#### **ORIGINAL PAPER**



### Electrochemical characterization tools for lithium-ion batteries

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#### Abstract

Lithium-ion batteries are electrochemical energy storage devices that have enabled the electrification of transportation systems and large-scale grid energy storage. During their operational life cycle, batteries inevitably undergo aging, resulting in a gradual decline in their performance. In this paper, we equip readers with the tools to compute system-level performance metrics across the lifespan of a battery cell. These metrics are extracted from standardized reference performance tests, also known as diagnostic tests, conducted periodically during battery aging experiments. We analyze the diagnostic tests from a publicly available dataset (Pozzato et al. in Data Brief 41:107995, 2022) that consists of the capacity test, high pulse power characterization test, and electrochemical impedance spectroscopy. We provide detailed calculation methodologies and MATLAB<sup>®</sup> scripts required to extract capacity, energy, state-of-charge, state-of-energy, open-circuit voltage, internal resistance, power, incremental capacity, and differential voltage. The MATLAB<sup>®</sup> scripts developed to generate the plots in this paper have been made accessible to the public (Ha et al. in Mendeley Data, V3, 2023). The primary objective of this paper is to provide an accessible guide for undergraduate and graduate students, educators, and researchers interested in characterizing the performance and health metrics of batteries. Such characterizations are critical to the development of battery aging models that can be used to improve cycle life estimation and advance battery management system algorithms.

**Keywords** Lithium-ion batteries  $\cdot$  Battery aging experiments  $\cdot$  Diagnostic tests  $\cdot$  Reference performance tests  $\cdot$  Capacity test  $\cdot$  High pulse power characterization (HPPC)  $\cdot$  Electrochemical impedance spectroscopy (EIS)  $\cdot$  Battery management system (BMS)

#### Nomenclature

Ε	Extracted energy [Wh]
$E_{dis}$	Discharged energy [Wh]
$E_{fade}$	Energy fade [%]
$\vec{E_n}$	Nominal energy [Wh]
$E_{target}$	Energy target [Wh]
Ι	Applied current [A]
$\Delta I_{chg}$	Charge pulse current in HPPC test [A]
$\Delta I_{dchg}$	Discharge pulse current in HPPC test [A]
N <sub>tot</sub>	Total number of diagnostic tests [-]
$OCV_{dchg}$	Open-circuit voltage in discharge [V]
P <sub>dchg</sub>	Discharge power [W]
P <sub>fade</sub>	Power fade [%]
P <sub>avail</sub>	Available power [W]

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Q	Extracted capacity [Ah]
$Q_{dis}$	Discharged capacity [Ah]
$Q_{\it fade}$	Capacity fade [%]
$Q_n$	Nominal capacity [Ah]
$Q_{stored}$	Stored capacity [Ah]
$R_0$	Ohmic resistance $[\Omega]$
$R_{0,chg}$	Charge ohmic resistance $[\Omega]$
$R_{0,dchg}$	Discharge ohmic resistance $[\Omega]$
R <sub>0,increase</sub>	Relative resistance increase [%]
R <sub>ct</sub>	Charge-transfer resistance $[\Omega]$
$R_p$	Polarization resistance $[\Omega]$
V	Cell terminal voltage [V]
$V_{max}$	Upper cutoff voltage [V]
$V_{min}$	Lower cutoff voltage [V]
$V_n$	Nominal voltage [V]
$V_0$	Equilibrium voltage just before $\Delta I_{dchg}$ is applied
	in HPPC test [V]

#### Subscripts

Diag.#N	<i>N</i> th Diagnostic test, $N = 1, 2,, N_{tot}$
pM	<i>M</i> th HPPC pulse number, $M = 1, 2,, 9$

Acronyms	
AC	Alternating current
BMS	Battery management system
BOL	Beginning-of-life
CC	Constant current
CV	Constant voltage
DC	Direct current
DOD	Depth-of-discharge
DV	Differential voltage
EIS	Electrochemical impedance spectroscopy
EOL	End-of-life
EV	Electric vehicle
eVTOL	Electric vertical take-off and landing
Gr	Graphite
HPPC	High pulse power characterization
IC	Incremental capacity
LAM	Loss of active material
LFP	Lithium iron phosphate
LIB	Lithium-ion battery
LLI	Loss of lithium inventory
NMC	Nickel-manganese-cobalt
OCV	Open-circuit voltage
RPT	Reference performance tests
RUL	Remaining useful life
SEI	Solid electrolyte interphase
Si-Gr	Silicon-graphite
SOC	State-of-charge
SOE	State-of-energy
SOH	State-of-health
UDDS	Urban dynamometer driving schedule

#### Introduction

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The lithium-ion battery (LIB) is considered one of the most effective electrochemical energy storage technologies due to its high energy and power densities [3]. Over the past decade, LIBs have revolutionized our lives, enabling the electrification of transportation systems and large-scale grid energy storage.

