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Reviving Aged Lithium-Ion Batteries and Prolonging their Cycle Life by Sinusoidal Waveform Charging Strategy

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Traditional high power constant current-constant voltage (CC–CV) charging leads to the degradation of Li-ion batteries. Thus, aging due to charging is a primary issue to be overcome in application technology. This study proposes the impacts of a sinusoidal waveform charging strategy for charging Li-ion batteries. Specifically, a negative voltage is introduced in the charging process to reverse passivation layer formation. After few cycles of sinusoidal waveform charging, aged cells can be revived. Tests reveal that the available capacity of an aged cell can be improved by a maximum of 18.7% relative to the original rated power. After 600 charging-discharging cycles of new cells, the cells charged using the sinusoidal waveform strategy possess approximately 15% more electrical capacity than do cells charged using the conventional CC–CV method, indicating an increase in battery cycle life. The suppression of interfacial resistance is characterized by electrochemical impedance spectroscopy. Sinusoidal waveform charging can reduce charging time by half and the maximum rise in temperature by 6 °C compared with the CC–CV charging method.

The rapid increase in the use of commercial Li-ion batteries in portable electronic devices and, more recently, electric vehicles and energy storage systems has engendered an urgent demand for considerable battery performance enhancement. Battery degradation is the primary limitation of Li-ion batteries used in the aforementioned applications. A major factor in battery degradation is the continuous passivation of solid electrolyte interphases (SEIs).[1] An SEI consists of solid Li complexes that are created due to the combination of Li ions and decomposed electrolyte with excess electrons attributed to charging.[2] Constant high-power charging was suggested to accelerate aging.[3] Therefore, considerable engineering efforts have been undertaken to stabilize the SEI over time. The development of charging methods would ensure that capacity loss would not be severe in the short term and enable long-term Li-ion battery utilization. Among constant-trickle-current charging, constant-current (CC) charging, and CC-constant-voltage (CC–CV) charging methods,[4] CC–CV is most extensively used. CC–CV charging involves charging a battery at a CC until its voltage reaches the predetermined limit, followed by CV charging until the current decreases to a predetermined low value. However, SEI formation can occur near the end of the CC-charging step during normal CC–CV charging if the charging current rate reaches or exceeds a certain value.[5] Thus, the charging performance of the CC–CV method cannot sufficiently satisfy the long-cycle-life requirement of the consumer. The development of charging methods that balance battery degradation and fast charging remains a challenge.

Reflex charging method applies a very short discharging pulse during pulse charging and resting periods. Because passivation layers in different types of batteries are grown mainly via reduction reaction, the discharging pulse in reflex charging method has been used to reduce unwanted chemical reactions at the electrode surface, such as side chemical formation, crystal growth, and passivation in nickel-cadmium batteries.[6] Charging techniques involving negative pulses have also been revealed to achieve high performance on Li-ion batteries. A study concluded that pulse charging can increase the battery charge capacity, reduce resistance, and thus delay the aging process.[7] Sinusoidal current charging was tested for a $LiFePO_4$ battery. Sinusoidal charging improved the charging time, charging efficiency, maximum rising temperature, and lifetime of the battery.[8] Although sinusoidal and negative pulse charging have been proposed for battery improvement, such charging strategies involving discharging stages have not been widely used due to lack of a theoretical basis for the charging voltage. Most experiments have been done without physiochemical aspects. Recently, density functional theory (DFT) calculations were applied to determine a moderate voltage exhibiting a sinusoidal waveform for charging Li-ion batteries;[9] the results revealed that a discharging step in the charging process might have resulted in elimination of SEI impedances. However, limited studies have been conducted on the effects of the sinusoidal waveform charging technique on $LiFePO_4$ battery performance. To address this gap in the literature, the current study explored the effects of sinusoidal waveform charging on Li-ion batteries. The charging voltage for the applied sinusoidal waveform charging strategy was determined

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according to a previous study,[9] and the charging strategy involves positive and negative voltages. In the positive voltage, Li ions can obtain sufficient energy to migrate through the SEI and graphite anode. In particular, the negative voltage may reverse the electrolyte reductions and eliminate SEI impedance. Notably, the charging method was determined to revive Li-ion batteries and prolong their cycle life.

