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A Study of the Factors that Affect Lithium Ion Battery Degradation

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SUMMARY

Due in part to concern over atmospheric carbon and global warming, the move from centralized fossil fuel-based power generation to renewable energy-based distributed generation is growing. Since the availability of renewable energy, e.g., photovoltaic and wind, is independent of electrical demand, battery energy storage systems (BESS) are also under development. Several battery types have been studied for use in BESS, but for a variety of reasons, most new energy storage systems are based on lithium-ion (Li-ion) batteries. Despite their advantages, however, Li-ion batteries degrade relatively rapidly under certain circumstances, which shortens their cycling lifespan, requiring costly replacement. This paper describes the results of a study of the influence of several factors on the degradation of Li-ion battery capacity during repeated charge/discharge cycling, including battery chemistry, ageing, cycling frequency, and temperature.

KEYWORDS

Energy Storage; Lithium Ion Batteries; Capacity Degradation; Cycling; Ageing; Temperature.

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INTRODUCTION

Due to the public's concern over the polluting and warming effects of generating electrical power by burning fossil fuels, the renewable energy industry has emerged and is growing rapidly. According to the International Energy Agency, for the next five years, 70% of global electricity generation growth is forecast to be met by renewable sources, with solar contributing the most, followed by wind, hydropower, and bioenergy [1].

When electricity generated by renewable power sources is injected into the grid, the voltage can increase above acceptable levels. Also, renewables like solar and wind are intermittent, which causes fluctuations in the generated energy, resulting in voltage flicker. Thus, renewables-produced voltage requires frequent adjustment by voltage regulators. 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 both the quality and efficiency of renewable power stations.

Because they have the ability to improve the operating capacities of the electric grid through peak shaving, frequency control, and energy storage, battery energy storage systems (BESS) play an important role in integrating variable renewable energy sources into grid power systems. BESS typically include batteries, hybrid inverters, energy management systems and thermal management systems. At grid scale, thousands of cells are connected in series and parallel to form battery modules for energy storage systems in megawatt level substations. The BESS are co-located with renewable energy sources, either to smooth the power supplied by the intermittent wind or solar source, or to save the energy for other times when the renewable sources cannot produce power directly. BESS are superior to most other energy storage techniques because of their 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 11 GWh in 2017 to between 100 and 167 GWh in 2030 [2].

Among many factors that impact the efficiency and cost of a grid-connected BESS, the type of battery used is one of the most important. When choosing the most suitable battery for an energy storage system, important considerations include specific energy or capacity, which relates to runtime; specific power, or the ability to deliver high current; life-span, reflecting cycle life and longevity; safety and toxicity; performance at various temperatures; charging speed; self-discharge and shelf life; and cost.

Several types of batteries continue to be developed for grid-connected renewable energy storage, but Lithium-ion (Li-ion) is currently the most popular. According to [3], in 2017 approximately 99% of new BESS energy storage was based on Li-ion batteries, and it has been predicted that Li-ion batteries will be the most competitive technology in the majority of applications in the coming decades [4]. A typical Li-ion battery can store 150 Wh of energy in 1 kilogram of battery [5]. It can be discharged to approximately 80% state of charge (SOC) at a rate of C/2 without any long-term damage. And, its cost per cycle is very low, typically $0.19 per cycle [5]. Thus, the Li-ion battery is attractive for intermittent source energy storage due to its long lifespan, high energy density, deep and fast discharge ability, and low cost per cycle.

Li-ion batteries are already used in many renewable energy BESS applications. Examples include the 36 MWh BESS of Younicos' 153 MW Notrees wind farm in Texas; the 32 MWh BESS in the Tehachapi 4,500 MW Wind Energy Storage Project in California; 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; the 6.6 MWh Angamos project in Mejillones, Chile; The 2 MWh BESS in Johnson City; 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.

Despite its popularity in grid-connected BESS applications, limited data is available on the influence of certain variables on the speed at which the Li-ion battery's capacity degrades and thus shortens its lifespan. Thus, this paper describes the results of a study of the influence of battery chemistry, ageing, cycling frequency, and temperature [6], [7] on the degradation of Li-ion battery capacity during repeated deep (>80%) charge/discharge cycling.