The growing demands of LIBs for electric vehicle (EV), aviation, and grid storage applications have underscored the importance of battery engineering infrastructure to ensure safety and reliability during real-time operation (Fig. 1). Incorrect battery operation in these contexts can lead to severe consequences from stranded EV drivers and fatalities in electric vertical take-off and landing (eVTOL) aircrafts. At the heart of this infrastructure lies the battery management system (BMS), wherein algorithms are developed to estimate and predict vital information about the battery, such as state-of-health (SOH) and remaining useful life (RUL) [4].



**Fig. 1** Growing demands of LIBs in transportation and energy storage systems [5]. Ensuring the safety and reliability of batteries is critical in these applications

Accurate SOH estimation and RUL prediction in the BMS rely on the development of degradation models using battery aging data. To obtain such aging data, the cycling protocol in a battery experimental aging campaign is designed to mimic the usage conditions specific to a particular application [1, 6, 7]. Throughout this cycling experiment, standardized reference performance tests (RPT), also referred to as diagnostic tests, are periodically conducted to assess and monitor the cell's performance. These non-invasive tests yield valuable insights into system-level performance metrics, such as capacity, energy, resistance, and power. Moreover, these metrics are monitored throughout the battery's lifespan and used to quantify aging in the form of health indicators.

To prepare students for the emerging needs in LIB industry, we have expanded upon the curriculum from Stanford University's graduate course, *ENERGY 295: Electrochemical Energy Storage Systems: Modeling and Estimation*, to create an educational resource on system-level analysis of LIBs. This course was built upon a series of manuals released by the US Department of Energy, namely the *Battery Test Manual For Plug-In Hybrid Electric Vehicles* [8] and *Battery Test Manual for Electric Vehicles* [9], which offer diagnostic test procedures and analysis methods for characterizing battery performance.

In this paper, a systematic set of tools is provided to quantify performance and health indicators using diagnostic tests from a publicly available battery aging dataset [1]. As far as the authors are concerned, this is the first paper of its kind to provide step-by-step procedures, MATLAB<sup>®</sup> scripts, and analysis on experimental data. The MATLAB<sup>®</sup>



**Fig. 2** Schematic of a LIB in discharging whereby the lithium-ions migrate from the negative to positive electrode through the separator via the liquid electrolyte. The electrons also move from the negative to positive electrodes via the external circuit to maintain charge balance in the electrodes

scripts developed to generate the results shown in this paper are available online [2].

The paper is structured as follows: brief information about the battery operation principles and aging phenomena are provided for context, followed by an overview of the diagnostic tests under analysis. The paper is then organized into modules, with each module serving as a dedicated lesson plan. Module 1 focuses on extracting capacity and energy from the capacity test, calculating capacity fade and energy fade to illustrate the cell's aging behavior. Module 2 outlines the calculation methods for state-of-charge (SOC) and state-of-energy (SOE), which are important internal states in the battery. Module 3 explains the estimation of the open-circuit voltage (OCV) curve using two methods: one based on the capacity test and the other utilizing the HPPC test. In Module 4, the high pulse power characterization (HPPC) test is used to quantify the direct current (DC) internal resistance and power capability while electrochemical impedance spectroscopy (EIS) is used to obtain impedance characteristics at different frequency regions. The cell aging is quantified in terms of resistance increase and power fade. In Module 5, the capacity test is used to obtain incremental capacity (IC) and differential voltage (DV) curves to highlight the voltage changes during battery aging.

