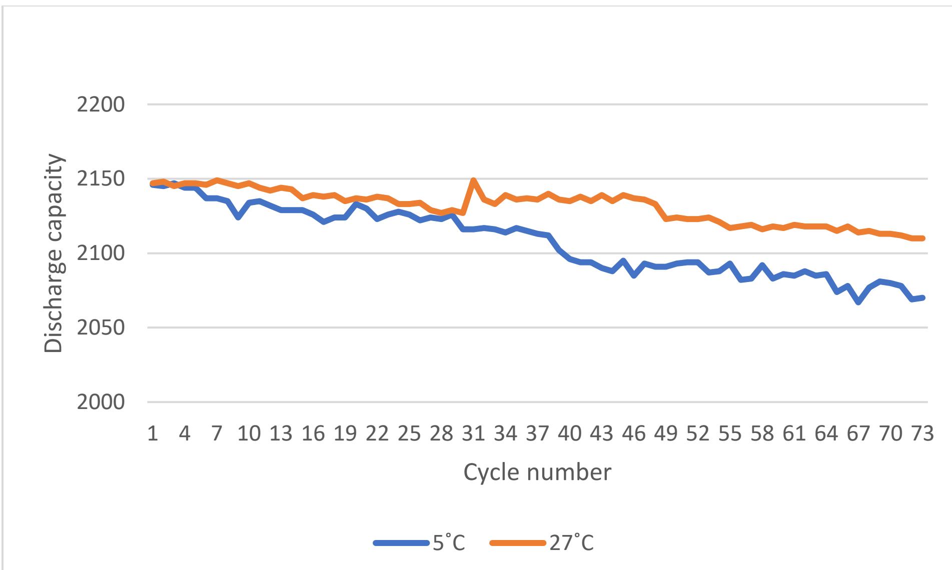

Figure 5.2 Capacity degradation of one INR-25R cell at 27˚C and 5 ˚C over 70 cycles

Another two batteries were cycled at 27 ˚C and 40 ˚C with the same voltage, current, and rest gap over 55 cycles. As shown in Figure 5.3, severe capacity loss is shown in the battery cycled at 40 ˚C while the one cycled at 27 ˚C had only a slight loss. This shows that high temperatures significantly reduce Li-ion battery lifespan.

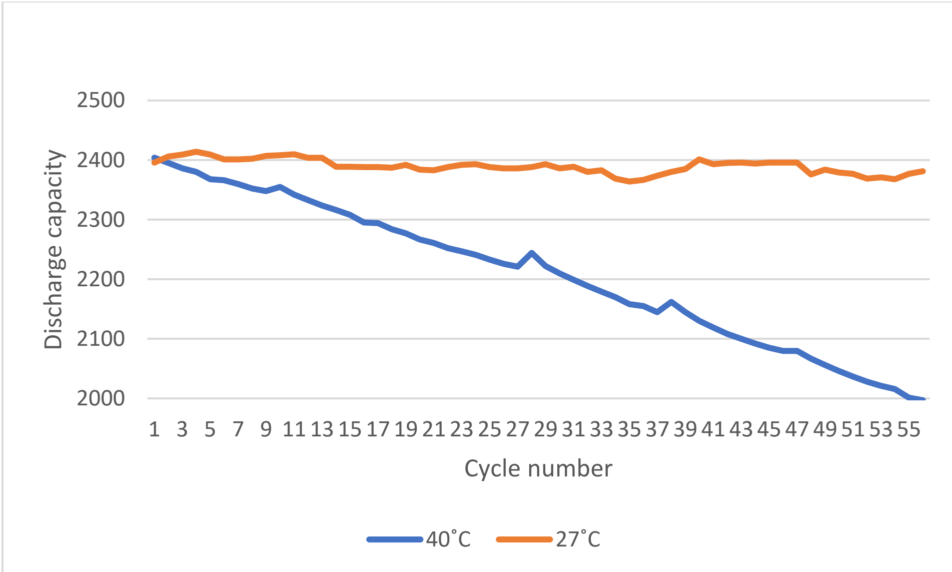

Figure 5.3 Capacity degradation of one INR-25R cell at 27˚C and 40 ˚C over 55 cycles

5.2.2 Performance comparison between INR and IMR 18650 Li-ion batteries

As mentioned in the description of Li-ion batteries characteristics in Chapter 2, the IMR has limited cycle and calendar life as well as relatively low capacity, while the INR has long lifespan and relatively large capacity. Thus, INR-25R batteries are expected to have a longer battery life than IMR-HE2 batteries under the same cycling conditions. One INR-25R cell and one IMR-HE2 cell were cycled at 27˚C, with 4.2V-2.5V cut-off voltage (100% DOD), 2.5A charge/discharge current, and a 20-minute rest gap between each charge and discharge, for 250 cycles. All the batteries used in this experiment were newly bought to reduce the errors due to battery aging or other factors. The capacity loss during the measurements is shown in Figure 5.4.

