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Fast Charging of Commercial Lithium-ion Battery Without Lithium Plating

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Abstract: Rapid charging of lithium-ion batteries (LIBs) enables the devices or systems powered by the batteries to provide services at faster rates or higher frequencies. However, fast charging of LIBs can cause lithium plating, resulting in rapid capacity degradation and even thermal runaway or fire in the batteries. Fast charging and lithium plating in a LIB are anode-centric events. Therefore, an anode-centric electrochemical model is critical for deriving a fast-charging protocol for LIBs. In this work, we developed an electric circuit model for the negative electrode using tests conducted on laboratory three-electrode lithium-ion cells, used the model to estimate the fast charging current, and compared the fast charging current derived using the model to the fast-charging current obtained from measurement. The fast-charging current obtained using the model agrees well with the measured fast charging current. Furthermore, we implemented this fast-charging protocol on commercial 18650 LIBs for 350 cycles using custom-built charging hardware and software and achieved an 80% state of charge in 29 minutes with acceptable temperature rise. The cell aging analysis revealed no significant capacity degradation nor lithium plating on the anode surface, as the protocol explicitly imposes control to protect the battery from lithium plating.

Keywords: Lithium-ion battery (LIB); Electrochemical Impedance Spectroscopy (EIS); Fast charging; Lithium plating; Three-electrode lithium-ion cell.

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1. Introduction

Lithium-ion batteries (LIBs) are widely used as power or energy sources in many electrical devices or systems. Fast charging of the LIBs enables the devices or systems to provide service at faster rates or higher frequencies. However, it is well known that fast charging commercial LIBs with high charging rates could cause metallic lithium deposition or lithium plating on the surfaces of the graphite anodes of the batteries [1-9], which, in turn, can cause rapid capacity fade and even thermal runaway or fire in the batteries [10, 11].

Several fast charging protocols have been proposed to reduce the charging time compared to the conventional constant current - constant voltage (CC-CV) charging protocol. Pulse charging (PC) is a fast charging technique that limits lithium concentration at the solid electrolyte interface (SEI) layer [12]. During a typical CC-CV charging process, the lithium concentration saturates once the cutoff voltage of the cell is reached. At this point, charging can encourage dendrite growth and a significant reduction in charging current is required. As a result, the CV stage of the charging protocol extends the charging

time to undesirable lengths, typically 2 to 4 hours. To mitigate the lithium concentration saturation problem, PC uses high current pulses of certain frequencies and amplitudes, with each pulse followed by a relaxation period, to charge the battery. The current pulses and rest periods balance the rate at which lithium migrates to the surface of the anode and the rate at which lithium diffuses into the graphite anode [12]. PC can achieve 100% state of charge (SoC) in the range of 45 minutes [12] to 82 minutes [13] for 250 cycles, which is significantly shorter than the CC-CV protocol. In addition, some authors reported that PC extends the battery life by more than 100 cycles than the conventional CC-CV protocol [14]. However, it was also reported that PC negatively affects the battery performance, such as increasing capacity loss due to the well-known effect of Ohm's law on nonlinear impedance [15]. It is also suggested that pulse profiles do not positively affect active materials or electrochemical processes that benefit the battery performance [15]. Furthermore, the selection of pulse characteristics, such as frequency, amplitude, and duty cycle, significantly impacts the cycle life and cell impedance, but there is no consistency in the pulse attributes for fast charging, and it is unclear if the pulse attributes depend on the electrode material properties.

Boost charging (BC) is similar to the typical CC-CV charging process but uses two CC stages and a final CV stage [16-18]. In this charging technique, cells are charged with higher C-rates in the first CC stage until the cutoff voltage is reached. Then the charging current is reduced to 1C to decrease the cell voltage below the cutoff voltage. The cell is charged at 1C until the cutoff voltage is reached again, and the charging is finished with a CV stage. BC can achieve 33% and 100% SoC in approximately 5 and 20 minutes, respectively, [16, 17] and accomplish 4500 cycles with the discharge capacity decreasing by only 14% [16]. This result is impressive compared to the conventional CC-CV and PC protocols. The BC protocol reported in [16] uses d.c. and the potential across the cell to measure the internal resistance of the cell and uses the calculated internal resistance to determine the charging current at the CC stages. The calculated internal resistance cannot capture several important events in the electrode/electrolyte interface, such as the diffusive transport of lithium into the bulk electrode, because the process is slow compared to the process where the d.c. or cell potential is applied to the cell for internal resistance measurement [19].

The varying current (VC) charging protocol charges LIBs with a hypothetical nonlinearly varying current created according to the cell d.c. resistance [20]. The charging current is low but gradually increases when the d.c. resistance is high to avoid generating large amounts of heat at low SoCs. The charging current peaks at mid-SoCs and exponentially decays afterward [20, 21]. The VC protocol can charge 2.2 Ah cells to 100% SoC in one hour [20]. While the VC method charges LIBs in an impressively shorter time than the CC-CV protocol, the cell is held close to the cutoff voltage for approximately

one-third of the charging time, encouraging cell aging and consuming active materials. Similar to the BC method, the protocol uses d.c. resistance to determine the charging current. As a result, the method also suffers from the problem that the d.c. resistance cannot capture the impedance associated with mass diffusive transport.

The multistage constant current (MSCC) charging method employs several monotonically decreasing constant current (CC) phases. This scheme applies the next lower charging current when the cell voltage reaches a predefined cutoff voltage, and the process continues for multiple and predefined stages [22, 23]. The MSCC method can charge LIBs to 75% capacity in 40 minutes and achieve 60% more cycle life than the conventional CC-CV method [22]. Complex algorithms are necessary to determine the appropriate charging current from a predefined look-up table (Taguchi approach) corresponding to specific CC stages. The protocol immediately pushes the cell voltage close to the cutoff voltage limit and continually charges with high currents, encouraging the evaporation of the electrolyte and unwanted side reactions within the cell. Several reports on other interesting fast charging methods targeting to lessen the charging time can be found in Refs. [24-27].

Although the cathode plays an important role in cell performance, fast charging and lithium plating in a LIB are anode-centric events [28]. During the charging of a lithium-ion cell, lithium ions are intercalated into the graphite anode in the voltage range of -0.06 to 0.2 V vs. Li/Li^+ [29]. Lithium deposition occurs thermodynamically if the electrochemical surface potential of the graphite is less than 0 V vs. Li/Li^+ . Therefore, the potential of the graphite anode can be used as an indicator for lithium deposition. It is important to note that none of the charging protocols discussed above uses anode potential explicitly while creating charging protocols. The methods are simply dedicated to achieving shorter charging time and assumed lithium plating would not occur if the full cell voltage was below the cut-off threshold. This assumption may not always be true, especially when higher C-rates are used to charge LIBs.

Seig et al. [30] proposed a fast charging protocol for a commercial graphite-anode high-energy lithium-ion pouch cell. An important feature of the protocol is that it keeps the anode potential above 0 V vs. Li/Li^+ to avoid lithium deposition on the anode surface. To develop the protocol, the authors built small three-electrode cells using materials from the commercial pouch cell and lithium reference electrodes and used the three-electrode cells to test the charging current that keeps the anode potential above 0 V vs. Li/Li^+ . The proposed protocol starts with a CC phase, where a high C-rate is employed to charge the cell. When the anode potential vs. Li/Li^+ reaches a predefined threshold slightly above 0 V, the charging current is reduced to maintain the anode potential above 0 V vs. Li/Li^+ . The charging process ends when the full cell voltage reaches the cut-off threshold. The charging current for the commercial pouch cell was found based on the charging current of the small three-electrode cells. Seig et al. [30] used the protocol to charge commercial pouch cells for 1800 cycles and achieved 80% SoC in 15 minutes. A similar charging protocol was also proposed by Remmlinger et al. [31] based on simulations. The fast charging current in the protocol presented in [30] was obtained from the measurement and was updated using the capacity loss or cell's d.c. resistance increase as the cell aged. The protocol does not provide insight into the relationship between the charging current, the open-circuit potential of the anode, the surface potential of the anode, and the various resistance and other elements

related to different electrochemical events in the cell. As a result, it is difficult to update the fast charging current accurately when the elements in the cell change as the cell is used.

In this work, to predict charging current that reduces the charging time significantly and ensures no lithium deposition on the negative electrode, we assembled three-electrode lithium-ion cells and performed galvanostatic electrochemical impedance spectroscopy (EIS) and open-circuit potential (OCP) measurement of the anode at various states of charge (SoCs). We predicted fast charging current using a model developed using kinetic/dynamic parameters of the negative electrode and compared it with the measured fast charging current. The predicted fast charging current obtained by simulation agrees well with the measured fast charging current. Furthermore, we used this predicted fast charging current to charge commercial LIBs, which significantly lowered the charging time (80% SoC in 29 minutes) than the conventional CC-CV (standard charging) method and prevented lithium deposition on the battery electrodes even after a long cycle test which is crucial for the performance and safety of the LIBs. The model used in the protocol provides insight into the relationship between the charging current, the anode potential, and other elements related to different electrochemical events in the cell. As a result, it is possible to use the model to update the fast charging current to keep the anode potential above 0 V vs. Li/Li^+ as the cell is used in the field.