#### Lithium-ion battery aging and diagnostic tests

#### Lithium-ion battery operation principles

A LIB consists of key components including the positive and negative porous electrodes, a porous separator layer, liquid electrolyte, and two current collectors as shown in Fig. 2. The current collectors play a crucial role as conductive foils attached to the electrodes, connecting the battery to an external circuit and facilitating the flow of electricity between the electrodes and the external circuit. In contrast, the separator layer is positioned between the electrodes, serving as a barrier to prevent electrical shorting. The positive and negative electrodes are reservoirs that contain the lithium-ions (positive electric charge) and the electrons (negative electric charge). During battery discharge, a spontaneous oxidation reaction occurs inside the negative electrode [10], which leads to movement of electrons from the negative to the positive electrode via the external electric circuit, generating usable electricity in the battery. Loss of negatively charged species causes a charge imbalance at the negative electrode. To offset this imbalance, the lithium-ions move from the negative to the positive electrode via a liquid medium called the electrolyte that permeates the pores in the electrodes and separator [10]. During charging, work is done on the battery by a power supply that causes electron movement from the positive to negative electrode, reversing the direction of electron and lithium-ion flow.

#### **Battery aging**

LIB aging occurs during both storage (calendar aging) and operation (cycling aging) and downgrades the performance in the form of capacity and energy loss and power fade. This degradation is attributed to various intricate micro-scale mechanisms, including the solid electrolyte interphase (SEI) layer growth, lithium plating, electrolyte decomposition, and active material particle fracture in the electrode [11]. These mechanisms collectively give rise to observable changes in the cell level, referred to as degradation modes. In LIBs, the dominant degradation modes are loss of lithium inventory (LLI) in the negative electrode due to SEI layer growth and loss of active material (LAM) in the positive and negative electrodes arising from active material particle cracking or delamination from the conductive binder [11]. The LLI causes a reduction in the cyclable lithium, and the LAM reduces the number of lithiation sites. Readers can refer to Edge et al. [11] for a comprehensive review of the battery degradation mechanisms and modes.

#### **Diagnostic tests**

Diagnostic tests, or RPTs, are standardized cell characterization tests performed periodically throughout the battery aging experimental campaign to evaluate and track the cell performance. In the dataset employed in this paper [1], ten LG INR21700-M50T cylindrical cells with cell names W3, W4, W5, W7, W8, W9, W10, G1, V4, and V5 were tested in a temperature controlled thermal chamber at 23 °C. These cells have a nickel-manganese-cobalt (NMC) positive electrode, specifically high-nickel NMC811, and silicon-graphite (Si-Gr) negative electrode with a nominal capacity of 4.85 Ah, an upper cut-off voltage of 4.2 V, and lower cut-off voltage of 2.5 V, as specified by the manufacturer (Table 1 of Appendix 2). Refer to Appendix Fig. 3 Diagnostic tests for cell W8. Light-to-dark grayscale indicates progressive battery aging. a Capacity tests conducted at C/20 in discharge. b EIS data at 50% SOC. c HPPC test current profile and voltage response. Discharge and charge pulse sequence applied (numbered from 1 to 9) at every 10% SOC increments. Positive current is for discharging, and negative current is for charging. d Zoomed-in window showing the 1st, 2nd, and 3rd discharge and charge current pulses and the 1C discharge pulses to remove 10% SOC. Following the 1C discharge, a 1-h rest period is enforced before the next current sequence is applied. e Zoomed-in view of the 3rd HPPC pulse sequence. Discharge current pulse ( $\Delta I_{dchp}$ ) applied for 12 s, rest period for 40 s, and charge current pulse  $(\Delta I_{chg})$  applied for 12 s, where  $\Delta I_{chg} = 0.75 \Delta I_{dchg} [9]$ 



2 for more information on the cycling protocol used in this dataset. While our analysis primarily focuses on cell W8, the accompanying code [2] developed for this paper allows users to reproduce the results presented here for all ten cells.

The diagnostic tests conducted in this dataset are the most widely adopted LIB diagnostic tests: the capacity test, EIS, and HPPC test. Note that there are other diagnostic tests such as the galvanostatic intermittent titration technique (GITT) and the pulsed multisine signal tests. Readers are referred to Barai et al. [12] for a comprehensive review of LIB diagnostic testing methods.

Figure 3 shows the applied current and measured voltage from the capacity test and HPPC test, and the EIS data from cell W8 for all the diagnostic tests conducted throughout the cycling experiment. The progressive aging is indicated by the light-to-dark grayscale colors from Diag.#1 to Diag.#15. The first set of diagnostic tests are conduced prior to the cycling experiment to quantify the fresh cell performance (Diag.#1). Subsequently, the diagnostic tests are conducted after a predefined number of cycles as shown in Table 3 of Appendix 2. Readers can refer to Pozzato et al. [1] for more information on the experimental setup.

