Optimized fast charging protocol for cylindrical lithium-ion battery based on constant incremental capacity algorithm

Li Lao¹ ² | Shangquan Wu¹ | Qingchuan Zhang¹

¹CAS Key Laboratory for Mechanical Behavior and Design of Materials, Department of Modern Mechanics, CAS Center for Excellence in Complex System Mechanics, University of Science and Technology of China, Hefei, China
²SINOEV Technologies Inc., Hefei, China

Correspondence
Shangquan Wu and Qingchuan Zhang, CAS Key Laboratory for Mechanical Behavior and Design of Materials, Department of Modern Mechanics, CAS Center for Excellence in Complex System Mechanics, University of Science and Technology of China, Hefei 230027, China.
Email: wushq@ustc.edu.cn (S. Z) and Email: zhangqc@ustc.edu.cn (Q. Z)

Funding information
National Natural Science Foundation of China, Grant/Award Numbers: 11627803, 11872354, 11872355; Strategic Priority Research Program of the Chinese Academy of Sciences, Grant/Award Number: XDB22040502

Summary
Reducing the charging time for electric vehicles (EVs) is considered as a crucial factor to promote consumer interest and improve the competitiveness of EVs in the automotive market. Therefore, the investigation of fast charging protocol becomes increasingly important. In this work, a novel self-adaptive fast charging protocol for cylindrical lithium-ion battery is proposed based on constant incremental capacity (dQ/dV) algorithm, the charging current of which is adaptively adjusted by the intrinsic properties of battery. The cycle test results show that the battery using the new fast charging protocol maintains a capacity of about 90% after 1150 cycles, indicating that the proposed charging protocol can improve the cycle life of the battery, while decreasing the charging time. The fatigue analysis has shown that the capacity fade results predominantly from the loss of active lithium ion and degradation of anode. The anode potential evaluation results show that the anode potential is always greater than zero volt with the proposed fast charging protocol, which avoids lithium deposition. Meanwhile, the post-mortem results of cycled battery indicate that the battery using the proposed charging protocol generate no lithium deposition on anode.

KEYWORDS
dQ/dV, fast charging protocol, lithium-ion battery, self-adaptive

1 | INTRODUCTION

Lithium-ion battery with advantages of high energy density, good cycle-life performance, and low self-discharge rate are becoming more widely used in electric vehicle (EVs) and energy storage systems.¹ Considering for convenience, consumers are increasingly demanding short charging time for EVs, which makes fast charging to be one of the most critical technologies for the application of lithium-ion batteries in EVs. However, fast charging requires a large current, which would have a negative effect on the battery life.² Moreover, the large charging current beyond the capacity of the battery might cause safety issues such as over temperature or even thermal runaway. Therefore, searching for an appropriate charging protocol is essential for the lithium-ion batteries to achieve a balance between an acceptable charging time and a long cycle life.

The most widely-used traditional charging strategy is the constant-current constant-voltage (CCCV) strategy, which can be easily implemented in a battery management system (BMS). However, the charging current and voltage limits for the CCCV protocol are usually too conservative, leading to long charging time.³ To accelerate the charging process, various fast charging strategies with variation of current have been proposed in recent years, which are mainly categorized as basing on the anode potential,³-¹² polarization,¹,¹³ temperature rise,¹⁴-¹⁷
algorithm, and experience. The charging protocol based on anode potential can prevent lithium deposition on the anode surface as well as potentially critical safety issues caused by Li plating. Since the anode potential of battery cannot be measured directly, there are two indirect potential evaluation methods, one is adding a reference electrode of Li metal and the other is to establish an electrochemical model. The reference electrode is not part of the battery product, therefore specific technologies are required to insert the reference electrode into the battery, making it different from the batteries that are used in EVs. The electrochemical model can predict the anode potential of fresh battery with high precision, while the effects of temperature and state of health (SOH) on model parameters need to be further investigated. Furthermore, the heavy computational load and complexity of the electrochemical model makes it difficult to be implemented in BMS for real-time application. The method based on polarization provides a variable charging current with constraints on battery polarization voltage. However, the polarization modeling and its quantitative effects on battery life are worth further examination. The charging protocol based on temperature rise is somewhat one-sided, since the anode potential is not taken into account. The protocol based on algorithms and experience is often lack of theoretical foundations in choosing charging current. Therefore, these methods are difficult to be applied in EVs, and it is worth to study new charging protocol.