2. The basic principle for prediction of fast charging current and implementation

The electrical dynamics within a LIB can be approximated using an equivalent circuit consisting of a voltage source, an internal resistor, and other circuit elements related to various electrochemical events in the cell electrodes. Fig. 1(a) represents a circuit model for representing the electrical dynamics of a LIB, where I is the cell current, V_{OCP} is the open circuit potential of the cell, V is the terminal voltage, Z represents the equivalent of the circuit elements related to the different electrochemical events in the electrode, and R_0 is the internal resistance of the cell. In this case, V_{OCP} depends on SoC, and in principle, R_0 and Z depend on SoC and temperature. In this work, we performed the fast charging at room temperature, and therefore values of Z and R_0 at room temperature were used. Once V_{OCP} , V , Z , and R_0 are known in Fig. 1(a), current I can be calculated using the circuit. In general, fast charging and lithium plating in a LIB are anode-centric events. Hence, only an anode-centric equivalent circuit/electrochemical model can accurately describe the fast and safe charging of LIBs. Therefore, the equivalent circuit model (ECM) shown in Fig. 1(a) is mainly based on the anode parameters measured using a reference electrode in a three-electrode lithium-ion cell. As described in the previous section, lithium plating occurs thermodynamically if the electrochemical surface potential of the anode is less than 0 V vs. Li/Li^+ . Therefore, the potential of the graphite anode is an indicator of lithium deposition, and the ECM uses 10 mV vs. Li/Li^+ as the terminal voltage of the anode to ensure the lithium-plating-free charging

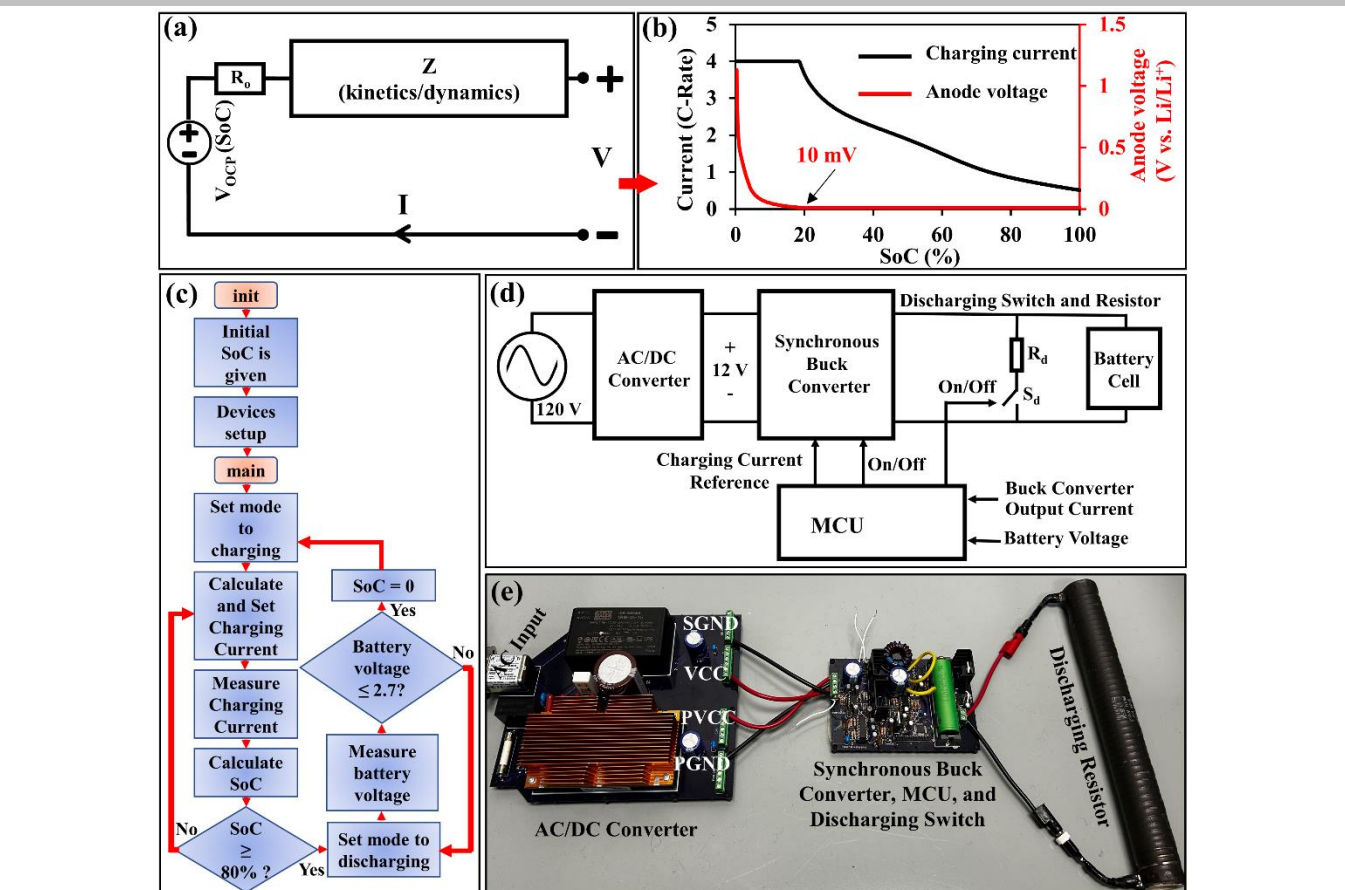


Figure 1. (a) Diagram showing electrical dynamics for a lithium-ion battery using an equivalent circuit model (ECM). (b) Example of fast charging current prediction using the ECM. (c) Flowchart for implementing the proposed fast charging protocol and conducting battery cycling test. (d) Block diagram of the charging/discharging hardware. (e) Photograph of custom-built charging/discharging hardware.

current. In addition, the ECM-based simulation uses anode OCPs and electric circuit elements associated with different electrochemical events, such as solid electrolyte interphase, charge transfer, and diffusion of charges into the bulk anode material according to the SoC, to accurately predict lithium-plating-free fast charging current, as shown in Fig. 1(b). The protocol further translates the charging current from the three-electrode test cell level to the commercial cell level using only a simple function like the capacity ratio.

We built our own charging hardware to implement the fast charging protocol and perform the cycling test on commercial LIBs. A flowchart for the cycle tests, a detailed block diagram of the modules, and a photograph of custom-built charging/discharging hardware are shown in Figs. 1(c-e). The cycle tests were controlled by Texas Instruments MSP430FR microcontrollers in the charging hardware. Circuits for discharging the batteries were also included in the hardware. First, the microcontroller initializes (init) all devices in the hardware, including the current sensor, temperature sensor, analog-to-digital converters (ADC), and digital-to-analog converters (DAC). Then, the microcontrollers read battery voltage, current, and temperature through sensors, calculate battery capacity and SoC, and set mode to charging. The charging process involves calculating and setting the desired (reference) charging current, measuring the actual charging current, and calculating cell capacity and SoC by integrating

the measured charging current. The cell is charged utilizing the charging protocol until the SoC reaches 80%. Once this occurs, the microcontroller activates the discharging circuit to discharge the cell to 2.7 V. While discharging, the cell voltage is read periodically, and the discharge continues until the cell voltage reaches 2.7 V. Once the cell voltage reaches this point, 0% SoC is assumed, and the charging process begins again, repeating the process.

3. Experimental

3.1 Cell assembly

The anodes (graphite coated on copper foils) and cathodes (NMC coated on aluminum foils) for assembling the three-electrode cells were harvested from a commercial LIB (Sony 18650VTC4, nominal capacity 2000 mAh @ 1C, Fig. 2(a)). The as-received battery was first discharged to the lower cutoff voltage (2.5 V) at a C/5 rate. The fully discharged battery was disassembled inside a glovebox with both moisture ($\text{H}_2\text{O} < 0.5$ ppm) and oxygen-controlled ($\text{O}_2 < 0.1$ ppm) environment, as shown in Fig. 2(b). The anode and cathode were carefully separated from the jelly roll, dipped immediately within dimethyl carbonate (DMC) to remove the electrolyte, and dried for 24 hours inside the glove box. The active material on one side of each

