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Article

Effect of Current Rate and Prior Cycling on the Coulombic Efficiency of a Lithium-Ion Battery

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Abstract: The determination of coulombic efficiency of the lithium-ion batteries can contribute to comprehend better their degradation behavior. In this research, the coulombic efficiency and capacity loss of three lithium-ion batteries at different current rates (C) were investigated. Two new battery cells were discharged and charged at 0.4 C and 0.8 C for twenty times to monitor the variations in the aging and coulombic efficiency of the battery cell. In addition, prior cycling was applied to the third battery cell which consist of charging and discharging with 0.2 C, 0.4 C, 0.6 C, and 0.8 C current rates and each of them twenty times. The coulombic efficiency of the new battery cells was compared with the cycled one. The experiments demonstrated that approximately all the charge that was stored in the battery cell was extracted out of the battery cell, even at the bigger charging and discharging currents. The average capacity loss rates for discharge and charge during 0.8 C were approximately 0.44% and 0.45% per cycle, correspondingly.

Keywords: lithium-ion batteries; coulombic efficiency; capacity loss

1. Introduction

Air pollution and global climate change are fundamental issues for today's society. New technological innovations are necessary to overcome these problems. Considerable eco-friendly changes have to be made for principal way of transport, which is mostly based on the internal combustion engine. One of the possibilities to have cleaner environment is the electrification of buses, cars, and trucks.

The applications of lithium-ion batteries are increasing in different sectors, such as space and automotive industries and consumer electronics to meet the power and energy requirements [1]. Notwithstanding, understanding a battery's rate of useful life or capacity loss in these applications is necessary, especially in automotive and space industry. In addition, determining the durability and performance of the lithium-ion batteries are critical [1].

Li-ion batteries have so many applications in different sectors. One of the problems related to these batteries is their lifetime. Their lifetime is not limitless, and they have a restricted lifetime due to some limitations in technology.

It is possible to expand their market by increasing their cycle life. In the past few years, substantial efforts have been accomplished for model development and to anticipate capacity fade in lithium ion batteries [1–3]. Notwithstanding, experimental data are necessary for the investigation of the capacity fading mechanisms and the aging processes of a battery system [1].

A factor influencing the rechargeable capacity of a lithium-ion battery cell was described [4]. It was seen that diminution resistive electrolytes and oxidation are essential to improve the discharge and charge coulombic efficiencies of both the negative and positive electrodes [4]. It was concluded that electrochemical investigations on the diminution of electrolytes and oxidation, accompanied with

the chemical investigation of reaction products, would assist anticipation in safety and advance cycle life for a lithium-ion cell [4].

Testing life cycle under many cycles such as fifteen thousand cycles and undergoing situation that simulate real application is significantly problematic due to the testing time, which is an extraordinarily long time. The capacity retention plays an important role in the lifetime of Li-ion batteries.

According to the data that were assembled from the cycle life experiments of two kinds of commercial lithium-ion battery cells containing NMC battery cells and LFP battery cells, which were experimentally studied the long-term coulombic efficiency development and its correspondence with the battery cell degradation. The findings demonstrate that NMC and LFP cells display two different aging behaviors [5].

A semi-empirical model that was obtained from the correspondence among battery degradation and coulombic efficiency was suggested to seize the capacity degradation behavior of several cylindrical lithium-ion batteries [6]. The suggested model seizes the convexity of the degradation arc competently, exhibits a superior goodness-of-fit than the generally employed square-root-of time model. In addition, it introduces an extreme robustness versus simulated data, with dissimilar aging shapes [6].

Coulombic efficiency and continuous-time energy efficiency of several lithium titanate batteries were investigated according to dissimilar discharge current rates and state of charge sections. The experimental outcomes demonstrated the coulombic efficiency and energy efficiency discrepancy in dissimilar state of charge sections and changing discharge rates [7].

Different investigations regarding the coulombic efficiency of lithium-ion batteries have been done. Notwithstanding, effect of different prior cycling and current rates on the coulombic efficiency of lithium-ion batteries were not precisely and comprehensively studied. Therefore, the main objective of this investigation was to determine the impact of important parameters such as current rate and prior cycling on the coulombic efficiency of the battery cell by accomplishing different experiments.