The incremental capacity ($dQ/dV$) curve of battery have attracted significant attention for battery diagnosis, where $Q$ is the charged capacity, $V$ stands for the terminal voltage, and $dQ/dV$ represents the differential of capacity $Q$ with respect to voltage $V$. This curve reflects the intrinsic properties of the battery, including reactions from $\text{LiC}_6$ to $\text{LiC}_0$, delithiating of the graphite, diffusion and electrode kinetics, and the reaction rate of lithium ions. Moreover, the $dQ/dV$ curve is used not only for degradation mechanism detection, but also for online SOH estimation. Researchers provided an approach to acquire $dQ/dV$ and other differential curves online and further used for battery diagnosis. However, there are few reports about charging protocol based on $dQ/dV$ curve. Since it is common to keep certain variables constant in the fast charging protocols, we have a hypothesis that keeps $dQ/dV$ constant during charge could be a possible solution.

In this article, a self-adaptive charging protocol is proposed based on constant $dQ/dV$ algorithm and illustrated with 2.75 Ah NCM811-based commercial 18 650 batteries. The cycle life test of battery with the proposed charging protocol was conducted and compared with traditional constant current charging protocol. Anode potential evaluation was and the fatigue mechanisms of battery after hundreds of cycles was reported. Post-mortem of aged batteries have been observed and analyzed. Moreover, the change of charging current and time during cycles was analyzed to explain the adaptive characteristics of the proposed protocol.

2 EXPERIMENTAL

2.1 Mathematical model

The mathematical model of charging protocol based on constant $dQ/dV$ can be deduced as follows: Firstly, the charged capacity can be expressed by Equation (1).

$$Q = \int_{0}^{t} i(\tau) d\tau$$

where $Q$, $i$ and $t$ represent charged capacity, current and time, respectively. Then taking the derivative of $Q$, we can get Equation (2).

$$dQ/dt = i(t)$$

The voltage of battery can be expressed by the Equation (3).

$$V = OCV(SOC) + i(t) * (R_\Omega + R_p)$$

where $SOC$, $V$, OCV, $R_\Omega$, and $R_p$ refer to state of charge, dynamic voltage, open circuit voltage according to SOC, ohmic resistance and polarization resistance of battery, respectively. Then derivative of $V$ with respect to $t$ can be expressed as Equation (4):

$$dV/dt = \frac{dOCV}{dSOC} * \frac{dSOC}{dt} + i'(t) * (R_\Omega + R_p)$$

where $C$ and SOH represent the initial capacity and the state of health, respectively. When SOC is larger than 20%, both the ohmic and polarized resistance have little change with SOC, as shown in Figure 1, so it is reasonable to consider the ohmic and polarized resistance as constant if SOC is larger than 20%. However, the polarized resistance would slowly change during the cycle test, which would be discussed later.
If \( dQ/dV \) is set to a constant value, assigned as \( D \), according to Equation (2) and (4), we can obtain Equation (5).

\[
D = \frac{dQ}{dV} = \frac{dQ/dt}{dV/dt} = \frac{dOCV/dSOC}{C \cdot SOH} \cdot \frac{i(t)}{i(t) + i'(t) \cdot (R_O + R_p)}
\]  

And Equation (6) is obtained by Equation (5).

\[
i'(t) = \frac{1 - \frac{dOCV}{dSOC} \cdot \frac{D}{C \cdot SOH}}{D \cdot (R_O + R_p)} \cdot i(t)
\]  

The coefficient is set to \( K \), and \( i'(t) \) can be expressed as Equation (7).

\[
i'(t) = K \cdot i(t)
\]  

\[
K = \frac{1 - \frac{dOCV}{dSOC} \cdot \frac{D}{C \cdot SOH}}{D \cdot (R_O + R_p)}
\]  

Note that the coefficient \( K \) varies with \( SOC \).

It can be seen from Equation (7) that, if the \( dQ/dV \) is set to constant during charging, the current would be adjusted automatically according to the intrinsic properties of the battery, including \( SOC-OCV \) curve, internal resistance, and SOH. Then the charging protocol could be implemented as a serials step of constant voltage charge, of which the only criteria is the quantity of electric charge. Since the constant \( D \) could be calibrated off-line and the quantity of electric charge could be measured directly, the proposed charging protocol could eliminate the heavy on-line computational load.