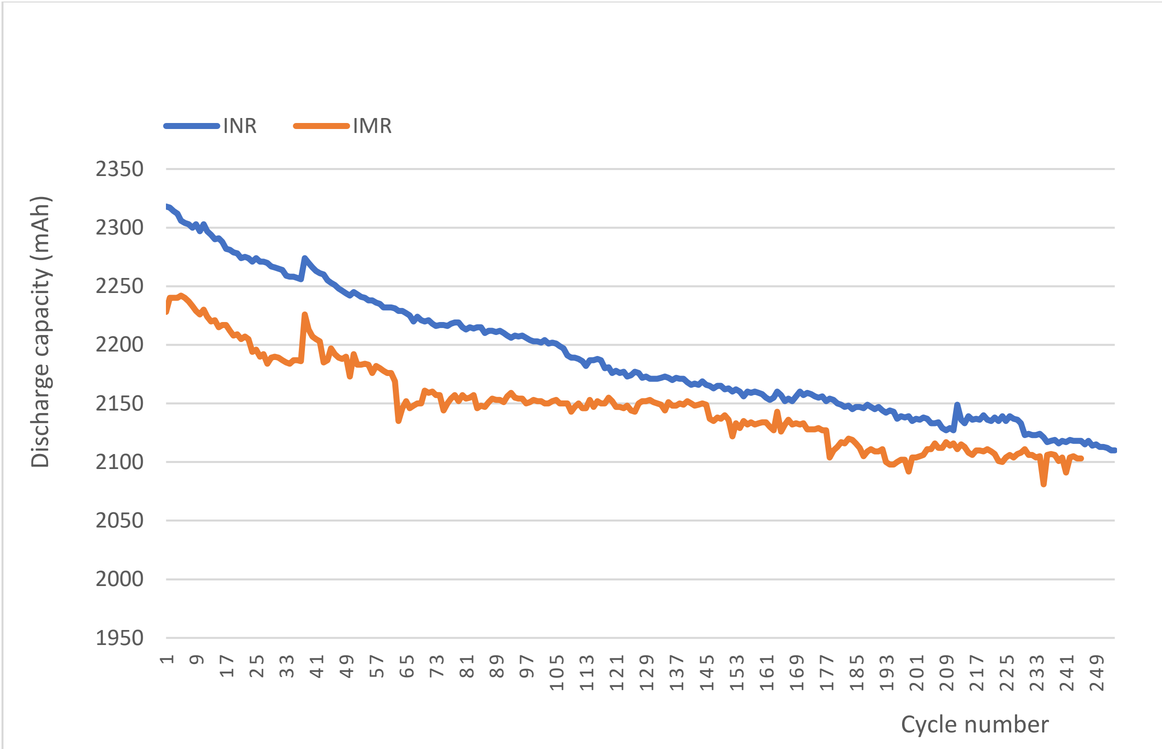

Figure 5.4 Degradation process of INR-25R and IMR- Li-ion batteries over 250 cycles at 27˚C

As shown in the plot, the INR battery has a higher discharge capacity than the IMR battery at the beginning of the cycling, but still below their initial capacity 2500 mAh. This could be due to several factors, including the battery degradation due to aging, self-discharge, and errors during manufacturing. Nevertheless, the data shows that the INR-25R battery can store more energy than the IMR-HE2 battery when they are purchased. However, what is also noticeable in the plot is that the INR battery and IMR battery degraded to approximately the same amount of discharge capacity at the end of the 250 cycles. This shows that the INR-25R battery experienced more capacity degradation than the IMR-HE2 battery during these 250 cycles. This means that the INR-25R battery degrades faster than the IMR-HE2 battery under the same conditions, which contradicts the expectation that INR batteries have longer lifespan.