Although many investigations about discharge and charge processes on lithium-ion batteries have been accomplished [8,9] most of them were accomplished by applying discharging and charging for different current rates. In this investigation, a comprehensive investigation of discharge and charge parameters of a lithium-ion battery was demonstrated. The coulombic efficiency of the lithium-ion battery at different current rates was determined. In addition, dependence and impact of the discharging and charging intensity, on the coulombic efficiency of the battery cell was studied.

2. Experimental

The CT0550 was used to test the battery cells. The CT0550 contains eighty channel cell tester, which is ideal for evaluating and testing battery cells. In addition, it is used for big volume testing. Two commercial lithium-ion battery cells were taken from suppliers to accomplish these experiments. The charging and nominal voltage of the battery is 4.2 V and 3.6 V, correspondingly. The battery cells were cycled between 2.6 and 4.2 V. Each of battery cell was cycled by using applied currents of 0.2 C, 0.4 C, 0.6 C, and 0.8 C at 25 °C.

The other experiments were done by using CT0550, which includes eighty independent 5 V/50 A channels per rack and 1 microprocessor per five channels. There is liquid cooling with central heat exchanger for stability and accuracy of high power and ultra-fast increase, decrease, and switching time between the charging and discharging modes. Three identical and new Li-ion batteries were employed for this experiment. Maximum discharge current of the batteries for continuous discharge is 8000 mA and for not continuous discharge is 13,000 mA.

3. Results and Discussion

3.1. Effect of Current Rate

The battery cells were cyclically discharged and charged at different current rates and between a lower and upper voltage limit. Figure 1 illustrates the current, voltage, and temperature profiles from the applied experiment for 0.4 C and 0.8 C.

When performing the test, each of the battery cells were initially rested for 24 h, and then being charged at a constant current rate equal to 0.4 C and 0.8 C. Following each of the charging processes, immediately, the battery cells were being discharged at a constant current rate equal to 0.4 C and 0.8 C, correspondingly. Lower and upper voltage limits were assigned as 2.65 V and 4.2 V to fulfill the lesser and uppermost voltage limit, correspondingly.

To automate the experiments, safety procedures were applied in the battery cycler to stop the experiment in the case special events are triggered. Each part of the experiment is finished if the measured voltage attains some limits, for example, 2.65 V and 4.2 V during discharging and charging, correspondingly.

In addition, another constraint was implemented, which was restricting the charging and discharging time. For example, in case the current rate is C/5, the battery cell needs maximum 5 h to attain each voltage limitation. This time was selected in such a way that the battery cells reach the lower and upper voltage thresholds. Because, stopping each discharge and charge cycle before reaching the threshold voltage leads to forcing the battery cells to settle to a dissimilar relaxed voltage. Two different loading profiles were applied to the batteries. One of them (number 1) was charged and then discharged with 0.4 C for 20 times and another cell (number 2) was charged and discharged with 0.8 C with the same amount of cycle number.