The capacity test is used to assess the discharged capacity and energy throughout battery life. The test consists of discharging the battery at constant current (CC) with a C-rate<sup>1</sup> of C/20 from a fully charged condition (4.2 V) until the lower cutoff voltage (2.5 V) is reached (Fig. 3a). A low current is employed during the capacity test [13] to minimize cell polarization and ensure the complete extraction of the battery's capacity. Although we employed C/20, a C/3 rate [12] can also be used in the capacity test, which reduces the testing

<sup>&</sup>lt;sup>1</sup> For the formal definition of C-rate, refer to Appendix 1.

duration from 20 h to 3 h. When performed at a sufficiently low C-rate, such as C/20 or lower, the capacity test can be used to approximate the OCV curve<sup>2</sup>, which is called the pseudo-OCV curve, and calculate the IC-DV curves that highlight the thermodynamic signatures of the cell. For greater accuracy, it is possible to use C/40 or C/50 at the expense of increasing the experiment time to 40 h and 50 h, respectively.

The HPPC test is used to extract the high-frequency DC resistance, which directly correlates to the power capability of the cell. The process involves characterizing the resistance by applying a sequence of discharge and charge current pulses at evenly spaced SOC values (numbered from 1 to 9 in Fig. 3c) while the battery is discharging. In this dataset, the current pulses are applied at every 10% SOC increments, where the first pulse is applied at 90% SOC and the last pulse (9th pulse) is applied at 10% SOC. Figure 3d shows the zoomed HPPC current pulse sequence consisting of a discharge current pulse  $(\Delta I_{dchg})$  applied for 12 s, rest period for 40 s, and a charge current pulse ( $\Delta I_{chg}$ ) applied for 12 s, where  $\Delta I_{chg} = 0.75 \Delta I_{dchg}$ as specified in the DOE battery testing manual [9]. Subsequently, a 1C discharge pulse is applied to remove 10% of the SOC, and the battery undergoes a resting period of 1-h before the next pulse sequence is repeated. For the dataset used in this paper, the HPPC test was exclusively conducted during battery discharging. However, the HPPC test can also be performed during the charging process if needed as noted in the DOE battery testing manual [9].

The EIS test is used to characterize the impedance in the battery by applying a small sinusoidal voltage signal over a wide frequency range and measuring the current response.<sup>3</sup> The EIS<sup>4</sup> data used in this paper is conducted at frequencies spanning from 10 mHz to 10 kHz at 20%, 50%, and 80% SOC [1]. EIS enables the deconvolution of complex electrochemical processes in the frequency domain due to the distinct relaxation times exhibited by different electrochemical processes in LIBs, such as charge-transfer reactions in the electrode and lithium-ion diffusion in the active material particles<sup>5</sup> [16]. The EIS results are typically presented in the

form of a Nyquist plot to characterize the frequency response in the complex plane [12], where the *x*-axis is the real part of the impedance, Re(Z), and the *y*-axis is the negative of the imaginary part, Im(Z). Figure 3b shows the Nyquist plot at 50% SOC throughout aging, with each point in the plot representing a measurement conducted at a specific frequency.

#### Module 1: capacity and energy

#### **Capacity calculation**

Extracted capacity Q quantifies the amount of charge stored in a battery. While the SI unit for capacity is coulomb (C), this unit is often too small to represent the typical amount of charge in LIBs [17]. For a more practical unit, engineers frequently use ampere-hours (Ah) with a conversion factor of 1 Ah = 3600 C. The extracted capacity is calculated by finding the area under the current versus time curve and given by the following equation:

$$Q(t) = \underbrace{\frac{1}{3600} \int_{t_0}^{t} I(\tau) d\tau}_{Ah}$$
(1)

where  $I(\tau)$  is the discharge current applied to the battery in ampere (A) at a given time instant  $\tau$  and Q(t) is the extracted capacity in Ah from an initial time  $t_0$  to a certain point in time t. Since  $I(\tau)$  is recorded at every time instant measured in seconds,  $\frac{1}{3600}$  is used to convert Q(t) from ampere-seconds (A · s) to Ah.