EXPERIMENTAL ARRANGEMENT

Two types of Li-ion rechargeable power cells were studied, the INR 18650-25R and the IMR 18650-HE2. Both batteries have the same specifications, including size (65 mm long and 18 mm in diameter), maximum capacity (2500 mAh), maximum discharge current (20 A), etc. However, due to their being based on different chemistries, some differences are found. The INR battery consists of lithium nickel manganese cobalt (LiNiMnCoO2), and the IMR battery consistes of lithium manganese oxide ($LiMn_2O_4$). The manganese in both batteries gives them high specific power, which provides good load capability. But the absense of cobalt and nickel in the IMR battery causes it to have lower specific energy (capacity) and shorter lifespan compared to the INR battery.

The batteries in question were studied using an iCharger 1010B+ Synchronous Balance Charger/Discharger, illustrated in Figure 1, to measure the decrease in battery discharge capacity during charge/discharge cycling. The charger can charge and discharge batteries in different modes, including Discharge, Balance Charge, Cycle, and so on, with customized voltage and current. The Cycle Mode was used, to ensure the continuity of decreasing battery life during cycling. Measured data, including temperature, current, voltage, power, capacity, and internal resistance, were recorded, plotted, and displayed using LogView, a menu-based package designed for such tasks.

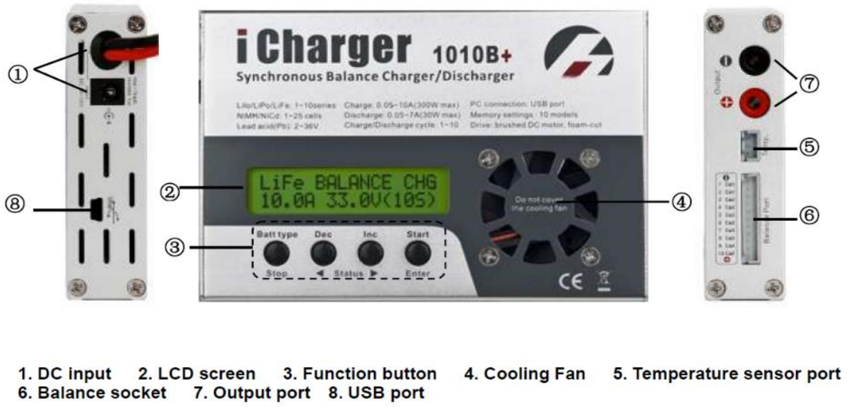

Figure 1. iCharger 1010B+ external controls and connections.

The standard charge process for Li-ion batteries is to apply a constant current of 1.25A (0.5C) until the voltage increases to 4.2V. The maximum charge current is 4.0A. It typically takes 180 minutess to fully charge a battery under a standard charge. The standard discharge process is to draw a constant current of 0.5A until the voltage drops to 2.5V. The maximum discharge current is 20A. Both batteries have a standard discharge capacity of 2500 mAh under 0.5A discharge current (0.2C). It typically takes five hours to fully discharge either battery under a standard discharge. Charged cells have a rated discharge capacity of 2450 mAh under a discharge current of 10A (4C). The higher the current, the lower the discharge capacity. Charging the batteries to above 4.2V or discharging them to below 2.5V can result in irreversible damage.

In this study, the battery capacity loss and its decreasing rate were used to determine battery degradation and lifespan. Full discharge capacity needs to be measured and should show a decreasing trend during usage. Although battery voltage is commonly used to estimate battery capacity for most batteries, it is difficult to do this for Li-ion batteries because of the way the voltage changes with capacity and state of charge (SOC). Therefore, the traditional full charge and discharge (100% depth of discharge (DOD)) cycle method was used to study the effects of battery chemistry, ageing, cycling frequency, and temperature on battery capacity degradation.

RESULTS

Battery chemistry effects

As stated above, the absense of cobalt and nickel in the IMR battery causes it to have lower specific energy (capacity) and shorter cycle life compared to the INR battery. To see these differences under cycling conditions, one INR-25R cell and one IMR-HE2 cell were charged and discharged 250 times, to 4.2V and 2.5 V, respectively, at 27˚C, with 2.5A charge and discharge currents, with a 20-minute delay between each charge and discharge. Note that all the batteries used in this experiment were newly purchased in order to minimize effects due to ageing. Figure 2 shows plots of the measured discharge capacity of the two batteries as a function of the cycle number.