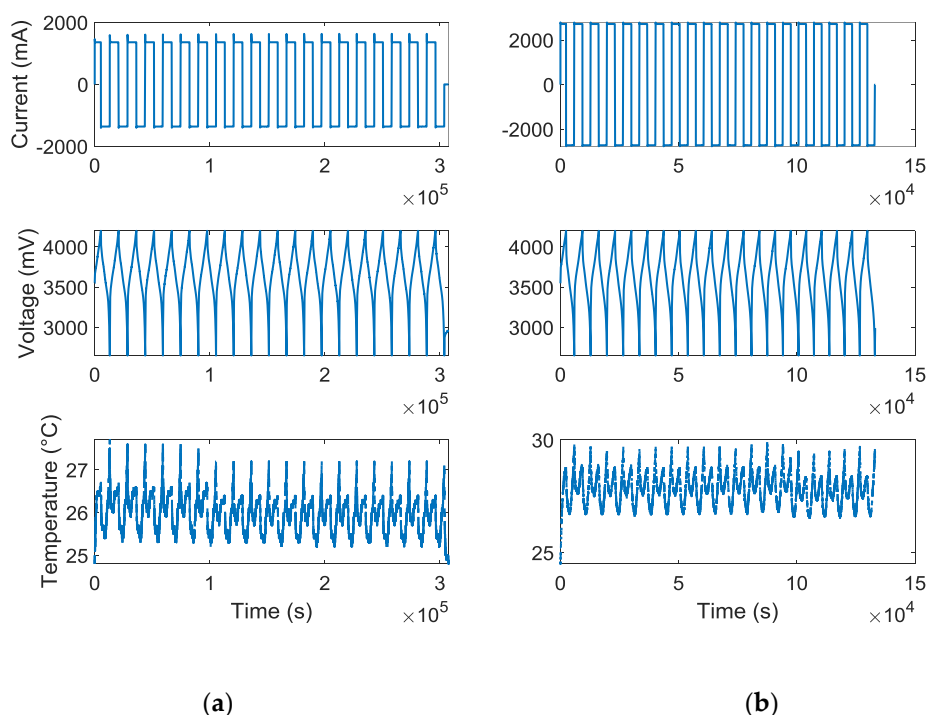


Figure 1. The load profile that was applied to the battery. (a) 0.4 C; (b) 0.8 C.

Charge End Capacity (CEC) and Discharge End Capacity (DEC) of the battery cells are illustrated in Figures 2 and 3, correspondingly. All of the end points of charge and discharge capacities continually decrease as lithium-ion cells are cycled and this could be a conventional feature of all lithium-ion battery cells.

The battery cell which was cycled at bigger C rates lose capacity quicker than another battery which was cycled at lower C rates. Discharge end capacity is less than charge end capacity for 0.4 C in all cycles. Notwithstanding, the cycling type less affects 0.8 C. In other words, the charge end capacity and discharge end capacity are almost the same for 0.8 C. The average capacity loss rates for discharge and charge during 0.4 C were approximately 0.076% and 0.09% per cycle, correspondingly. This was calculated over the 19 cycles.

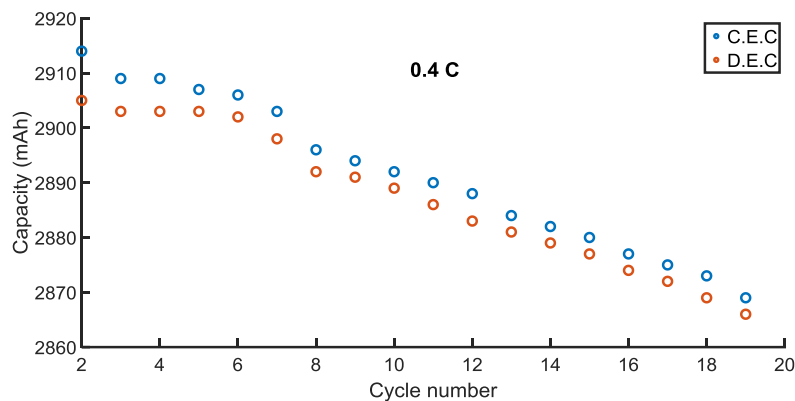


Figure 2. End Capacities for 0.4 C.

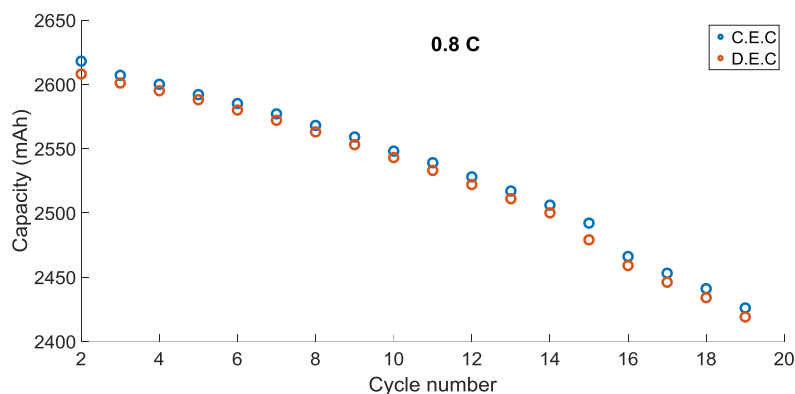


Figure 3. End Capacities for 0.8 C.