The effects of the sinusoidal waveform charging strategy on battery performance were demonstrated using commercial $LiFePO_4$ 18650 batteries (EP1500, Pihsiang Energy Technology Co., Ltd., Taiwan) with a typical rated capacity of 1450 mAh. Figure 1 illustrates the sinusoidal waveform charging strategy. The offset voltage was set at 3.65 V, i.e., the cell voltage of a $LiFePO_4$ battery with full capacity. The waveform comprises positive and negative voltages separated by cell voltage. The positive voltage step was designed to offer sufficient energy for Li-ion transport through materials during charging. Li-ion migration through the SEI is the energy-determining step and is primarily demonstrated through ion exchange. A lithium-bonding network may assist with Li transfer via ion-exchange the SEI bridge.[10,11] Thus, DFT calculations suggested the amplitude of the positive voltage to be 0.7 V.[9] The negative voltage step was designed to reverse SEI formation. The amplitude of the negative voltage was set at 0.1 V to obtain inverse reduction at room temperature. The frequency was set at 1000 Hz because it matches the Li-ion migration time between two electrodes during charging. Besides, Chen et al. concluded that the minimum-ac impedance frequency (1000 Hz for 18650 cells) is the optimal frequency for charging Li-ion batteries by using a sinusoidal waveform.[8]

In addition, controlled experiments involved charging the $LiFePO_4$ batteries through a conventional CC–CV charging method by applying constant current and voltage of 5 A and 3.65 V, respectively. First, the battery was charged at a CC, which made the battery voltage approach 3.65 V. The CC was set at 5 A (3.45 C), which is comparable to that of practical supercharger of an electric vehicle. Subsequently, the battery was charged at a CV of 3.65 V. Because charging current would decrease due to the full capacity of the battery, both charging processes were performed until the charging current reached 0.0725 A (0.05 C). The discharge condition was defined as a CC mode involving a CC of 5 A, and the corresponding cutoff voltage was 2.5 V. The state of health (SOH) of a battery is defined as the discharge capacity divided by the rated capacity (1450 mAh).

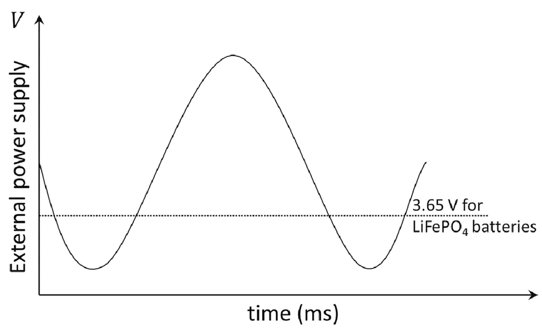

Figure 1. Sinusoidal waveform charging method.

Reviving experiments were conducted on three aged cells. The cells were aged using CC–CV charging and CC discharging cycles at 45 °C in an oven. The aged cells were then charged using the sinusoidal waveform strategy to revive their activation at room temperature. Furthermore, the sinusoidal waveform strategy was demonstrated to extensively prolong the cycle life of the Li-ion batteries. Sinusoidal waveform charging and CC–CV charging were performed at room temperature. Three cells were used for each charging protocol. The SOH deviation of the three cells did not exceed 2%. The cell with intermediate performance in each protocol was selected for discussion. The charging and discharging processes were switched manually; therefore, batteries have at least a 15-minute rest between cycles, a 12-hour rest very day, and a 60-hour rest very weekend. The long rest avoided pseudo capacity fade of batteries.

The cells were charged using a commercial charging instrument (N6786A, Keysight Technologies, Inc., Santa Rosa, CA, USA); the measurement deviation was determined to be less than 0.04%. The discharging measurement was performed using battery automation test systems (BAT-778B 20 V5 A 8Ch, Acutech Systems Co., Ltd., Taiwan), with the error specification being 0.1%. Electrochemical impedance spectroscopy (EIS) was conducted through an impedance measurement system (KFM2150 660-01 A, Kikusui Electronics Corp., Japan). Impedance spectra were recorded in the range 2 kHz to 0.1 Hz with a current amplitude of 200 mA. The data analysis and equivalent circuit fitting were performed using EIS spectrum analyzer software.