### 2.2 Fast-charging protocol

Commercial 18 650 batteries with nominal capacity of 2.75 Ah and internal resistance (at 1KHz) of 42 m\( \Omega \) are used, whose cathode is NCM811 and anode consists of graphite and Si. All the batteries were charged and discharged by battery tester system (Neware CT-4000-5V6A, Shenzhen, China). This type of battery is a high specific energy and non-fast charge battery, the internal resistance are shown in Figure 1. The purpose of this charging protocol is to ensure a relatively fast charging speed while extending battery life.

In order to verify the influence of constant \( D \) in Equation (5), different values of \( D \) have been tested. Figure 2A shows that the current of the proposed protocol depends on the initial current value. For the protocol based on constant \( dQ/dV \) that starts charging at zero current, the current is kept at a small level when SOC is below 20\%, which is marked in black line. Based on the anode potential results and engineering experience, the lithium-ion battery could accept large current at low SOC, so the constant \( dQ/dV \) could be combined with a large constant current (CC) charge at low SOC to shorten the charging time, as shown in Figure 2B. Since every \( dQ/dV \) step could be a constant voltage configuration, the current shows a decreased shape for each step, which could be explained by the first- or second-order model of battery. The inflection point of the current is always around 40\% SOC regardless of the value of \( dQ/dV \) and the initial current, so we suspect that it is related to the battery
characteristics, and the constant current stage should not exceed SOC at inflection point. Since the SOC calculation has error due to the estimation algorithm, capacity fade and truncation error, and so on, the cutoff condition of constant current charging can be set to voltage cutoff instead of SOC cutoff for engineering convenience.

Finally, both the current in CC stage and value of \( \frac{dQ}{dV} \) could be determined by the requirement of charging time. In this case, it takes one hour to charge the battery from 0% to 80% SOC.

The current of the proposed charging protocol applied in this article is shown in Figure 3 in black line, and the voltage curve is marked in blue line. This protocol includes two steps, constant current and constant \( \frac{dQ}{dV} \) charging. The battery is firstly charged to 3.72 V at 1C (2.75 A) constant current, assigned as step 1. Next, the battery is charged to 4.08 V in constant \( \frac{dQ}{dV} \) mode, with 45mAh per 10 mV, assigned as step 2. More specifically, the battery is charged 45mAh at 3.73 V with constant voltage, then charged 45mAh at 3.74 V constant voltage, and so on, finally charged 45mAh at 4.08 V with constant voltage. As a result, when step 2 is completed, the battery SOC reaches 80%.

A comparative CC (without CV stage) charging experiment has also been conducted, and the current and voltage curve are shown in Figure 2. Both CC (0.8 C) and the proposed protocols could charge the battery from 0% to 80% SOC within one hour.

### 2.3 Cycle life tests

To evaluate the charging protocol effects on the cycle life, two battery samples were prepared for cycle test with each protocol. The variation in capacity and internal resistance of all the fresh batteries is very small, specifically less than 40 mAh and 1 mΩ, respectively. In order to simulate the field application of fast charge, all the batteries are charged to 80% SOC and discharged to 2.75 V at 1C rate. There was no rest after charge, while 30 min rest was inserted between each cycle. For every 50 cycles, the batteries are carried with a standard 0.5C-charge-1C-discharge test to calibrate the actual capacity, and a followed 0.1C-charge-1C-discharge test to analyze the fatigue mechanism. Since a liquid thermal management system is applied in the EV to keep the battery temperature between 25°C and 35°C, all the experiments are
conducted at 25°C. All batteries were disassembled after cycle test for post-mortem investigation.