The life cycle of a lithium-ion battery cell is not unlimited, because of smart parts of battery cell ingredients that are utilized by parasitic reactions throughout the time of each cycle likely constructing electrolyte oxidation and capacity fade [10]. The quantity of these parasitic reactions could be displayed by accurate measurements of coulombic efficiency [10]:

$$\text{Coulombic Efficiency} = \text{charge out/charge in}$$

Figure 4 illustrates the coulombic efficiency vs cycle number. The presence of these reactions could be distinguished by a coulombic efficiency fewer than 1.000. The coulombic inefficiency vs cycle number is shown in Figure 5. Coulombic inefficiency divided by time of each discharge and charge cycle vs time is illustrated in Figure 3.

The quantity of parasitic reactions that happen for a specified cycle is straightforwardly the time of each cycle multiplied by the parasitic reaction rate. This causes a conventional expression for the coulombic inefficiency for any particular cycle [10]:

$$(1 - \text{CE}) = (\text{time of one cycle}) \times k(T, t)$$

where t : Calendar time; $k(T, t)$: The parasitic reaction; T : The cell temperature.

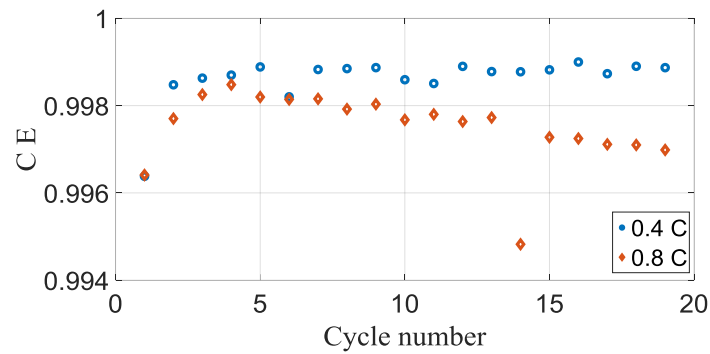


Figure 4. Coulombic efficiency vs cycle number.

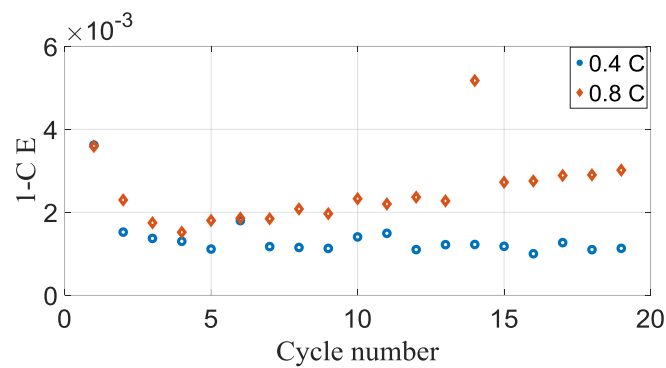


Figure 5. Coulombic inefficiency vs cycle number.

Reaction processes that use electrolyte ingredients or active lithium in lithium-ion battery cells are frequently considered as parasitic reactions [11]. As was mentioned before, parasitic reactions that occur in the battery cell and $k(T,t)$ are related to this parasitic reaction rate, which is as a function of the battery cell calendar time and temperature. As could be seen from Figure 6, these parasitic reactions are higher for 0.8 C when compared to 0.4 C.

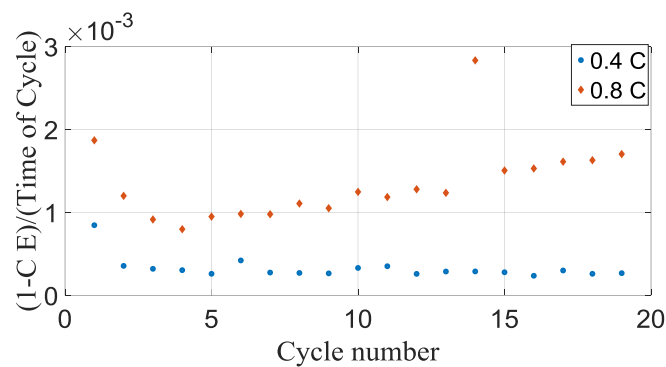


Figure 6. Coulombic inefficiency divided by time of each cycle vs cycle number.