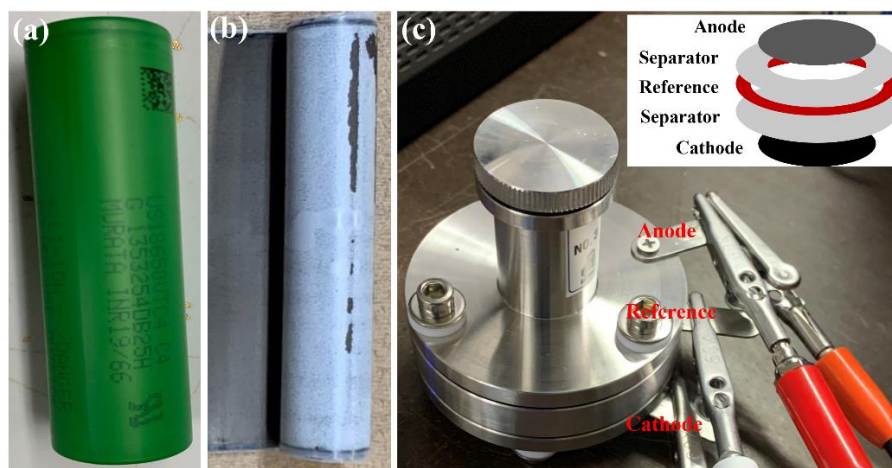


Figure 2. (a) As-received commercial Sony 18650VTC4 lithium-ion battery. (b) Jelly roll exposed after cell disassembly inside the glove box. (c) MTI three-electrode split cell kit and schematic of the cell component arrangement inside a three-electrode lithium-ion test cell.

electrode was carefully removed using cotton swabs and N-Methyl-2-Pyrrolidone (NMP) and was left to dry for another 12 hours. Then, anode and cathode disks of 12 mm diameter were punched out inside the glovebox. On the other hand, lithium rings (99.9 %, Sigma-Aldrich) were used as the reference electrodes in the three-electrode configuration facilitated by MTI split cell kits, as shown in Fig. 2(c). Polypropylene films (Celgard® H2013, thickness 20 μm , PP|PE|PP) were used to insulate the anode, cathode, and reference electrode in a three-electrode cell. Also, 1 M lithium hexafluorophosphate (LiPF_6) dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (v/v = 1:1) (Sigma-Aldrich, battery grade, $\geq 99.99\%$ trace metals basis) was used as the electrolyte. The test cells were rested for 24 hours for electrolyte wetting before performing electrochemical properties tests.

3.2 Electrochemical properties measurement

3.2.1 Cell conditioning test

Before Electrochemical Impedance Spectroscopy (EIS) and fast-charge measurement, three-electrode test cells were subjected to five initialization cycles using the LBT21084HC Arbin cycler. The initialization cycles were performed between 2.5 V and 4.2 V in the full cell configuration using CC-CV charging at C/5 rate with C/20 as the CV stage termination condition, CC discharging at C/5, and five minutes rest between charge and discharge. This initial test is important to confirm stable performance, determine capacity, and set a well-defined SoC of the cell.

3.2.2 Electrochemical Impedance Spectroscopy (EIS) measurement

The Electrochemical Impedance Spectroscopy (EIS) tests were performed in the galvanostatic mode using a Gamry Reference 3000 potentiostat/galvanostat. The lithium reference electrode in a three-electrode cell facilitates monitoring and measuring the electrochemical properties of individual working electrodes. Therefore, the EIS of the anode and cathode was measured using the reference electrode in a three-electrode configuration, while the full cell EIS was measured in the two-electrode configuration. The a.c. amplitude was set to 5% of the cell capacity to ensure linearity and a reasonable

signal-to-noise ratio so that errors due to the nonlinearity of the electrochemical cell could be minimized. Unless otherwise mentioned, the EIS tests were conducted in the frequency range between 100 kHz and 0.05 Hz using an automatic sweep mode from high to low frequency.

In order to measure the anode EIS at various SoCs, the test cell was fully discharged first, then charged at C/5 and stopped at a certain SoC to measure EIS. The EIS measurements were carried out at each SoC step once the cell was stabilized after resting for three hours. The confirmation of cell stability after a three-hour resting period is reported in our previous work [32]. The anode OCPs were also measured at different SoCs before measuring EIS, which exhibited a non-linear function of SoC, as shown in Fig. S1(a).

On the other hand, EIS and OCP measurements were also carried out while discharging from a fully charged state at various SoCs. An example is shown in Fig. S2. However, this research mainly focuses on finding an appropriate fast charging current while maintaining the battery health; hence, only the anode EIS as a function of SoC measured while charging from a fully discharged state will be discussed in detail in the paper.

3.2.3 Fast charging current measurement using three-electrode cells

We measured the fast charging current with different starting maximum currents in the potentiostatic mode using a three-electrode test cell. As shown in Fig. S1(b), the charging currents were measured at different C-rates with the anode potential held at 10 mV vs. Li/Li^+ . As mentioned before, theoretically, this anode potential can be as low as 0 mV vs. Li/Li^+ and can shorten the charging time. However, in practice, it is desirable to keep some margin from the theoretical limit as local anode surface potential can vary due to the physical morphology of the electrode and non-thermodynamic conditions at high C-rates. While choosing the holding anode potential, verifying the full cell's safe voltage limit is essential to protect the cathode from over-discharging. During this charging process, the anode potential decreases until the holding potential is reached, and the cell is charged with the maximum current. Then, the charging current decreases until the SoC reaches 100%, as shown in the inset of Fig. S1(b). This method helps to

charge the cell with a higher average current than the standard charging protocol (1C, CC-CV), resulting in a much shorter charging time. This type of measurement is already shown in [30]. The current curves for different C-rates overlap very well after the anode potential reaches the holding potential, suggesting that C-rate values corresponding to a specific SoC are very similar. The reproducibility and reliability of this behavior were assessed for different cells.

3.2.4 Fast charging current measurement using three-electrode cells

As described in Section 2, the fast charging protocol implementation and electrochemical properties test of commercial 18650 LIBs were carried out using our custom-built charging hardware. During this process, LIBs were charged utilizing the fast charging current until the SoC reached 80%. While discharging, a constant resistance discharge was chosen instead of a typical constant-current discharge, meaning that the discharging current was determined by the cell voltage divided by the load resistance, as per Ohm's Law. The discharge resistance chosen here was 1.019Ω , which results in discharge currents from 4A (1.9C) to 2.7A (1.3C). Furthermore, the cell voltage, cell temperature, and ambient temperature were sampled during the entire cycle test procedure.

3.2.5 Standard charging of commercial lithium-ion batteries (LIBs)

The standard charging (or reference performance test) of the as-received commercial 18650 LIBs was carried out using the conventional 1C constant current – constant voltage (1C CC-CV) charging scheme with C/10 as the CV stage termination condition. The LIBs were cycled for 350 cycles using the LBT21084HC Arbin cycler at room temperature ($\sim 23^\circ\text{C}$). Also, LIBs were cycled between 2.5 V and 4.2 V cutoff potentials as per the manufacturer's suggestion.

4. Results and discussion

4.1 Anode impedance measurement

Fig. 3(a) shows the Nyquist plots of the graphite anode impedance recorded at different SoCs during the charge. Each anode EIS spectrum includes two depressed semicircles above the real axis and a small semicircle below the real axis, followed by an inclined line at low frequencies in all SoCs. The small semicircle below the real axis, where $-\text{Im}(Z) < 0$ and is often referred to as an inductive loop, is frequently observed in the low-frequency region of the graphite anode impedance spectrum [33–37]. Although the presence of inductive loops in anode impedance spectra has been reported in the literature, the cause of such loops is credited to contrasting reasons. A detailed explanation of such loops in the EIS spectra is outside the scope of this work. Recently, we have reported detailed research on the origin of

such inductive characteristics in the low-frequency region of the graphite EIS spectrum [32] and hence will not repeat here.

The high-frequency ($>1 \text{ kHz}$) semicircle with a small diameter can be related to solid electrolyte interphase (SEI) developed on the anode surface due to the electrolyte reduction, while the second semicircle located at the medium frequency range can be attributed to the impedance related to the charge transfer [38–40]. The inductive loop occurs at low frequencies between 6 Hz and 0.63 Hz, depending on the SoC. The straight lines inclined to the real axis at the low-frequency region can be ascribed to the lithium diffusion process within the graphite anode [41]. Fig. 3(b) displays an equivalent circuit model (ECM) for fitting the anode EIS spectra, and the ECM fits measured spectra well, as shown in Fig. 3(a). The EIS spectra were validated by analyzing their reproducibility by Kramers-Kronig (K-K) compliant equivalent circuits before fitting with ECM [42, 43]. Moreover, the full cell impedance was compared with the combined spectrum of anode and cathode to examine the full cell impedance variation per anode and cathode impedances, as shown in Fig. S2.