The capacity test consists of slowly discharging the battery at C/20 with a CC amplitude from  $t_0$  to  $t = t_f$ , where  $t_0$ corresponds to 100% SOC at the upper cutoff voltage  $V_{max}$ = 4.2 V and  $t_f$  corresponds to 0% SOC at the lower cutoff voltage  $V_{min} = 2.5$  V. The total extracted capacity from the capacity test is called the discharged capacity ( $Q_{dis}$ ) and calculated as

$$Q_{dis} = \frac{1}{3600} \int_{t_0}^{t_f} I(\tau) d\tau$$
  
=  $\frac{1}{3600} \cdot I \cdot (t_f - t_0)$  (2)  
where  $\begin{cases} t_0 : 100\% \text{ SOC at } V_{max} = 4.2 \text{ V} \\ t_f : 0\% \text{ SOC at } V_{min} = 2.5 \text{ V}. \end{cases}$ 

It is worth noting that  $Q_{dis}$  is dependent on temperature. Figure 4 shows the comparison of the fresh cell  $Q_{dis}$  at 10 °C, 23 °C, and 40 °C ( $Q_{dis} = 4.79$  Ah at 10 °C,  $Q_{dis} = 4.84$  Ah at 23 °C, and  $Q_{dis} = 4.89$  Ah at 40 °C). At 10 °C,  $Q_{dis}$  is 1% lower than the  $Q_{dis}$  at 23 °C, and at 40 °C, the  $Q_{dis}$  is 0.7% higher than the  $Q_{dis}$  at 23 °C. This temperature-dependent

<sup>&</sup>lt;sup>2</sup> Galvanostatic intermittent titration technique (GITT) can be used instead of the capacity test to estimate the OCV curve with higher accuracy but at the expense of a longer experiment duration (~70 h) compared to 20 h for the C/20 capacity test [12].

<sup>&</sup>lt;sup>3</sup> An AC (alternating current) can be applied, and the voltage response can be measured instead [12].

<sup>&</sup>lt;sup>4</sup> To conduct an EIS test, dedicated EIS hardware is required. For more information on the hardware used, refer to Pozzato et al. [1].

<sup>&</sup>lt;sup>5</sup> To interpret EIS data, one can employ electrical circuit models (ECM), which utilize circuit elements to represent different impedances, such as resistors for ohmic resistance and capacitors and resistors in parallel for the charge-transfer resistance [14]. Alternatively, model-free approaches like distributed of relaxation times (DTR) analysis can also be used for impedance deconvolution and interpretation [15]. In this paper, we limit our discussion to extracting internal resistance metrics from the Nyquist plots.



**Fig. 4** Discharged capacity  $Q_{dis}$  at 10 °C, 23 °C, and 40 °C from C/20 capacity tests conducted on a fresh INR21700-M50T cell. As expected,  $Q_{dis}$  increases with higher temperature since the chemical reaction rate and the electrochemical transport properties such as conductivity and diffusivity in the electrolyte and electrode increase according to the Arrhenius equation [18]

variation is expected and attributed to the fact that as temperature decreases, less capacity is extracted due to sluggish kinetics and slower lithium-ion diffusion [18].

Listing 1 shows a MATLAB<sup>®</sup> function to calculate Q and  $Q_{dis}$  using the commands cumtrapz and trapz. These functions are used to perform numerical integration using the trapezoidal method, which approximates the area under the graph by subdividing the area into a series of trapezoids [19]. In the code displayed in Listing 1,  $Q = 1/3600 \times \text{cumtrapz}(t, I)$  computes the cumulative trapezoidal integral of the vector I with respect to the spacing defined in the vector t. This operation yields the vector Q, with each element representing the cumulative sum of the integrated values at each point in t [19]. In contrast,  $Q_{dis} =$ 

1/3600\*trapz(t, I) calculates the scalar value Q\_dis, which is the total integral of the vector I with respect to the spacing defined in the vector t [20]. By definition, the last element in the vector Q is equal to the Q\_dis value.

Using the output Q from Listing 1, the command plot (Q, V) is utilized to plot the measured voltage during the C/20 capacity test as a function of the calculated Q. Figure 5 shows the plots for cell W8 at every diagnostic test. The zoomed-in window shows that  $Q_{dis}$  can be extracted from the intersection of the voltage curve with the x-axis when the cutoff voltage 2.5 V is reached, helping to visualize capacity fade as the battery ages. The fresh cell discharged capacity is  $Q_{dis,\text{Diag},\#1} = 4.88$  Ah whereas at the last diagnostic test it is  $Q_{dis,\text{Diag},\#15} = 4.46$  Ah.