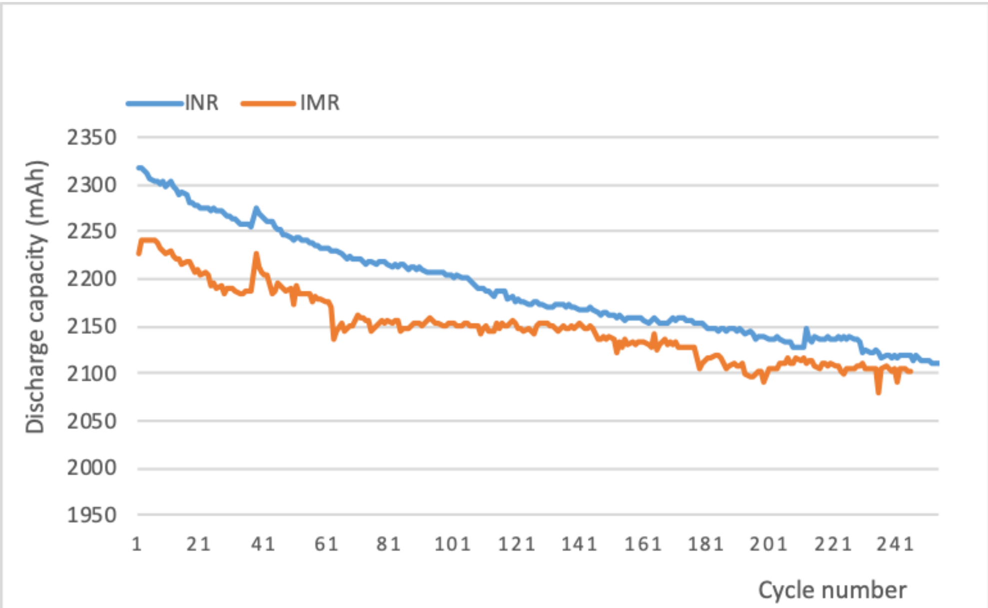

Figure 2. Measured decrease in discharge capacity of INR-25R and IMR-25 batteries over 250 cycles at 27˚C.

As shown in Figure 2, the INR battery has a higher discharge capacity than the IMR battery at the beginning of the cycling, as would be expected. However, it can also be seen in the figure that both batteries degraded to approximately the same discharge capacity at the end of the 250 cycles. Thus, the INR battery degraded faster than the IMR battery under the same conditions, but if lifespan is defined in terms of a battery's capacity decreasing to a certain level, then both batteries had approximately the same lifespan, which contradicts the expectation that INR batteries have longer lifespan.

Ageing effects

In order to examine the impact of time on Li-ion battery degradation, an INR-25R battery, which had been purchased two years earlier and cycled once at the time of purchase (to obtain initial discharge capacity data for the new battery), was cycled once again two years later to obtain initial discharge capacity data for the same, but two year older, battery. The battery had been in storage and remained inactive during those two years. During both charging and discharging, the current was 2.5A, the charge/discharge voltages were 4.2V and 2.5V, respectively, and the temperature was 27˚C. The initial and final (two years later) discharge capacities of the battery were 2409 mAh and 2142 mAh, showing that approximately 267 mAh of capacity were lost during the two years of storage. This is more than the capacity loss during 250 cycles (208mAh) for the INR battery (upper, blue curve in Figure 2). Thus, battery ageing alone can significantly shorten battery lifespan.

Cycling frequency effects

Frequent cycling of a battery without allowance for recovery during cycles can add stress to the battery, partially because of the increase of cell temperature during cycling and the lack of sufficient cooling time. Thus, under the same cycle environment (i.e., temperature, current, voltage, etc.), batteries that have longer recovery time during cycles should have slower degradation and longer cycle life.

Two IMR-HE2 Li-ion batteries were cycled at 27˚C, with a 4.2V-2.5V voltage range, and a 2.5A charge/discharge current, but with either a 2 minute delay after each charge and discharge, or a 20 minute delay after each charge and discharge, for 100 cycles. The discharge capacity degradation data are shown in Figure 3. As shown in the figure, both batteries experienced the same amount of capacity loss after 100 cycles, meaning that, for these two cycling frequencies at least, the battery discharge capacity was independent of frequency. Further measurements with shorter and longer recovery periods would be needed to say more about this result.