The ECM includes serial resistance (R_s), which represents the ohmic resistance of the cell, two parallel resistor-CPE (constant phase element) networks, a resistor-inductor (R_L - L_L) parallel network that represents the inductive loop present in the low-frequency region of the impedance spectrum, and two parallel RC networks. The two resistor-CPE networks represent the high-frequency semicircle related to the SEI resistance (R_{SEI}) and the higher-to-medium frequency semicircle above the real axis (Z' axis) related to the charge transfer resistance (R_{CT}), respectively. Furthermore, two RC networks (R_1 - C_1 and R_2 - C_2) simulate the Warburg impedance related to the lithium diffusion process. The ECM uses CPEs to simulate depressed semicircles in the anode EIS spectra, commonly used for electrodes with inhomogeneous surface morphology and varying thickness or composition of active materials coating [44]. A resistor-CPE (R-CPE) parallel network can be approximated with a resistor-capacitor (R-C) parallel network, and the capacitance C can be calculated using the equation $C = [(R^*Q)^{1/\alpha}]/R$, where R and Q are the resistor and the CPE in the R-CPE network; α is an empirical constant representing how close the CPE's behavior is to a resistor ($\alpha = 0$) or a pure capacitor ($\alpha = 1$) [45]. Table 1 presents anode OCP and resistance and capacitance values related to various electrochemical events according to SoCs estimated by fitting the anode EIS spectra using the ECM, which are essential for predicting the fast charging current of the LIB. In Table 1, C_{SEI} and C_{DL} are the capacitance values used to approximate the CPEs for the SEI and charge transfer process, respectively.

4.2 Prediction of fast charging current

Predicting the fast-charging current for a lithium-ion cell that ensures no lithium plating during the charging process is a complex task. It should involve accurate information about the kinetic and mass transport processes in the cell's electrode/electrolyte interface. In this

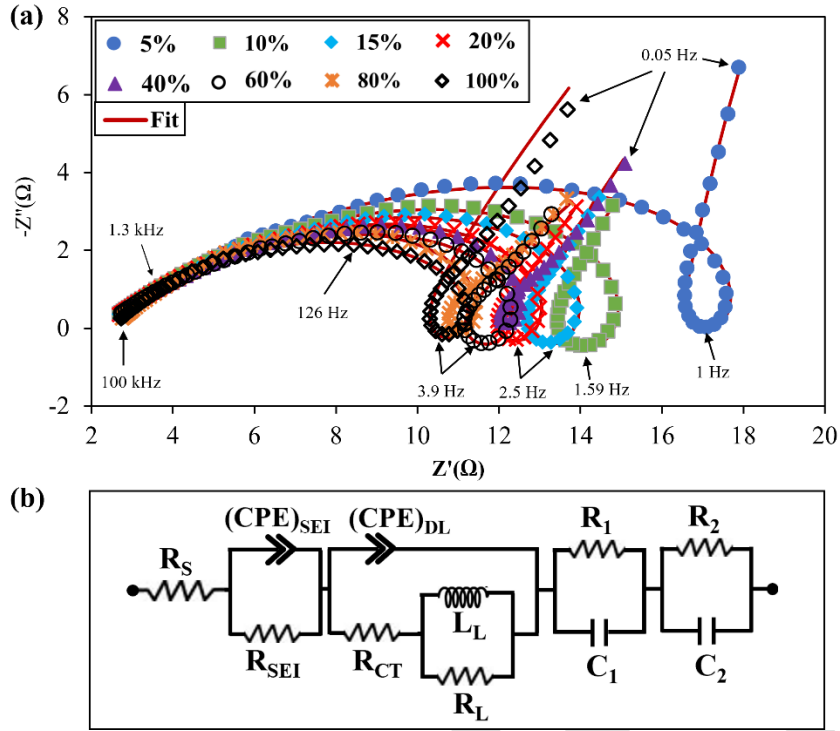


Figure 3. (a) Impedance spectra of the graphite anode measured at different SoCs during the charge. (b) The equivalent circuit model (ECM) used to fit the anode impedance spectra shown panel (a).

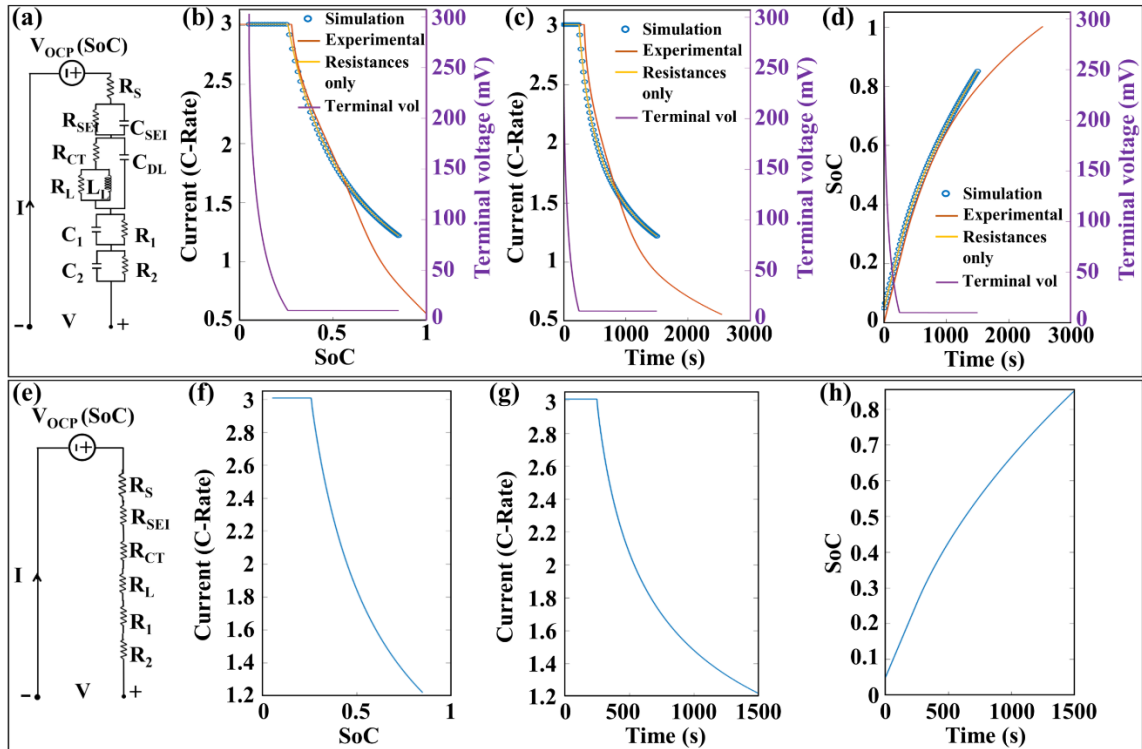


Figure 4. (a) Electrical circuit model for predicting a fast-charging current for a LIB test cell. Graphs showing experimental and simulation results for (b) charging current (C-Rate)/terminal voltage (anode) vs. state of charge (SoC), (c) charging current (C-Rate) /terminal voltage (anode) vs. charging time, and (d) state of charge (SoC) /terminal voltage (anode) vs. charging time. (e) Electrical circuit model for predicting a fast-charging current for a commercial 18650 LIB. Graphs showing simulation results for (f) charging current (C-Rate) vs. state of charge (SoC), (g) charging current (C-Rate) vs. charging time, and (h) state of charge (SoC) vs. charging time of the commercial 18650 LIB.

Table 1. Element values according to SoCs obtained after fitting the anode EIS spectra of a small three-electrode test cell using the ECM shown in Fig. 3(b).

SoC (%)	OCP (mV)	R_s (Ω)	R_{SEI} (Ω)	C_{SEI} (μF)	R_{CT} (Ω)	C_{DL} (μF)	L_L (mH)	R_L (Ω)	R_1 (Ω)	C_1 (F)	R_2 (Ω)	C_2 (F)
5	310	2.411	3.167	58.56	12.29	529	508	4.520	23.80	1.108	0.623	0.304
10	209	2.392	3.102	55.45	10.12	869	258	5.340	0.815	0.041	10.35	1.143
15	160	2.396	3.139	50.47	9.088	629	141	4.021	10.71	1.100	0.341	0.597
20	130	2.395	3.014	56.71	8.336	755	135	4.702	7.448	1.053	0.688	0.163
40	105	2.42	3.007	51.44	7.604	577	73	3.526	0.731	0.238	7.610	1.117
60	70	2.448	2.949	56.28	7.370	660	62	3.751	0.792	0.681	7.625	1.070
80	56	2.439	2.809	58.78	6.656	605	118	4.606	8.834	1.407	0.847	0.891
100	37	2.513	2.706	59.79	6.552	816	119	3.181	9.075	1.028	1.587	0.109

Table 2. Open circuit potentials (OCPs) and resistances as a function of SoCs calculated for the anode of commercial 18650 LIB.