Reviving aged batteries. The ceaseless formation of SEI passivation is key to the understanding of severe aging problems of Li-ion batteries. Inappropriate charging methods lead to constant pumping of electronic energy into a battery, thus engendering SEI growth. For example, while using ethylene carbonate as an electrolyte, the reaction usually started with the formation of a $LiOCO_2C_2H_4$ radical for an excess electron. Then, $LiOCO_2C_2H_4$ radical can extensively react to form more stable and irreversible solid molecules. Such radical isomer is ably reversed as long as no new molecules have been produced. Therefore, an appropriate charging strategy may enable reversing the chemical reaction and reduce the radical precursors before the SEI grow into a solid passivation layer.[9] The effects of the sinusoidal waveform charging strategy on the revival of aged batteries were then tested. After the degradation operation in the oven, the three cells are at SOH levels of 60%–70%, 70%–80%, and 80%–100%, and each of the cells was denoted as *Ps#1*, *Ps#2*, and *Ps#3*, respectively. The battery classification mainly considered commercial use: an SOH of 80% is the available battery standard for electric vehicles, SOH of 70% is the available battery standard for most portable devices, and SOH of less than 60% indicates that the cost of continuous use would be higher than the cost of replacing the battery. The SOH (and discharge capacity) values of the cells are 64.7% (938.1 mAh), 78.8% (1143.2 mAh), and 84.9% (1231.2 mAh) respectively. Experiments were then performed

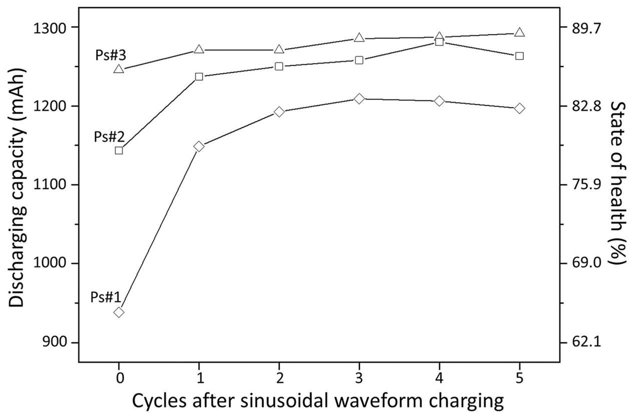

Figure 2. Reviving discharge capacity of an aged battery after sinusoidal waveform charging.

using the sinusoidal waveform strategy to charge the aged cells, and Figure 2 presents the results. After the first cycle involving charging using the sinusoidal waveform, the SOH considerably increases. In the subsequent few cycles, the SOH slightly improves and remains at a relatively high level. After revival, the highest SOH (and discharge capacity) values are 83.4% (1209.1 mAh), 88.3% (1281.0 mAh), and 89.1% (1292.2 mAh). The rated power of *Ps#1* improves by 18.7% relative to the original rated power, indicating the highest improvement among the cells. Because *Ps#1* has a greater degree of damage, it can be revived to a higher degree. The rated power levels of *Ps#2* and *Ps#3* improve by 9.5% and 4.2% relative to the original levels, respectively.

After revival, the capacity of the cell charged using the CC–CV method is at a high grade level. Thus, we can confirm the improvement of the passivation inside the battery. The reviving effect was not a momentary phenomenon. These results demonstrate that the sinusoidal waveform charging strategy is superior to the CC–CV charging method.

Charging time and maximum increase in temperature. The sinusoidal waveform charging strategy not only revives an aged cell but also reduces the charging time. As presented in Table 1, the CC–CV method requires approximately 50 min to charge a new cell. The sinusoidal waveform strategy fully charges a new cell in 25 min. Because the CC–CV method used in this study involved a high current (i.e., CC of 5 A) comparable to a supercharger, time saving was considered crucial. Although certain commercial superchargers cancel CV charging to reduce charging time, batteries cannot be full-charged with CC only. In the test, CC charging takes 20 min to achieve ca. 83% capacity (1208.5 mAh) of the new cell.

Table 1. Experimental values of charging a new cell.

Charge method	Sinusoidal waveform	CC–CV
Battery notation	*Ps#4*	*Ps#5*
Charging time	25 min	49 min
Discharging capacity	1464 mAh	1447 mAh
Increase in temperature	9 °C	15 °C

Suppressing temperature rises during charging is a major concern for the utilization of Li-ion batteries.[12,13] A temperature rise induces cell degradation as well as electrolyte vaporization and cell expansion, which may result in possible safety issues. As listed in Table 1, using the CC–CV method results in a maximum temperature rise of 15 °C, whereas using the sinusoidal waveform charging strategy engenders a temperature rise of 9 °C. Although the initial discharge capacity of *Ps#4* achieved using sinusoidal waveform charging is 17 mAh higher than that of *Ps#5* achieved using CC–CV charging, the difference of approximately 1% is considered negligible considering the inconsistency of cells.