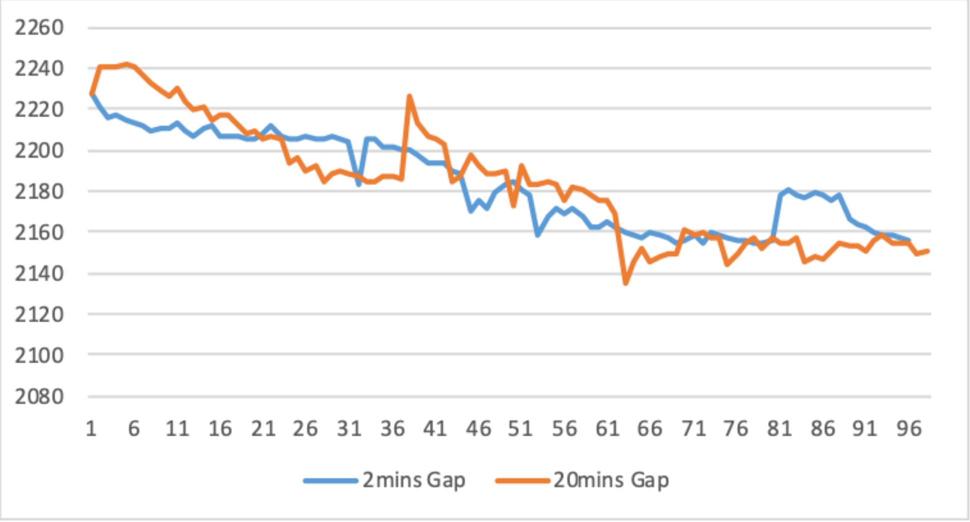

Figure 3. Measured decrease in discharge capacity (in mAh) of two INR-25R cells at 27˚C over 100 cycles. Charge/discharge delay times were 2 minutes (blue curve) and 20 minutes (orange curve).

Temperature effects

INR batteries have high load capacity and thermal stability. Thus, INR-25R batteries should ideally be able to withstand extreme temperatures without significant capacity change. It has been reported that Li-ion batteries function best at room temperature (27˚C) and achieve optimal battery life at 20˚C [8]. Higher or lower ambient temperatures can thus accelerate battery capacity degradation. Four INR-25R batteries were cycled under various controlled temperatures to observe the temperature effects on battery life.

First, two batteries were cycled, one at 27˚C and the other at 5˚C, with a 4.2V-2.5V voltage range, a 2.5A charge/discharge current, and a 2 minute delay after each charge and discharge. The capacity degradations of these two batteries over 73 cycles are plotted in Figure 4. The battery cycled at 5˚C shows obviously faster capacity loss than the one cycled at 27˚C, which shows that low temperatures can accelerate battery degradation and decrease battery life.

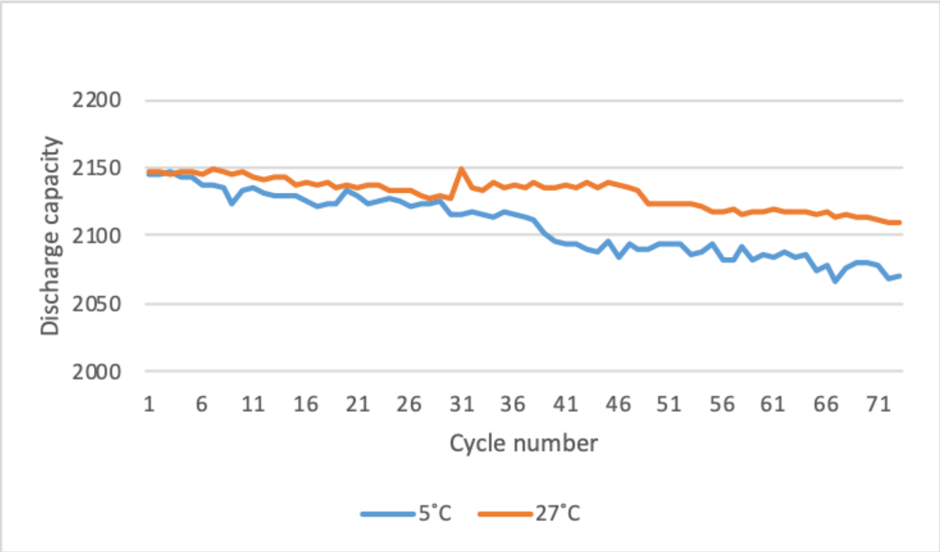

Figure 4. Measured decrease in discharge capacity (in mAh) of INR-25R cells at 27˚C and 5˚C over 70 cycles.