SoC (%)	OCP (mV)	R_s (m Ω)	R_{SEI} (m Ω)	R_{CT} (m Ω)	R_L (m Ω)	R_1 (m Ω)	R_2 (m Ω)
5	310	2.030	2.667	10.35	3.806	2.030	2.667
10	209	2.014	2.612	8.520	4.497	2.014	2.612
15	160	2.018	2.643	7.653	3.386	2.018	2.643
20	130	2.017	2.538	7.020	3.960	2.017	2.538
40	105	2.038	2.532	6.403	2.969	2.038	2.532
60	70	2.061	2.483	6.206	3.879	2.061	2.483
80	56	2.054	2.365	5.605	3.159	2.054	2.365
100	37	2.116	2.279	5.517	2.679	2.116	2.279

work, the fast charging current prediction uses open-circuit potentials (OCPs) and impedance information obtained from the EIS spectra analysis according to the SoC of the graphite anode, as shown in Table 1. Fig. 4(a) represents the ECM that emulates a LIB cell. All the simulations were performed using MATLAB R2020a with a built-in Simulink in a desktop computer with a 1.6 GHz processor. Figs. 4(b-c) shows an example of a fast charging current simulation starting at a 3C rate as a function of SoC and time using the information shown in Table 1. In addition, Fig. 4(d) displays the SoC versus charging time graph. The figures also compare simulation results with experimental results and show good agreement between them for most SoCs, although there is some discrepancy at high SoCs.

The fast charging process, which takes tens of minutes, is much longer than the time constants of the resistor-capacitor parallel networks or the inductor-resistor parallel network in the circuit model shown in Fig. 4(a). As a result, the capacitors in the circuit model can be approximated with open circuits and the inductor can be approximated with a short circuit. This approximation significantly simplifies the circuit model. To evaluate the error caused by the simplification, the fast charging current was also simulated using the

circuit model shown in Fig. 4(a) while all the capacitors were replaced with open circuits and the inductor was replaced with a short circuit. As shown in Figs. 4(b-d), the comparison of fast charging currents simulated with and without capacitances and inductances in the circuit model displays no difference in the charging current. This result indicates that a purely resistive circuit model can accurately emulate the LIB cell and can be useful for predicting the fast charging current because of its simplicity. We note that a purely resistive circuit model does not necessarily eliminate the need for EIS and a d.c. internal resistance is not sufficient to accurately characterize the overall cell resistance, although it can partly measure the cell resistance, such as electrodes' ohmic resistances and electrolyte resistance. However, the d.c. internal resistance cannot measure resistances related to several other important electrochemical events in the electrode/electrolyte interface, most importantly the resistance related to the diffusive transport of lithium into the bulk electrode (Warburg resistance), because the process is too slow compared to the process where a d.c. potential is applied to the cell for internal resistance measurement [46, 47]. The inclusion of Warburg resistance in the resistive circuit is very important because it represents a significant

portion of the total cell resistance (sum of R_1 and R_2 in Tables 1 and 2) and can be critical for deciding the fast charging current. Furthermore, the resistance values associated with various electrochemical events were translated from the three-electrode test cell level to the commercial cell level using only the capacity ratio. The estimated values are presented in Table 2. Based on this information, the fast charging current starting at 3C rate was simulated for the commercial 18650 LIB using the simplified circuit model shown in Fig. 4(e). The simulation results are shown in Figs. 4(f-h).

Several studies [48-50] have suggested that fast-charging current schemes based only on the anode potential measurement using low-capacity three-electrode cell configurations and translating the schemes to higher capacity cells may not correlate most accurately, especially at non-thermodynamic conditions where C-rates are higher than C/2. Also, it has been shown that there is no direct correlation between the C-rates of half-cells and full cells due to different electrolyte and electrode compositions, fabrication processes, different mechanical (i.e., electrode pressure) and thermal environments in different cell formats. These differences yield uncorrelated kinetics on impedances and overpotentials, which are key for the design of the charging scheme. However, the approach undertaken in this work can provide valuable data and insights on fast charging of LIBs without the risk of lithium plating.

In addition, although the reference electrode in a three-electrode cell configuration can help to measure individual electrode potentials and develop fast charging protocols that can avoid lithium plating, it has been suggested that the anode potential measured using a reference electrode may underestimate the actual surface potential of the anode. As a result, the protocol may overestimate the likelihood of lithium plating on the anode surface [48]. This means that the anode may not suffer lithium plating even when its potential drops below 0 V vs. Li/Li^+ (theoretical limit) when measured using a reference electrode at a fixed distance away from the anode. It has been suggested that this uncertainty is about iR' , which is C-rate dependent and can vary with cell design. Hence, the anode potential (ϕ) measured vs. the reference electrode can be modified as $\phi \approx \eta - |iR'|$ [48], where η is the local anode surface potential, i is the cell current, and R' is the electrolyte resistance between the reference electrode and the anode surface. We measured R' using EIS and estimated the voltage measurement error in our measurement as 2.947 mV/C-rate and 8.842 mV at 3C (see supporting information and Fig. S3). We simulated the charging current and charging time to reach 80% SoC with anode potential fixed at 0 V vs. Li/Li^+ (theoretical limit) and with and without correcting the iR' error (see supporting information and Fig. S4). Simulation results revealed that by correcting the iR' error in our protocol, the charging time could be lowered by 11.85%. However, we note that the protocol used for charging commercial LIBs in the article was not updated with the anode voltage measurement error.

4.3 Cycling test of commercial lithium-ion battery (LIB)

This section presents the implementation results of the proposed charging strategy on the commercial LIB (Sony 18650VTC4). As described in section 3.2.5, the reference performance test (or standard test) of the as-received commercial 18650 LIB was performed using the 1C CC-CV charging scheme. The test was conducted between 2.5 V and 4.2 V cutoff potentials for 350

cycles. Fig. 5. compares the performance of commercial LIBs in terms of charging voltage, charging time, and cell capacity that were cycled using the proposed fast charging and standard charging (CCCV) protocols. Fig. 5(a) compares the charging voltages of the fast charging protocol and the standard charging protocol at different cycles, such as the 1st, 100th, 200th, 300th, and 350th cycles. The voltage profiles of fast charging quickly increased to ~3.9 V compared to the voltages of the standard charging protocol. This rapid increase in cell voltage while fast charging was mainly due to the high C-rate charging (max. 3C) at low SoCs. The voltage remained almost similar until ~55% SoC and again increased slowly until the end of the cycle (80% SoC). We note that the final voltage always remained below 4.2 V (upper cutoff voltage). The maximum voltage reached at the end of the charging process can give insights into the health of the cell. The results indicate that the proposed protocol not only charges the LIB fast but also maintains battery health. The voltage profiles also showed slight variations in the voltage data regarding final voltages and charging time and showed no clear relation to the cycle number. The variations may be related to the noise and measurement errors in the charging system.

Fig. 5(b) shows the charging time comparison between the fast charging protocol and the standard charging protocol at different cycles, such as the 1st, 100th, 200th, 300th, and 350th cycles. The charging time comparison shows that cells can be charged significantly faster (80% SoC in ~29 minutes) using the proposed protocol compared to the standard charging protocol (80% SoC in ~50 minutes). This charging time can be further reduced to ~25 minutes using the fast charging current starting with the maximum C-rate of 5C. A fair comparison of battery charging time should involve factors such as battery chemistry, electrode and electrolyte materials, temperature, SoC, C-rates, safety, and capacity retention. Nevertheless, the charging time achieved in this research is shorter or comparable to the fast charging time achieved by using different charging protocols reported in the literature [16-18, 20, 22, 51].

Furthermore, long cycling tests were performed on the commercial LIBs using the fast charging protocol and the standard charging protocol. Fig. 5(c) shows the discharge capacity of the commercial LIBs for 350 cycles. During these tests, commercial LIBs were charged to only 80% SoC using the fast charging protocol, while they were fully charged in the case of the standard charging protocol. The capacity of the commercial LIB was ~1.9 Ah in the standard charging, which is close to the manufacturer's suggested capacity of 2 Ah at 1C. The long-term cycling tests showed that the LIBs did not exhibit a noticeable capacity loss during the 350 fast charging cycles or the 350 standard charging cycles. Also, it should be noted that during the fast charging cycle test, the measured charging capacity was consistent, while the discharging capacity showed some variations and groupings, as shown in Fig.5(c). These groupings can be attributed to cycling occurring only during working hours with a researcher present in the lab as a safety precursor. For this reason, the battery rest time was not regulated either, although the rest time between charge and discharge was allocated as 5 minutes. The discharging capacity also shows a slight upward trend, indicating Coulombic efficiencies of more than 1. This trend is possible for the following two reasons. The first reason could be the use of constant resistance (1.019 Ω) discharge, which resulted in discharge currents from 4 A (1.9 C) to 2.7 A (1.3 C). This discharge scheme resulted in a