The intensity of these parasitic reactions decreases as the battery cells age for the reason that coulombic inefficiency comes within reach of unification [10]. This is unquestionably attributable to the growing of interface layers between the electrolyte and electrodes [10].

As could be seen from the Figure 4, the battery cells demonstrated well capacity retention throughout the beginning twenty cycles. However, there are clear differences in the coulombic efficiency for both cases, which would cause differences in the capacity retentions. The coulombic efficiency outcomes demonstrated that all the battery cells that were discharged and charged have coulombic efficiency less than 1000.

The rate of battery capacity loss is proximate to the divergence of the coulombic efficiency from 1000. This correspondence is to be assumed in the application which Li absent at the negative electrode by becoming more concentrated of solid electrolyte interphase that the derivation of the coulombic inefficiency is [12]. It is essential to contemplate the experimental factors that should be controlled to measure the coulombic efficiency accurately during a constant current discharge and charge among fixed voltage limits. There are several factors that need to be contemplated, such as accuracy of voltage, currents, battery cell temperature, and time among voltage measurements [12].

3.2. Effect of Prior Cycling

The investigation of rechargeable batteries, particularly lithium-ion battery cells, in the present circumstances, is of great technological and scientific attentiveness. Additionally, experimental investigations targeting at engineer more accomplished batteries. A considerable quantity of modeling has been attempted to comprehend the electrochemical processes that happen throughout battery application.

To satisfy the demands for some applications, it is needed to prolong the lifetime of Li-ion batteries. For instance, solar and wind energy storage systems have more demanding lifetime requirements. The capacity of the Li-ion batteries decreases during cycling. In an automotive application, this lessening in Li-ion battery capacity demonstrates a lessening in the uttermost driving scope of an electric vehicle. Li-ion battery cell capacity, accordingly, is an appropriate metric for characterizing the state of health of a Li-ion battery cell [13–15].

The lithium-ion batteries are distinguished rechargeable batteries. In these batteries, lithium ions are commuted internally between two electrodes, during which electrons are carried by the external circuit and perform the electrical function. The electrodes are generally inserting porous electrodes that, in a perfect instance, reversibly keep lithium in their construction. The electrode that is at the greater electrochemical potential is considered the positive electrode and another that at the lesser potential is considered the negative electrode.

An electrolyte is employed as surroundings of transmission for the lithium ions among the electrodes. A separator that permits ion transportation is employed to stop physical contact among the electrodes.

From beginning to end of charging, lithium ions are transferred from the positive electrode to the negative electrode by the separator and electrolyte. Electrons relocate in the corresponding direction by the exterior circuit. The opposite process happens throughout discharging.

The effectiveness of lithium-ion batteries worsens over time, even if they are used or not. Ageing without and with use are called calendar ageing and cycle ageing, correspondingly.

The two principal outcomes of ageing are power and energy fade. In an electric vehicle utilization, for example, the power specifies the utmost acceleration the vehicle could gain, and the energy specifies the utmost distance that the vehicle could travel through a single charge.

Energy declining could be induced through a diminution of battery capacity or in the increase of the impedance. Diminution of counterbalancing of the active electrode material or the cyclable lithium is the principal origins of capacity fade.

The increase in impedance is attributable to the physical or chemical conversion of the diverse interfaces and materials. An increase in impedance consequently results in a power fade moreover to an energy fade. Typically, both power and energy fades happen contemporary and their comparative importance relies on the specific application. For example, power fade is less critical than energy fade in an electric vehicle.

Lithium-ion batteries have different classifications of ageing mechanism. They could be either mechanical or chemical in character. The mechanisms are dissimilar on the negative electrode side and on the positive electrode side. The most essential ageing mechanism on the negative electrode side is the development of a solid electrolyte interphase, which utilizes the cyclable lithium.