Prolonging battery cycle life. Because the sinusoidal waveform charging strategy was demonstrated to be beneficial for passivation layer elimination, regular use of the strategy can be assumed to prolong the cycle life of Li-ion batteries. Accordingly, tests were conducted to validate the effectiveness of sinusoidal waveform charging in prolonging battery cycle life. The cycle life specifications of the commercial cell are outlined as follows: more than 1500 cycles (2.2 A charging/2.9 A discharging) and 80% rated capacity. In this paper, the experiments were performed under room temperature and the cells were subjected to sinusoidal waveform charging and CC–CV charging strategies. The SOH of the aged cell (*Ps#4*) that was charged using the sinusoidal waveform strategy was compared with the SOH of the aged cell (*Ps#5*) that was charged using the conventional CC–CV method. After charging-discharging cycles, two types of SOH degradation can be observed. As shown in Figure 3, the SOH decay in CC–CV charging is more severe than that in sinusoidal waveform charging. In the first 200 cycles, the difference in SOH between the two cells is not large. As the number of cycles increases, the SOH decay of *Ps#5* is more rapid and obvious. After 600 cycles, SOH (capacity) of *Ps#4* is 94.7% (1373.1 mAh) and that of *Ps#5* is 80.2% (1363.2 mAh). The difference in fading capacity between *Ps#4* and *Ps#5* is approximately 210 mAh, nearly 15% of the SOH. Therefore, the sinusoidal waveform charging strategy can delay the degradation of Li-ion batteries.

Precise control of chemical reactions in a cell is difficult. Thus, the fading lines are not smooth in Figure 3, exhibiting an oscillatory decline curve. Both curves demonstrate temporary increase, and this is because the measurement process involved

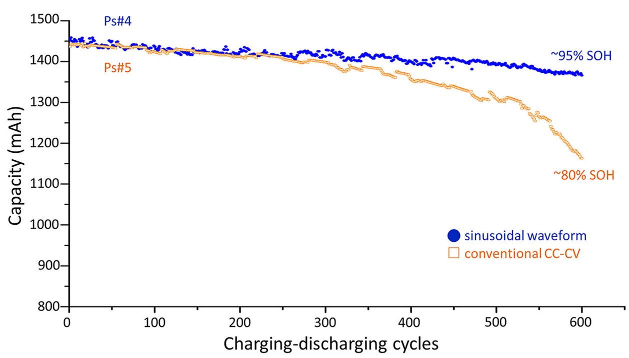

Figure 3. State of health degradation by charging using the sinusoidal waveform or CC–CV methods.

a resting time of approximately 60 hours. The capacitance of the batteries temporarily rebounds, and the rebound effect is less than 2% (17 mAh). The rebound can be regarded as temporary pseudo-rise, which would not affect the results of the degradation trends.

Electrochemical characterization. To characterize the SEI structures during operation cycles remains a challenge, because currently available direct observation technologies would destroy the structures before they could be observed. In addition, given that internal Li-ion battery chemistry involve side reactions and impurities, SEI structures are even complicated. Uncertainty and inconsistency of various SEI formation processes have made it very difficult to discriminate the changes in the size of the SEI film. However, EIS may provide the preliminary information of SEI resistance correlated to the effect of the different charging strategies. Figure 4(a). illustrates the EIS spectra of *Ps#4* and *Ps#5* observed after 600 charging-discharging cycles. The equivalent circuit fitting with reference to the Li-ion battery model[14] is shown in Figure 4(b). The ohmic resistance (R_0) represents the resistance of the electrolyte, current collectors, battery terminals, and internal connectors. The ohmic resistance of the new cell is 47.34 mΩ. The ohmic resistance of *Ps#4* increases to 49.25 mΩ. By contrast, the ohmic resistance of *Ps#5* reaches 62.44 mΩ. This increase indicates that sinusoidal waveform charging is helpful in improving the ohmic resistance in the electrolyte and cell components.