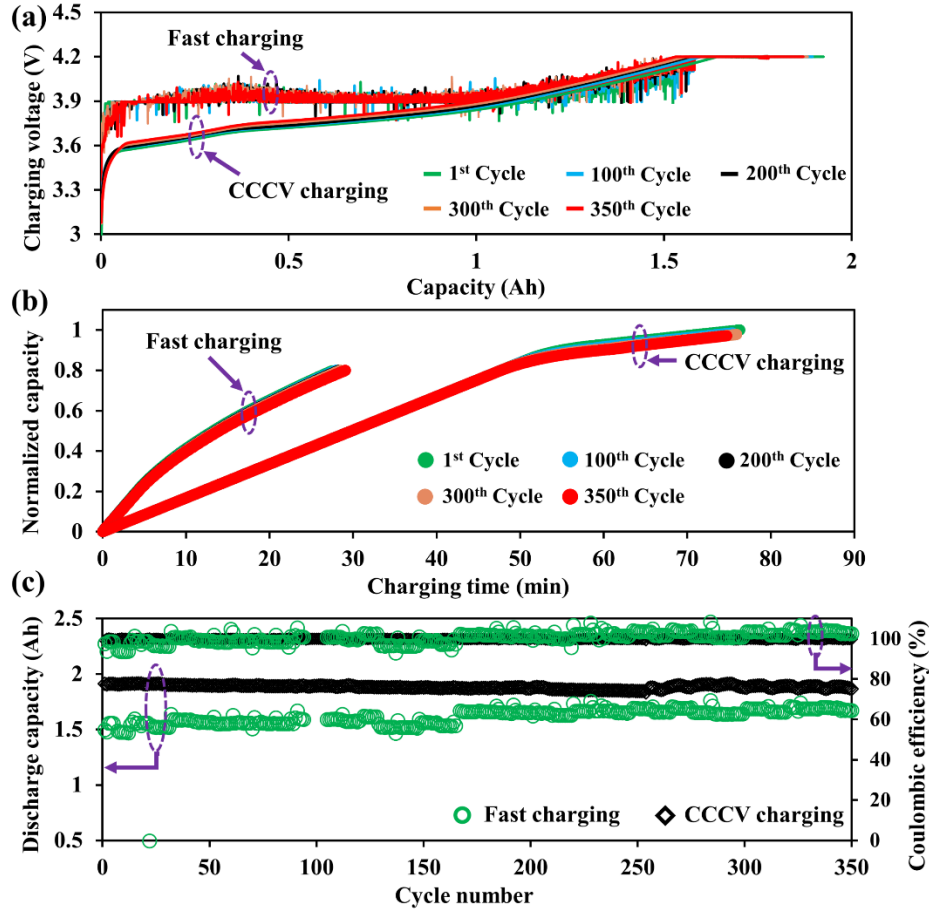


Figure 5. Cycling test of commercial LIB (Sony 18650VTC4) using the proposed fast charging protocol. Performance comparison of cells using fast charging and standard charging (CCCV) protocols in terms of (a) charging voltage vs. capacity, (b) normalized capacity vs. charging time, and (c) discharge capacity vs. cycle number.

slightly smaller average discharging current than the average charging current, leading to slightly higher discharging capacities than the charging capacities. The other source of the upward trend of discharging capacity could be an error in the current sampling and capacity calculation using the integral of the sampled current.

We implemented an algorithm for Coulomb counting to determine cell SoC during charging. This method relies on current sensing and discrete time integration. Current sensing is often susceptible to electrical noise and component tolerances. Also, discrete time integration introduces the sample-and-hold phenomenon, where the sampled value is assumed to be constant during a short period while the microprocessor completes the requisite computations. During this process, some error is inevitable, leading to the cell being charged/discharged to slightly different SoCs. This problem can be mitigated through the use of high-precision components and a high-speed microprocessor. Furthermore, a small gap in the cycling test at about the 100th cycle, as shown in Fig. 5(c), is because of the data loss during the data transfer process from the memory device in the charging hardware to a desktop computer for data processing and plotting.

In order to ensure safety and monitor battery health, the temperature of the LIB and charging hardware was monitored during the fast charging cycling. While the temperature sensor physically touches the cell, heat generated by other parts of the hardware can also affect the overall temperature of the system. Several important

data points are graphed to visualize the different stages of the charging process, as shown in Fig. 6. These points include the maximum and average temperature during charging and discharging and the ambient temperature. Overlaying the ambient temperature allows for visualizing the temperature rise caused by the charging/discharging process. The cell was charged with a maximum 3C charging current while it was discharged with a maximum of 2C, so the charging process is expected to generate more heat than the discharging process, which is apparent in the graph. Furthermore, the figure shows a semi-constant but small temperature rise (maximum temperature rise of about 14 °C) above the ambient temperature, which signifies that the fast charging protocol is not aging or stressing the LIB beyond reasonable limits. Again, the clear grouping of the cycles can be attributed to the cell and the hardware warming up from room temperature and then reaching equilibrium after several cycles.

We note that the protocol used for charging commercial LIBs was not updated throughout the testing period. That means the same charging current profile was used for charging the LIB for 350 fast charging cycles. However, it is desirable to update the charging protocol as the cell ages because degradation of electrodes (especially the anode in our case) in terms of active materials loss and anode slippage, and hence noticeable increase in the electrode impedances, are almost inevitable during the long-term fast charge cycling[52]. This update is crucial regarding cell health and, hence, for the long cycle life of LIBs. This may include gathering information

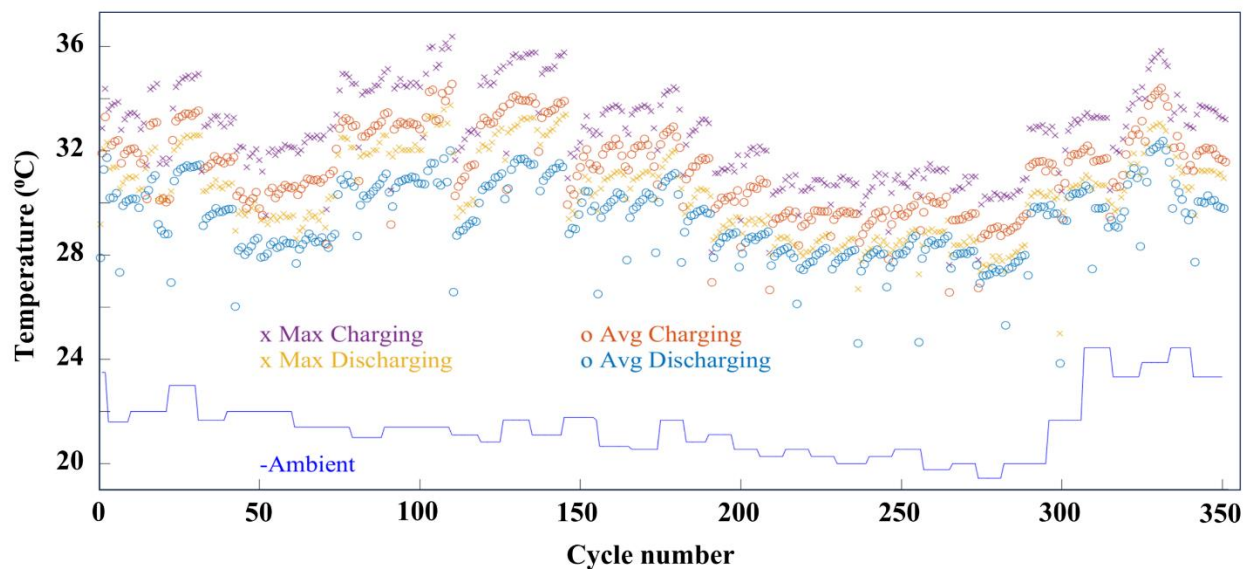


Figure 6. Variation in ambient and cell temperature while cycling the commercial 18650 LIB using the proposed fast charging protocol.

regarding electrode and electrolyte impedance evolution as the cell ages through a series of three-electrode cell measurements, which will require the disassembly of cells at different cycle ages. Requiring cells at different cycle ages and their disassembly can make the whole process complex and challenging as different cells may not

necessarily degrade in the same manner and may result in different current profiles, in addition to the issues with correlating half-cells to full cells, as mentioned in Section 4.2. However, this process is plausible and can result in improved performance in lithium plating control.