This interphase layer between the electrolyte and graphite is produced due to the fact that the functioning graphite potential on the surface is greater than the stability range of the mostly utilized carbonate electrolytes.

Generally, configuration cycling is accomplished in a lithium-ion battery after battery cell structure where the commencing solid electrolyte interphase is made. Notwithstanding, continuing cycling induces the graphite particles to thicken and construct cracks in the solid electrolyte interphase layer. This revealing novel surface is responsible for supplementary solid electrolyte interphase expansion.

The solid electrolyte interphase enlargement declines at rate that is accompanied by time. Nevertheless, it proceeds over the length and breadth of the lifetime of the battery cell and it uses the cyclable lithium [16].

As was mentioned before, there are different types of ageing mechanism. There is ageing mechanisms within the confines of the graphite that comprise gas development, lithium plating, graphite depilation, and current collector erosion. A considerably slim impervious layer of the electrolyte oxidation production establishes on the electrode surface that brings about the increase in the battery cell impedance.

Life cycle is essentially necessary in implementations of rechargeable batteries. Nevertheless, lifetime prognostication is predominantly based upon empirical trends, instead of mathematical models. In practicable lithium-ion batteries, capacity fade happens over a large amount of cycles, which is restricted by sluggish electrochemical processes, for instance, the creation of a solid-electrolyte interphase in the negative electrode.

Throughout the discharge and charge of a lithium-ion battery cell, the active lithium-ion in the battery cell is inserted out of and into the negative electrode, correspondingly. For the duration of each cycle a tiny quantity of that active lithium-ion reacts with the intention of thickening a passive layer on the surface of the electrode. This is identified under the name of solid electrolyte interphase.

The life cycle of a lithium-ion battery cell is not boundless because little fractions of battery cell ingredients are used up by parasitic reactions throughout each cycle. These undesirable reactions could appear by several different processes, such as solid electrolyte interphase repair and growth, electrolyte oxidation, progression metal ions from out of the positive electrode, and destruction of the positive electrode. Each of these processes could have different reasons for instance solid electrolyte interphase growth and repair is because of lithium-ion loss at the negative electrode [17].

The significance of the coulombic efficiency was acknowledged in a thoughtful research paper on factors that influence capacity retention of lithium ion cells. In the mentioned research paper, it was declared that matched coulombic efficiencies for the negative and positive electrodes, notwithstanding could result in outstanding life cycle for full Li-ion battery cells [4].

It was shown that accuracy measurements of coulombic efficiency are achievable and could lead to bigger comprehension of the degradation processes to be accomplished at the electrodes of Li-ion battery cells [4].

As mentioned before, coulombic efficiencies for the Li-ion battery cells were calculated as the ratio of the capacity of the discharge instantaneously following the previous charge capacity. Consequently, for the Li-ion battery cells:

$$CE = Q_d/Q_c$$

where: Q_d : Discharge capacity; Q_c : Charge capacity

Three new Li-ion battery cells were selected for the experiments. Two of the Li-ion battery cells were discharged and then charged at 25 °C by using currents corresponding to 0.4 C and 0.8 C. Another Li-ion battery cell was discharged and charged at the same temperature, but with the currents corresponding to 0.2 C, 0.4 C, 0.6 C, and 0.8 C.

Figures 7 and 8 demonstrate the coulombic efficiency of the new and cycled commercial battery cells plotted vs cycle number. Figure 9 demonstrates the result of coulombic efficiency measurements of Li-ion battery cells for different current rates. It can be seen from Figures 7 and 8 that cases coulombic efficiencies of the new cell is approximately bigger than the cycled battery cell for both 0.4 C and 0.8 C.

Another observation from the figures is an almost similar pattern of coulombic efficiencies for both 0.4 C and 0.8 C cases.

Figure 9 shows a comparison between coulombic efficiencies for different current rates from 0.2 C and 0.8 C. It is clear from the figure that the coulombic efficiency for 0.8 C is lesser than other cases and, in addition, it follows an almost different pattern as compared to other C rates.