3  |  RESULT AND DISCUSSION

3.1  |  Impact of the charging protocol on cycle life

The cycle life test results with the proposed charging protocol and CC charging protocol are compared and are shown in Figure 4. Figure 4A shows the change of actual capacity with cycle number. All batteries have the same capacity at the initial two cycles, and the capacity of the proposed protocol remains higher than that of CC protocol during cycles. As shown in Figure 4B, the capacity retention ratio of batteries charged with the proposed protocol is about 90% after 1150 cycles, while the batteries with CC protocol remain approximately 80% of capacity after 700 cycles. The capacity retention of batteries charged with the proposed protocol shows a good consistency between test cycles and calibration, while the capacity retention with CC protocol during the test cycles is worse than that during calibration. The two CC charged batteries show an accelerated capacity decrease after 200 and 600 cycles, respectively. Besides, the cycle life of two batteries charged with CC protocols diverges after 200 cycles, while the cycle life with the proposed protocol shows a good consistency and a stable trend. Since all the four batteries are mass manufactured from the automated production line, and there is very small initial variation in the chosen four batteries, the divergence could be attributed to the charging protocols. This might imply that the 0.8C-CC charging protocol has less tolerance, so that inevitable small variations in batteries (such as the inconsistency of the electrode thickness, the amount of electrolyte, etc.) could result in a dramatic divergence of cycle life. As a result, the proposed charging protocol outperforms the CC protocol not only in cycle life, but also in consistency, which is important to engineering application in EVs as it reduces the work load of balancing.

3.2  |  Self-adaptive current adjusting

The capacity retention ratio in Figure 4B(CC-1, CC-2) shows an accelerated decline, which may be due to that the current is not adjusted as the capacity fade. Therefore, the SOH change should be taken into consideration in charging protocol. However, it is complicated to get the SOH accurately enough in the engineering application. The proposed charging protocol could keep the capacity fade in a stable and slow velocity, as shown in Figure 4B \( \frac{dQ}{dV} \)-1, \( \frac{dQ}{dV} \)-2, which can be attributed to automatically adjusted current. Figure 5A shows the current curves of fresh and aged batteries in the proposed charging protocol. It can be seen that although the experiment settings are not changed during the cycle, the current decreases as cycle number increases. The current is adaptably adjusted due to the gradual change of the intrinsic properties of the battery, and could be deduced from Equation (8): (a) The parameters of \( R_\Omega \) and \( R_p \) would increase as SOH changes; (b) the SOC-OCV curve would change due to the material changes on the anode and cathode. The qualitative analysis according to Equation (8) shows that the current would change as the capacity fade, which contribute to a longer life. The charging time of the proposed protocol continuously increases as the cycle number increases, as shown in Figure 5B.

3.3  |  Anode potential evaluation

Lithium deposition on the anode surface is one of the major causes of abnormal capacity fading of lithium-ion
battery, which can even cause thermal runaway. When lithium is deposited, it is likely to become dead lithium once isolated from the anode basis, which accelerates the capacity fading. The occurrence of lithium deposition can be detected by measuring the anode potential. In order to evaluate the anode potential during charging, a customized device is designed to reconstruct a three-electrode battery and tested with battery test system (Neware CT-4000-5V10mA, Shenzhen, China). The anode, cathode and separator are from disassembled electrode, and a lithium plate is added as the reference electrode. These components are installed in a stainless-steel shell and pressed tightly by screws, as shown in Figure 6A. The anode potential during charging with two protocols are shown in Figure 6B. During the charging process with the proposed protocol, the anode potential is always greater than 0 V, which means that lithium deposition on the anode is prevented. On the contrast, during the CC charging process, the anode potential is less than 0 V when SOC is larger than 60%, which would result in the lithium deposition and accelerated decay of capacity. As a result, the proposed charging protocol is superior to the CC protocol because lithium deposition is prevented.

### 3.4 Fatigue mechanism of aged battery

To identify the dominant degradation mechanism, differential voltage curves \((dV/dQ)\) are derived by 0.1C
constant current charging. Figure 7A shows the potential curves and Figure 7B shows the differential voltage curves, including full cell, cathode and anode. The position of peaks in the $dV/dQ$ curve of full cell is determined by those of cathode and anode. Specifically, for the batteries tested in this article, the location of peaks is dominated by anode, while SOC is below 60%, and dominated by the cathode, while SOC is above 60%.

The $dV/dQ$ curves of aged batteries during 0.1 C constant current charging are shown in Figure 8, with a fresh battery as reference. Here, q1, q2, q3 represent the intervals between different peaks of fresh battery. The change of q1 represents the degradation of anode, q2 represents reduction of active lithium ion, and q3 represents the cathode active material, respectively. And corresponding values with single quotes and double quotes represent the properties of aged battery cycled with CC protocol and the proposed charging protocol, respectively.