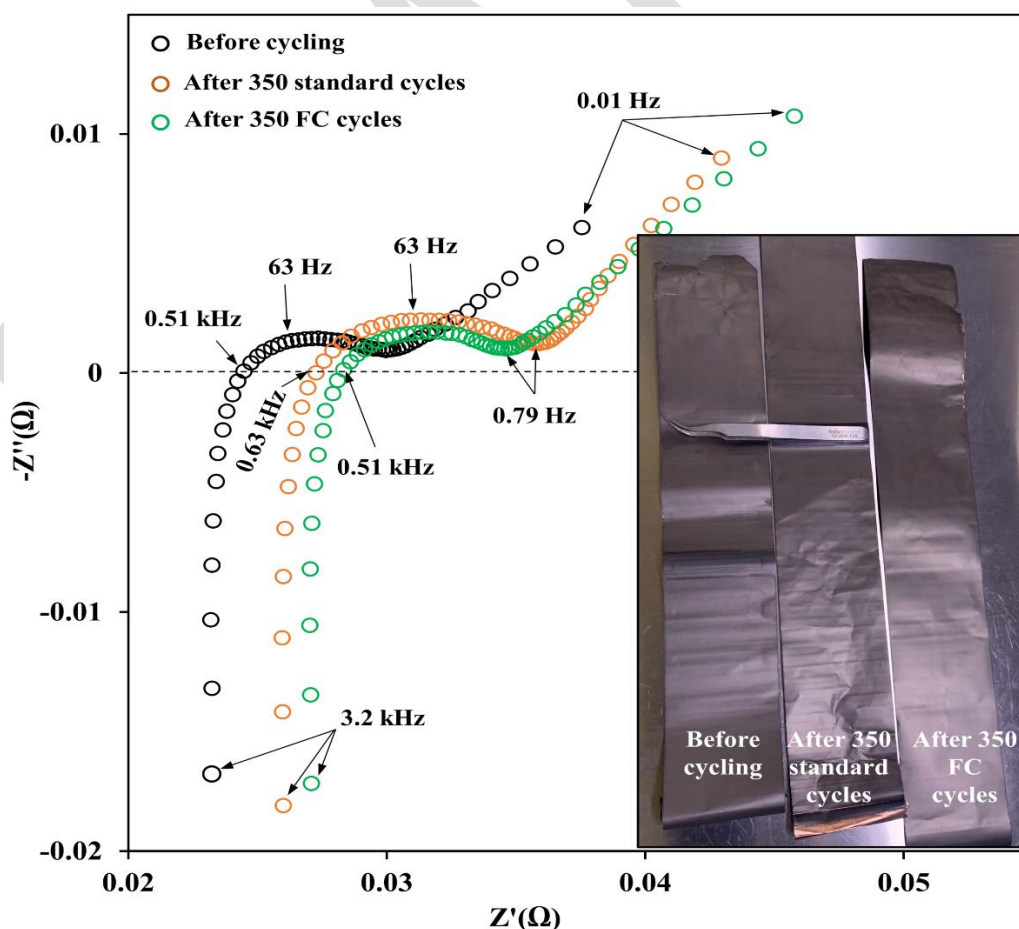


Figure 7. Electrochemical impedance spectra (EIS) of new and aged commercial LIBs. The insets show the optical photographs of the graphite anodes disassembled from the new and aged commercial LIBs.

Finally, the cell aging analysis was carried out using non-destructive and destructive methods. Electrochemical impedance spectroscopy (EIS) tests were conducted on new and aged (standard charge/discharge and fast-charged/discharged for 350 cycles) commercial LIBs. In order to make a fair comparison of LIB impedances, EIS tests were conducted at 3.6 V, and the data are shown in Fig. 7. Although EIS experiments were carried out in the frequency range of 100 kHz and 0.01 Hz, only data points below 3.2 kHz are shown in the graph. The EIS spectra show inductive behavior at high frequencies for all batteries, which can be attributed to the connecting leads of the instrument. Such an inductive effect has been frequently reported for large-capacity commercial LIBs [53, 54]. Apart from that, the impedance spectrum for each LIB consists of a semicircle in the medium-to-low frequency region related to the charge transfer and a straight line inclined w.r.t. the Z' axis related to the solid state diffusion process. As expected, the impedance of the aged LIBs increased slightly compared to the new LIB. However, it is important to note that both aged LIBs exhibited similar impedance evolution with the cycling.

This result further implies that the fast charging protocol is not significantly aging or stressing the LIB compared to the standard charging protocol. Furthermore, we also compared the discharge capacities of the new and aged LIBs (350 fast-charged and standard-charged cycles) using the standard charging/discharging scheme and found no obvious capacity degradation after the fast charging process, as shown in Fig. S5. Finally, the new and aged commercial LIBs were disassembled inside the glovebox to analyze the graphite anode surface. As shown in the inset of Fig. 7, the optical photographs show no signs of obvious lithium plating on both graphite anodes (standard and fast charged) after 350 cycles. Hence, the results obtained from cell aging analysis using non-destructive and destructive methods suggest that the proposed fast charging protocol can rapidly charge the commercial LIBs without lithium plating on the negative electrode, preventing significant cell aging and safety issues.

4. Conclusion

In summary, in this research, we developed an anode-centric fast charging protocol using kinetic/dynamic parameters of the negative electrode measured using a three-electrode lithium-ion cell. Furthermore, we compared the predicted fast charging current with the measured fast charging current at a small cell level. The predicted fast charging current agrees with the measured fast charging current very well. The resistance values associated with various electrochemical events were translated from the three-electrode test

cell level to the commercial cell level using a simple function such as the capacity ratio, and the fast charging current for commercial LIB was predicted. The developed fast charging protocol was employed for cycling commercial LIBs for 350 cycles. This charging method achieved an 80% state of charge (SoC) in 29 minutes, with a maximum temperature rise of 14 °C from the ambient temperature. The time is significantly shorter than that achieved by the 1C CC-CV protocol and comparable to the time achieved by various fast charging protocols reported in the literature. Furthermore, the non-destructive and destructive methods for analyzing cell aging revealed no significant cell capacity degradation nor lithium plating on the anode surface, even after a long cycling test. This important result can be attributed to the fact that the protocol explicitly imposes control over the anode potential to protect the battery from lithium plating. In addition, if the element values in the ECM can be updated as the battery is used, the fast charging current can be updated online or in the field. Therefore, the proposed method paves the way for the development of an adaptive fast charging method that can update the fast charging current as the elements in the battery change.

CRedit authorship contribution statement

Arun Thapa: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft. **Noah Hedding:** Investigation, Hardware, Software, Formal analysis, Writing - original draft, Review & editing. **Hongwei Gao:** Conceptualization, Methodology, Discussion, Formal analysis, Validation, Funding acquisition, Supervision, Review & editing.

Conflict of interest

The authors declare no conflict of interest.

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Supporting Information

S1. Short description of the charging hardware block diagram

The custom cycling system is comprised of an AC to DC converter (TUNS300F12 by Cosel), a synchronous buck converter, a discharging circuit, and a microcontroller unit (MCU). The AC to DC converter converts the 120V AC input from the grid into 12V DC while performing power factor correction. The synchronous buck converter receives the 12V DC from the AC to DC converter and supplies the fast charging current to the battery during charging. The discharging circuit is comprised of a semiconductor switch S_d and a resistor R_d and discharges the battery when S_d is gated on. The MCU controls the synchronous buck converter and the discharging circuit to perform the charging/discharging cycle testing. During charging, the MCU disables the discharging circuit by turning off switch S_d in the discharging circuit and enables the synchronous buck converter by

turning on the PWM controller of the synchronous buck converter. Meanwhile, the MCU samples the output current of the synchronous buck converter and the battery voltage, uses the sampled current and voltage to find the SoC of the battery, and calculates the reference fast charging current according to the proposed fast charging protocol. The control circuitry of the synchronous buck converter implements the closed-loop average current control to ensure the output current of the synchronous buck converter tracks the reference fast charging current provided by the MCU. During discharging, the MCU disables the synchronous buck converter by turning off or shutting down the PWM controller of the synchronous buck converter and enables the discharging circuit by turning on switch S_d in the discharging circuit.

The flow chart for the charging/discharging cycle testing is depicted in Figure 1(c) (main manuscript).

S2. Anode potential and charging current measurement using a three-electrode cell

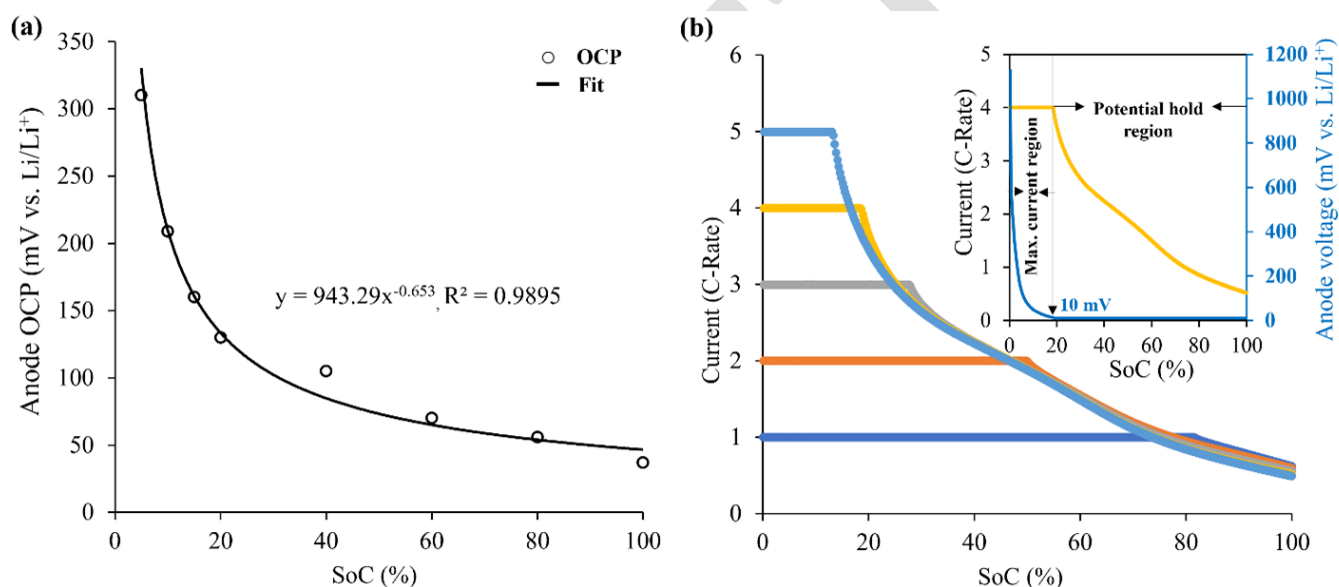


Figure S1. (a) The anode open circuit potential (OCP) measured at various SoCs. (b) Charging currents with different constant C-rates as starting currents measured with the anode potential held at 10 mV vs. Li/Li^+ . The inset in Fig. S1(b) represents the variation of anode potential corresponding to the charging current with the 4C starting current.