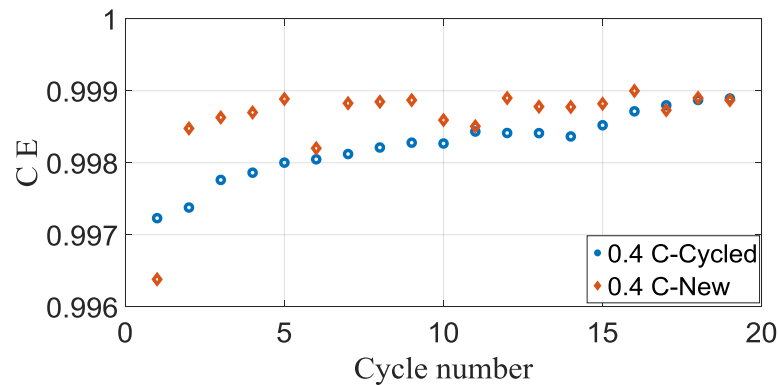


Figure 7. A comparison between coulombic efficiencies for 0.4 C.

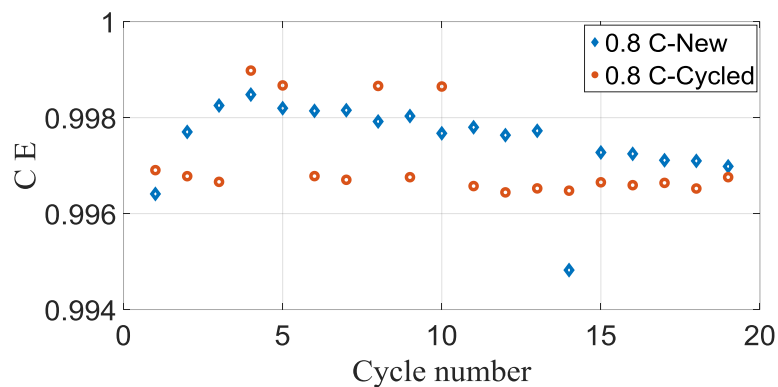


Figure 8. A comparison between coulombic efficiencies for 0.8 C.

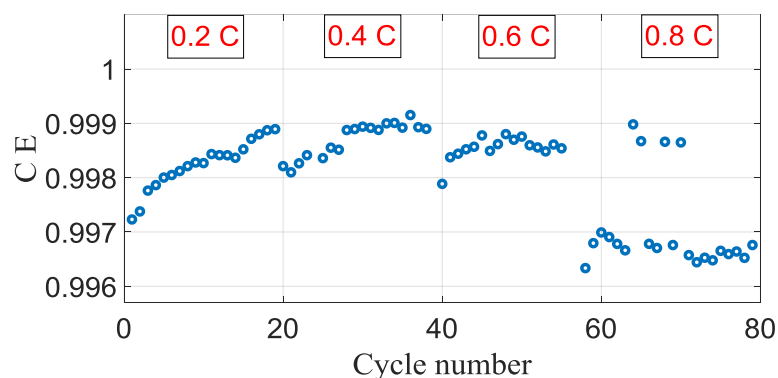


Figure 9. A comparison between coulombic efficiencies for different current rates.

4. Conclusions

The effects of the current rates on the coulombic efficiency of the lithium-ion batteries were studied. The battery cells experienced continuous discharge and charge cycles under constant discharging and charging currents. Three different load profiles were applied to the battery cells. The achieved results demonstrated an approximately identical capacity fade vs cycle number for the dissimilar current rates at the same temperature. The discharge and charge end point capacities decreased together with cycle number for 0.4 C. However, at a considerably sluggish rate when compared to the discharge

and charge end point capacities for 0.8 C. The battery cell that was cycled with 0.8 C demonstrated a considerable and obvious capacity loss in relation to cycle number as compared to 0.4 C. It was concluded that parasitic reactions of the battery cells moved away more greatly from unification as the cycling rates were increased.

Author Contributions: S.S.M. proposed the idea of the paper; S.S.M. wrote the paper; E.S. provided suggestions on the content and structure of the paper; S.K.K. and E.S. has been reviewing the draft manuscripts.

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