In addition to a little bit shifting to the right, the spectrum shape of *Ps#4* overlaps on the spectrum shape of the new cell. According to electrochemical models,[15] the high-frequency

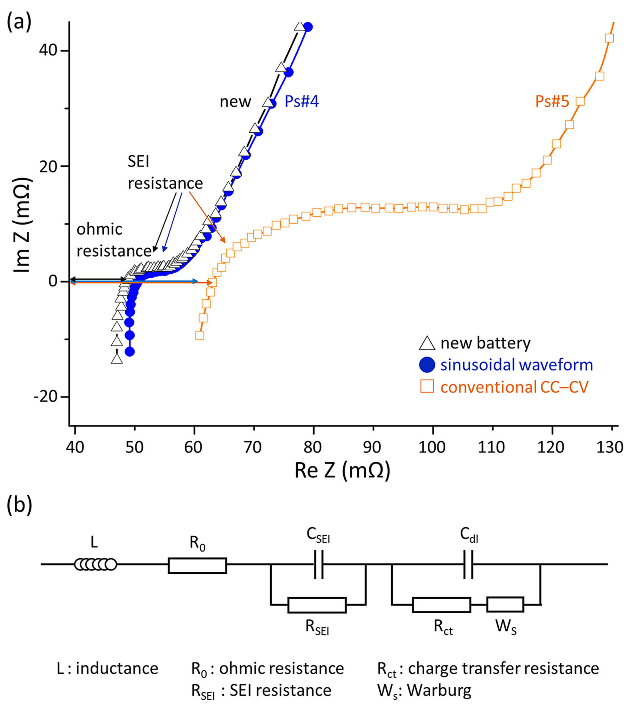

Figure 4. (a) Impedance spectra of the new cell, cell charged using sinusoidal waveform method, and cell charged using CC–CV method. (b) Equivalent circuit of Li-ion battery related to the impedance spectrum.

semicircle (>600 Hz) is ascribed to an SEI resistance behavior (R_{SEI}). The R_{SEI} of the new cell is 5.89 mΩ. *Ps#4* has an R_{SEI} of 5.96 mΩ after 600 cycles of sinusoidal waveform charging, only a very tiny increase compared to the new battery. After 600 cycles of CC–CV charging, the high-frequency semicircle of *Ps#5* shifts to the upper right, and the size of the semicircle increases. The R_{SEI} of *Ps#5* is 13.67 mΩ. The considerable increase in the R_{SEI} of the cell is caused by the growth of the SEI passivation layer, which coincides with the loss of recyclable Li ions. The sinusoidal waveform charging strategy thus effectively inhibits SEI formation. The aged cell based on the sinusoidal waveform (*Ps#4*) has a higher discharge capacity than does that based on CC charging (*Ps#5*), which signifies that more available Li ions can be extracted from active electrode materials. On the other side, the positive voltage (~0.7 V) of the sinusoidal waveform is required for activating to migrate and extract the Li ions from SEI and graphite, which was concerned in company with the reductive decomposition of electrolytes. However, the EIS reveals no obvious degradation on *Ps#4*. The cycle life of a Li-ion battery depends on the stability of the electrode materials and the interfaces of the anode and electrolyte. Therefore, we can conclude that sinusoidal waveform charging is superior to CC–CV charging because it can successfully inhibit SEI passivation layer formation and prolong battery cycle life.

This study investigated the functions of a sinusoidal waveform charging strategy for charging Li-ion batteries. The sinusoidal waveform charging strategy requires a shorter cell charging time and engenders a lower cell temperature rise compared with the traditional CC–CV charging method. In addition, the sinusoidal waveform charging strategy can notably revive aged batteries and prolong battery cycle life. Three batteries were aged to different SOH levels by using CC–CV charging. The aged cells are revived after several cycles of sinusoidal waveform charging because the negative voltage in the sinusoidal waveform effectively reverses SEI passivation layer formation. The highest increase in SOH is from 64.7% to 83.4%. Furthermore, the regular use of sinusoidal waveform charging can prolong the cycle life of a cell. Degradation tests were performed under room temperature. After 600 cycles of charging, a cell charged using sinusoidal waveform charging exhibits approximately 15% higher electrical capacity relative to that of a cell charged using the CC–CV method. Electrochemical characterizations were also conducted using EIS. The resulting spectra reveal that sinusoidal waveform charging can successfully inhibit the increase in R_{SEI} caused by charging. In summary, this paper proposes a simple and low-cost charging approach for improving battery performance and may provide information regarding the electrochemistry of Li-ion battery charging. Because consumers' demands require considerable pumping power for charging a battery, battery charging methods exhibiting improved safety, low cost, rapid charge rates, and long cycle lives are essential. The sinusoidal waveform charging method not only exhibits superior performance to the CC–CV charging method but also has the competitive advantage of low replacement and time costs.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Sinusoidal waveform · Charging strategy · Reviving Li-ion battery · Prolonging cycle life

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