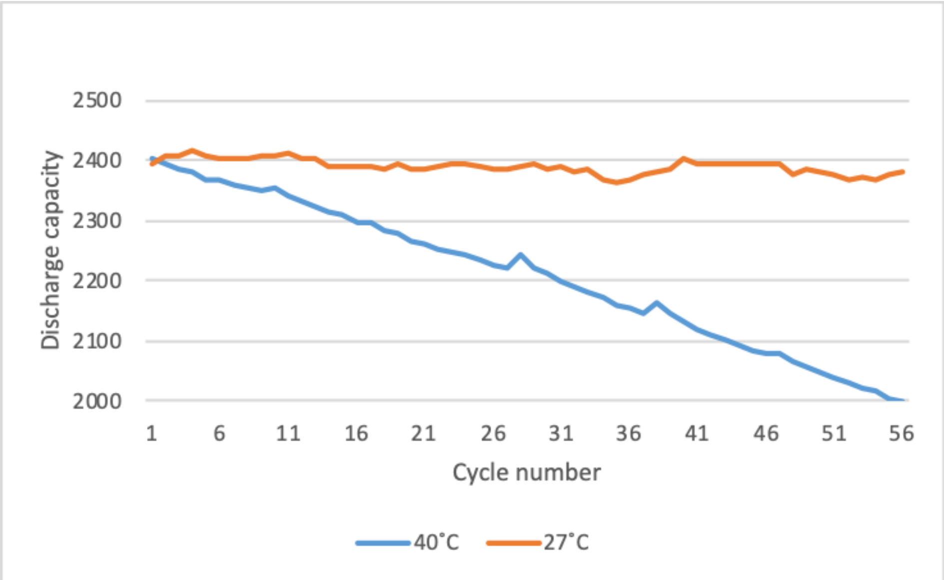

Figure 5. Measured decrease in discharge capacity (in mAh) of INR-25R cells at 40˚C and 27˚C over 55 cycles.

Next, two other batteries were also cycled, one at 27˚C and the other at 40˚C (instead of 5˚C), also with a 4.2V-2.5V voltage range, a 2.5A charge/discharge current, and a 2 minute delay after each charge and discharge. The capacity degradations of these two batteries over 55 cycles are plotted in Figure 5. As can be seen, significant capacity loss occurs in the battery cycled at 40˚C while the battery cycled at 27˚C had a much smaller loss of capacity (as in Figure 4). This shows that high temperatures can significantly reduce Li-ion battery lifespan.

CONCLUSIONS

Li-ion batteries are becoming increasingly popular for use in renewables-based battery energy storage systems, but there is still only limited data available on the influence of certain variables on the speed at which their capacity degrades, leading to shortened lifespan. This study has used an iCharger 1010B+ Synchronous Balance Charger/Discharger to initially examine the influence of battery chemistry, ageing, cycling frequency, and temperature on the degradation of Li-ion battery capacity during deep (>80%) charge/discharge cycling. In the INR/IMR chemistry comparison measurement, the INR battery degraded faster than the IMR battery, but both batteries had approximately the same lifespan, contradicting the expectation that INR batteries have longer lifespan. In the battery ageing experiment, a battery that had been inert for two years lost as much discharge capacity as a new battery that underwent 250 charge/discharge cycles. In the cycling frequency experiment, with frequency determined by delay times of 2 minutes and 20 minutes between charging and discharging, the loss of battery discharge capacity was independent of frequency. Finally, the temperature dependence measurements showed that battery capacity degrades rapidly if the battery temperature is much above or below room temperature.

Continuing measurements are being made with additional types of Li-ion batteries, delay times during charge/discharge cycles, and temperatures in order to establish more definite conclusions. Lithium polymer (LiPo), (relatively low self-discharge rate, high conductivity, and high specific energy), and lithium titanate (relatively high capacity) are of particular interest.

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