S3. Electrochemical Impedance Spectroscopy (EIS)

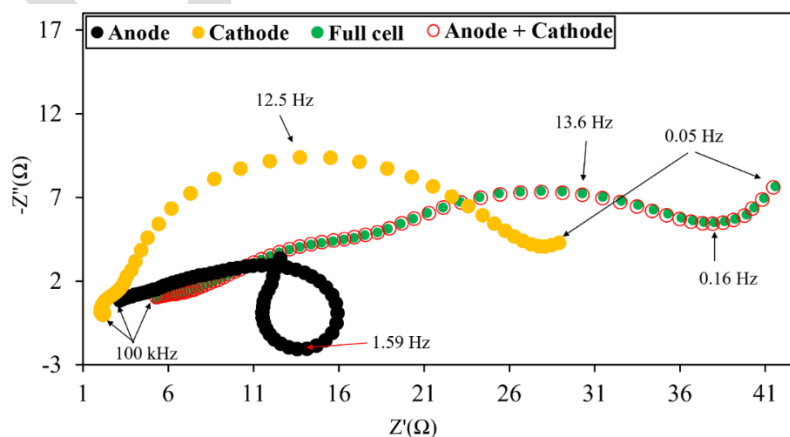


Figure S2. (a) Anode, cathode, full cell, and the sum of anode and cathode impedance spectra measured at 10% SoC while discharging from high to low SoCs.

Fig. S2 shows Electrochemical Impedance Spectroscopy (EIS) of the anode, cathode, and full cell measured at 10 % SoC. The anode and cathode EIS were performed using a reference electrode in the three-electrode configuration, while full cell EIS was recorded in the two-electrode configuration. In addition, the figure also shows an impedance spectrum obtained after adding the anode and cathode EIS spectra. The figure demonstrates that the measured full-cell impedance overlaps very well with the one obtained by adding anode and cathode impedance, implying the full cell impedance variation as per anode and cathode impedance and, hence, a well-functioning test cell.

S4. Estimating the measurement error of the anode potential vs. Li/Li^+ in a three-electrode setup

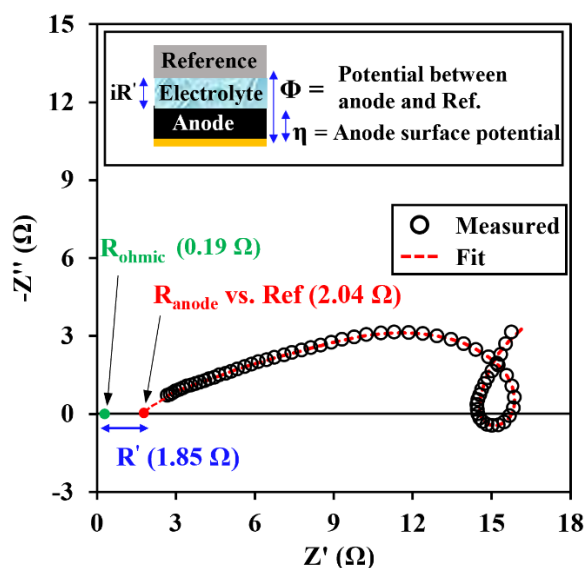


Figure S3. Estimating the measurement error of the anode potential in the three-electrode set up using anode impedance spectrum measured at 10% SoC while charging from low to high SoCs. The inset shows the three-electrode cell structure with different potentials; cathode is not shown for simplicity and clarity.

We estimated the voltage measurement error of the anode potential vs. Li/Li^+ in a three-electrode cell setup using electrochemical impedance spectroscopy (EIS). For this, we adopted the method reported in Ref. [48]. Fig. S3 represents an anode impedance spectrum measured at 10% SoC while charging from low to high SoCs. The green symbol indicates the ohmic impedance of a single graphite (anode) electrode (R_{ohmic}) after subtracting the contribution of cabling (0.04Ω at 100 kHz). The red symbol represents the anode impedance vs. the reference electrode ($R_{\text{anode vs. Ref.}}$) measured using a three-electrode setup. The fitted line was extrapolated to determine the high-frequency (100 kHz) intercept at the Z' -axis. The resistance between the anode and the reference electrode ($R' = 1.85 \Omega$) in the three-electrode cell was determined by subtracting the R_{ohmic} from the $R_{\text{anode vs. Reference electrode}}$. This resistance, R' , is the resistance of the electrolyte between the reference electrode and the anode, as shown in the inset of Fig. S3. Then, the error in the measurement of the anode potential or potential correction factor can be given as $iR' = (\phi - \eta)$ [48], where i is the cell current. In this work, 1C current at a small three-electrode cell level is

1.6 mA. Therefore, the potential correction factor iR' can be calculated as 2.947 mV/C-rate, and at 3C charging, $iR' = 8.842 \text{ mV}$.

S5. Comparison of charging current and time with and without iR' correction

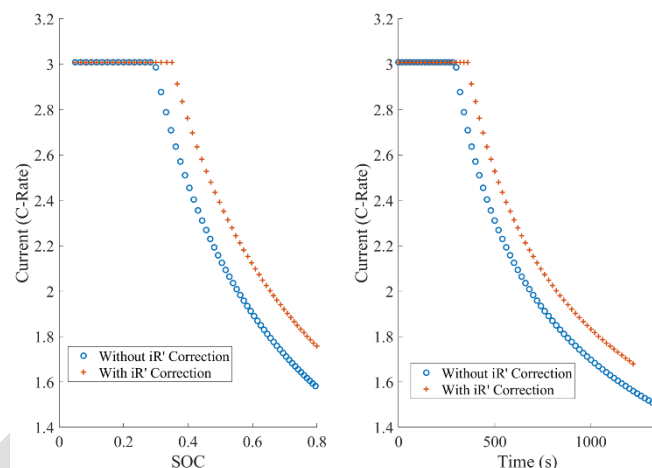


Figure S4. Comparison of charging current and time with and without iR' error correction and with anode potential fixed at 0 V vs. Li/Li^+ . Simulated graphs of (a) C-rate vs. SoC and (b) C-rate vs. time.

We simulated the charging current (max. 3C) and charging time to reach 80% SoC with anode potential at 0 V vs. Li/Li^+ (theoretical limit), with and without correcting the iR' error. Results are depicted in Fig. S4. Simulation revealed that the charging protocol takes 22.52 minutes to reach 80% SoC without the iR' error correction, while with the iR' error correction, the charging time is reduced to 19.85 minutes, an 11.85% improvement in the charging time.

S6. Comparison of discharge capacity of new and aged (350 cycles) commercial Sony 18650VTC4 LIBs

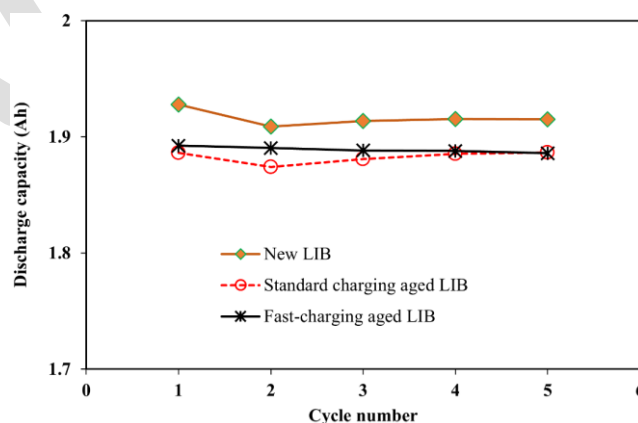


Figure S5. Comparison of discharge capacities of new and aged (350 cycles) commercial LIBs for five cycles.

Fig. S5 compares discharge capacities of new and aged (350 standard and fast-charged cycles) commercial LIBs. In this comparison, the first five cycles from the new LIB, five cycles after 350 cycles from the standard (1C CC-CV) cycled LIB and five cycles from the fast-charged LIB were considered. Furthermore, commercial LIBs were charged to 4.2 V using the 1C CC-CV method and discharged with a 1C constant current to 2.5 V. The figure displays no significant degradation ($< 2\%$) in the discharge capacity for both aged LIBs.

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GRAPHICAL ABSTRACT