5.2.3 Degradation under different cycle frequency

Frequent cycling without allowance for rest during cycles adds stress to Li-ion batteries, partially because of the increase of cell temperature during cycling and the lack of time for cooling down. Thus, under the same cycle environment (i.e., temperature, current, voltage, etc.), batteries that have longer rest time during cycles should have longer cycle life and slower degradation.

Two IMR-HE2 Li-ion batteries were cycled at 27˚C, with 4.2V-2.5V cut-off voltage (100% DOD), 2.5A charge/discharge current, but with 2 min and 20 min rest gaps between each charge and discharge, respectively, for 100 cycles. The discharge capacity degradation data are shown in Figure 5.5.

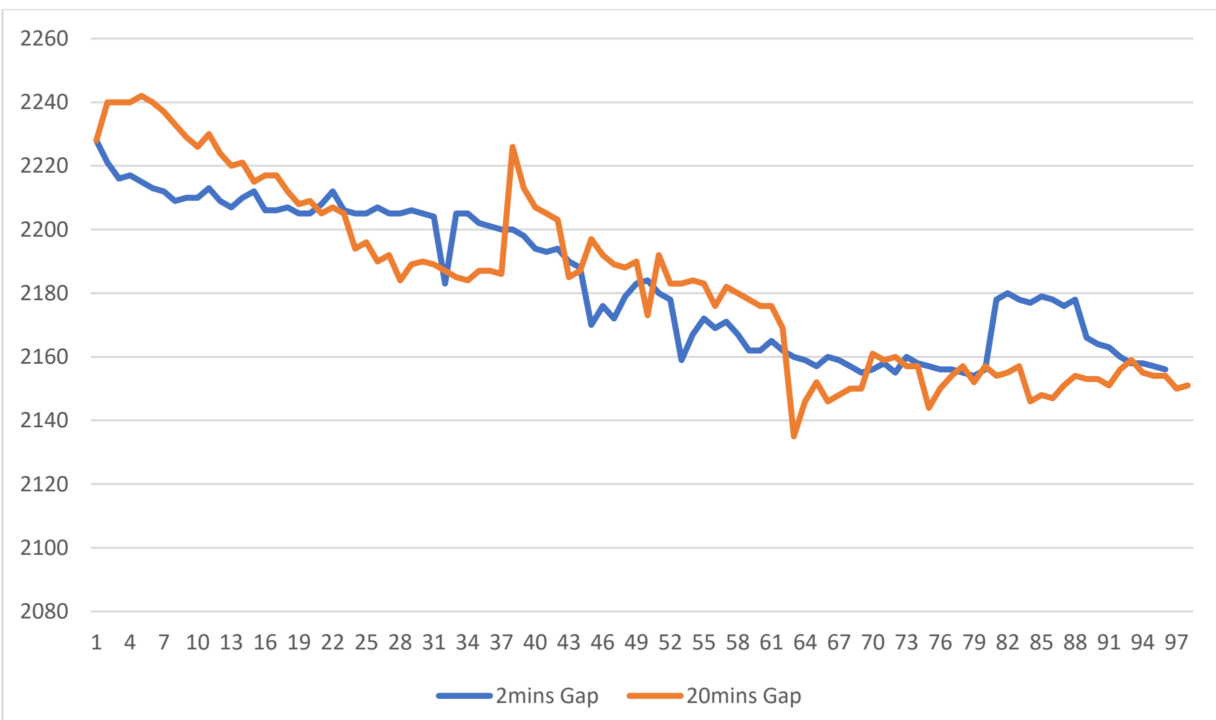

Figure 5.5 Degradation of IMR-HE2 batteries under different frequency over 100 cycles

As shown in the figure, even though the capacity of both batteries fluctuated during the 100 cycles, in contrast to what was expected, the IMR-HE2 battery that was allowed 20 minutes rest actually experienced the same amount of capacity loss after 100 cycles as the battery that had only 2 minutes rest. This shows that the difference in rest time between charge and discharge is inconsequential, at least for 2-minute and 20-minute rest times.

In Figure 5.5, the fluctuation of discharge capacity is noticeable because the total number of cycles is small. In addition, the large capacity increase such as in the red plot around cycle 40 and in the blue curve around cycle 82 were due to a 24-hour delay in restarting the cycles, which gave the batteries more time to rest.