For the proposed charging protocol, $q1'$ is shorter than q1, which indicates the degradation of anode. And $q2'$ is also shorter than q2, indicating a loss of active lithium ion. However, there is little change between $q3'$ and $q3''$, meaning almost no loss in the cathode active material. For the CC charging protocol, $q1''$ is obviously shorter than q1, which indicates degradation of the anode which may cause lithium deposition on the anode surface. The change is observed between $q2'$ and $q2''$, indicating reduction of active lithium ion. For $q3$, there are very minor changes detectable. Moreover, $q1''$ is obviously shorter than $q1'$, and $q2''$ is slightly shorter than $q2'$. This might be caused by the lithium deposition, as it would cover the surface of the anode, thereby reducing the effective surface area of the anode. Overall, the analysis of q1, q2, and q3 has shown that the capacity fade results predominantly from a loss of active lithium ion and degradation of the anode.

3.5 Post-mortem analysis of lithium deposition

As shown in Figure 9, a post-mortem observation was conducted to compare the surface morphologies of anode from cycled batteries which were, respectively, charged by 0.8 C CC protocol and the proposed charging protocol, since the main cause of the capacity fading is the

**FIGURE 8** The $dV/dQ$ curves of batteries, including fresh battery, aged battery with CC charging protocol and aged battery with the proposed charging protocol [Colour figure can be viewed at wileyonlinelibrary.com]

**FIGURE 9** The post-mortem observation of anode from A, fresh battery, B, aged battery with the proposed charging protocol, and C, aged battery with CC charging protocol. Their corresponding SEM images are shown in figures d-f [Colour figure can be viewed at wileyonlinelibrary.com]
degradation of the anode. All the batteries were discharged to 2.75 V at 1C current before morphologies observation. Figure 9A shows that the anode surface of fresh battery is black and clean. Figure 9B shows that the anode surface of battery under the proposed charging protocol is similar to that of fresh battery, indicating that no lithium deposition occurred during the charging. The anode surface of battery (Figure 9C) with CC charging protocol shows some greyish white areas marked by red elliptical line, indicating the occurrence of lithium deposition. A Hitachi S4800 scanning electron microscope was used to take the scanning electron microscope (SEM) images. The SEM images of anode electrode surface from fresh battery, battery cycled with the proposed charging protocol (1150 cycles) and battery cycled with CC protocol (800 cycles) are displayed in Figure 9D-F, respectively. Compared with the fresh battery, the anode surface after cycled with the proposed charging protocol is somewhat rough, but the particles of anode still have clear boundaries. The anode surface of battery cycled with CC protocol has a layer of attachments, which may be caused by lithium deposition. The post-mortem observation and SEM images show that the proposed protocol could keep the integrity of anode better than the CC protocol.

4 | CONCLUSIONS

In this article, a novel self-adapted fast charging protocol is proposed based on constant incremental capacity algorithm. The parameters of the algorithm could be calculated or calibrated offline, and the current is adjusted by the intrinsic properties of battery automatically. The test results show that batteries with the proposed protocol exhibits a good cycle life. Specifically, commercial NCM811/graphite-Si 18 650 batteries with the proposed charging protocol keep a capacity retention ratio of 90% after 1150 cycles, highlighting its advantages over CC protocols for 80% after 700 cycles. The anode potential evaluation and the post-mortem analysis show that the proposed protocol could prevent lithium deposition and keep the integrity of the anode effectively. The proposed charging protocol can effectively improve the battery life and extend the service time of electric vehicles while achieving fast charging, which would significantly improve the overall economic benefits of electric vehicles.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (grant nos. 11872355, 11872354, and 11627803) and the Strategic Priority Research Program of the Chinese Academy of Sciences (grant no. XDB22040502).

ORCID

Li Lao https://orcid.org/0000-0003-4184-0877

REFERENCES

14. Vo TT, Chen XP, Shen WX, Kapoor A. New charging strategy for lithium-ion batteries based on the integration of Taguchi method and state of charge estimation. J Power Sources. 2015;273:413-422.
16. Chen Z, Shu X, Xiao RX, Yan W, Liu Y, Shen J. Optimal charging strategy design for lithium-ion batteries considering...


25. Li XK, Kang JQ, Yang YF, Yan F, du C, Luo M. A study on capacity and power fading characteristics of Li(Ni1/3Co1/3Mn1/3)O2-based lithium-ion batteries. *Ionic.* 2016;22(11):2027-2036.


How to cite this article: Lao L, Wu S, Zhang Q. Optimized fast charging protocol for cylindrical lithium-ion battery based on constant incremental capacity algorithm. *Int J Energy Res.* 2020;1–9. https://doi.org/10.1002/er.5915