5.3 Degradation effect on battery performance

Another INR-25R battery that was purchased two years prior and had been severely cycled (> 500 deep cycles) at that time. It was then charged and discharged once at 27 ˚C, with 4.2V-2.5V cut-off voltage (100% DOD), and 2.5A charge/discharge current. Its discharge capacity and discharge time are recorded in Table 5.2. As shown in both Table 5.2 and Table 5.3, after two years of storage or severe cycling, INR-25R batteries experienced a large decrease in discharge capacity and a slight decrease in discharge time.

	Discharge capacity	Discharge time
Before degradation	2408 mAh	58 mins
After degradation	2104 mAh	50 mins

Table 5.3 Discharge capacity and discharge time of one INR-25R Li-ion battery before and 2 years after severe cycling

Figures 5.6 and 5.7 show the power and voltage changes of the INR-25R battery during a full discharge before and two years after severe cycling, which show no significant difference. These figures show that the battery degradation does not affect the battery voltage or power. Thus, besides the capacity loss, the only noticeable difference between the degraded battery and the new battery is the discharge time. This means that the battery degradation only causes the decrease of discharge time and discharge capacity, but not the other performance parameters, such as power, voltage, current, etc.

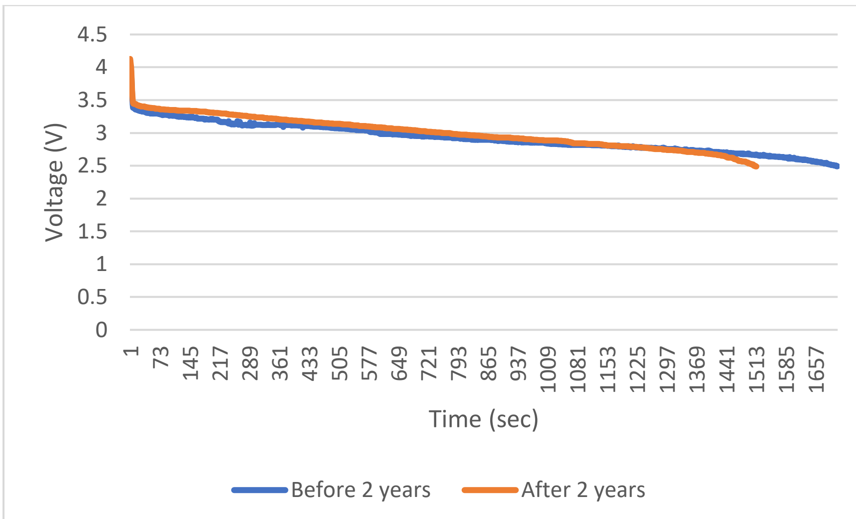

Figure 5.6 Voltage change during discharge of one INR-25R cell before and 2 years after severe cycling

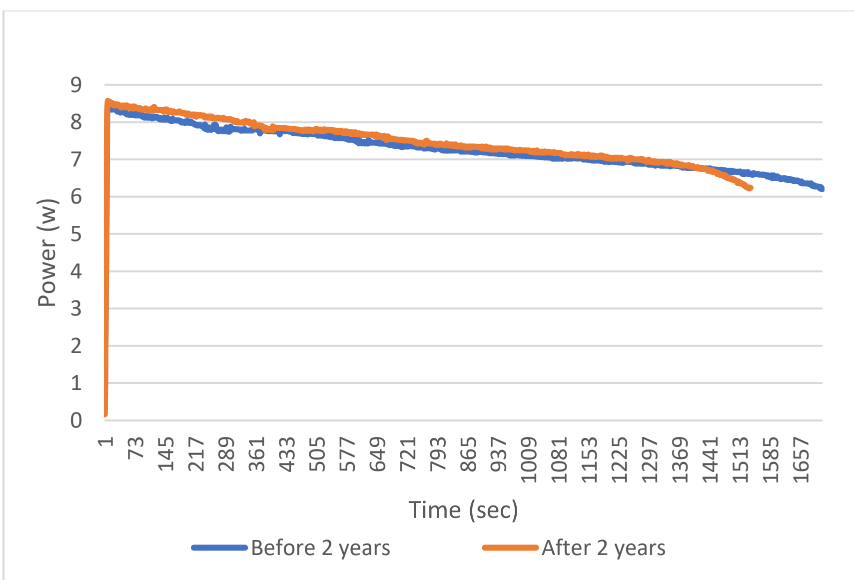

Figure 5.7 Power change during discharge of one INR-25R cell before and 2 years after severe cycling

Another thing to notice is that one INR-25R battery experienced a capacity loss of 304 mAh and a decrease of discharge time of 8 mins (Table 5.2) after two years of cycling for more than 500 deep cycles, while another one experienced a capacity loss of 267 mAh and a decrease of discharge time of 6 mins (Table 5.1) after two years of storage without being used. By comparing the data, the capacity loss due to severe cycling is less than 50 mAh. This shows that the battery calendar life loss is much more severe than the cycle life loss and it should be the main concern when it comes to the prolonging of battery life.

Chapter Six

Conclusions and Recommendations for Future Work

The purpose of this thesis project has been to study the conditions that affect Li-ion battery lifespan. A review of existing literature, which describes the conditions, including temperature, DOD, charge voltage, cycle bandwidth and charge current, that affect Li-ion battery lifespan and the best conditions to prolong Li-ion battery life can be found in Chapter 3. Chapters 4 and 5 describe the project conducted to study how some other conditions, which have rarely been addressed in the literature, such as cycle frequency and battery chemistry, affect Li-ion battery life. Chapters 4 and 5 also describe observations of some Li-ion battery characteristics, including how cycling and aging cause battery degradation and how degradation affects battery performance.

6.1 Conclusion

Previous studies have shown that temperatures between 5°C and 20°C are recommended to prolong battery life when storing Li-ion batteries, 20°C or slightly below is recommended to prolong battery life when cycling Li-ion batteries, and 27°C is recommended for maximum battery runtime. When storing Li-ion batteries, 50% of SOC is recommended because the higher the SOC, the faster the battery degradation. Too low a SOC also accelerates capacity degradation and increases battery IR. When cycling Li-ion batteries, the cycle bandwidth from 25% to 85% SOC is used by industrial devices such as EV to prolong battery life [16]. The charge voltage of 3.92V [16] and DOD of around 50% are recommended to achieve optimal battery life [19]. For energy Li-ion batteries, a C-rate of 0.8 C or below is recommended to prolong battery life. The higher the C-rate, the faster the Li-ion battery degrades. For power Li-ion batteries, C-rates are specified by manufacturers and are much higher than for energy ones.

The project was done using several iCharger 1010B+ synchronous balance chargers, to cycle several INR-25R 18650 and IMR-HE2 18650 Li-ion batteries at different temperatures and frequencies. LogView and Excel software were used to record and plot the data, which includes voltage, current, capacity, temperature, and power. Cycle frequencies used in this project, which were two minutes and twenty minutes rest time between each charge and discharge session, were found to have no impact on battery degradation rate. This is different from the assumption that frequent cycling accelerates Li-ion battery degradation due to chemical and mechanical stress [15]. INR-25R 18650 Li-ion batteries are found to degrade faster than IMR-HE2 18650 Li-ion batteries under the same conditions, which is contrary to the research that INR batteries have longer cycle life than IMR batteries [29]. The project also verifies the relationship between temperature and Li-ion battery degradation rate [22], which shows that Li-ion batteries degrade faster at high temperatures (40˚C) and low temperatures (5˚C) than at room temperature (27˚C). In addition, the data shows that the discharge time of a degraded Li-ion battery is shorter than a new one, but its voltage, current and power are the same.

This research had several limitations including that there were only a few batteries used in the measurements, which doesn’t show the replicability and generalizability of the data; there were interruptions during the experiment that caused slight reversal of capacity loss; and the batteries tested were not all purchased from the same manufacturers, which may have caused errors in the results due to different quality of the batteries.

6.2 Suggestions for future work

- For the cycle frequency experiment, longer rest difference should be used between sets of batteries (such as 2 mins and 1 hour) and a larger number of batteries should be used to improve the replicability.
- When comparing the data of the INR-25R and IMR-HE2 batteries, the INR battery was shown to degrade faster than the IMR battery. This is contrary to the literature, which states that INR batteries have longer lifespan than IMR batteries because of the component of cobalt in INR batteries [29]. Further investigation should be done addressing this issue.
- In addition, there are lots of literatures introducing life-predicting models for Li-ion batteries. Future research may fit the data found in this thesis (temperature, DOD, C-rate, etc.) into different models to see if models can predict the optimal battery life with these data, and to compare the optimal battery life conditions predicted by models with the conditions recommended in real life.

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