#### **Energy calculation**

Energy is another metric used to measure the battery performance. The SI unit for energy is joules (J) while watt-hours (Wh) is commonly used for battery characterization and BMS applications. Unlike capacity, which quantifies the charge stored in a battery, energy provides information about the battery's work capability, considering not only the charge content but also the electrical potential associated with that charge.

The extracted energy E(t) is calculated as

$$E(t) = \underbrace{\frac{1}{3600} \int_{t_0}^t V(\tau)I(\tau) d\tau}_{Wh}$$
(3a)

<pre>Listing 1 capacity_ energy_calculations.m</pre>	<pre>function [Q, Q_dis, E, E_dis]=capacity_energy_calculations(t, I, V) % INPUTS: % t = current and voltage acquisition time vector [s] % (for this dataset, sampling rate is 1 s) % I = current vector applied to the cell [A] % (positive I: discharging) % V = measured voltage vector [V] % OUTPUTS:</pre>	1 2 3 4 5 6 6 7 7 8 8 9 9 1 1 1 1 1 1 1 1 1 1 1 1
	<pre>% Calculate the discharged capacity Q_dis % NOTE: Q_dis = Q(end) Q_dis = 1/3600*trapz(t, I); % Calculate the discharged energy E_dis % NOTE: E_dis = E(end) E_dis = 1/3600*trapz(t, V.*I); end</pre>	2 2 2 2 2 2 2 2 2



**Fig. 5** Voltage from C/20 capacity test plotted against extracted capacity Q at each diagnostic test for cell W8. The intersection of the *x*-axis with the voltage curve corresponds to the discharged capacity  $Q_{dis}$ . This visualization method provides a clear way to track the diminishing capacity of the battery over time. Discharged capacity of the fresh cell is  $Q_{dis,\text{Diag},\#15} = 4.88$  Ah whereas for the aged cell it is  $Q_{dis,\text{Diag},\#15} = 4.46$  Ah

$$=\underbrace{\frac{1}{3600}\int_{t_0}^{t}P(\tau)\,d\tau}_{Wh}$$
(3b)

where  $I(\tau)$  is the discharge current applied to the battery in ampere (A) at a given time instant  $\tau$ ,  $V(\tau)$  is the measured terminal voltage in volts (V) at time  $\tau$ ,  $P(\tau)$  is the measured power in watts (W) at time  $\tau$ , and E(t) is the extracted energy in Wh from an initial time  $t_0$  to a certain point in time t. Since  $I(\tau), V(\tau)$ , and  $P(\tau)$  are recorded at every time instant measured in seconds,  $\frac{1}{3600}$  is used to convert E(t) from wattseconds (W  $\cdot$  s) to Wh. Equation (3a) can be used with available current and voltage data. If the direct power measurement is available, the power can be integrated as a function of time to calculate E(t) as shown in Eq. (3b).

We define the discharged energy  $(E_{dis})$  as the total energy extracted from the battery from  $t_0$  (100% SOC at  $V_{max} = 4.2$  V) to  $t_f$  (0% SOC at  $V_{min} = 2.5$  V) during the C/20 capacity test.<sup>6</sup> The total discharged energy  $(E_{dis})$  is calculated as

$$E_{dis} = \frac{1}{3600} \int_{t_0}^{t_f} V(\tau) I(\tau) d\tau$$
  
=  $\frac{1}{3600} \int_{t_0}^{t_f} P(\tau) d\tau$  (4)  
 $t_0 : 100\%$  SOC at  $V_{max} = 4.2$  V

where  $\begin{cases} t_0 : 100\% \text{ SOC at } V_{max} = 4.2 \text{ V} \\ t_f : 0\% \text{ SOC at } V_{min} = 2.5 \text{ V}. \end{cases}$ 



**Fig. 6** Voltage from C/20 capacity test plotted against extracted energy *E* at each diagnostic test for cell W8. The intersection of the *x*-axis with the voltage curve corresponds to the discharged energy  $E_{dis}$  to visualize the energy fade at each diagnostic test. The fresh cell discharged energy is  $E_{dis,\text{Diag},\#1} = 17.9$  Wh whereas for the aged cell it is  $E_{dis,\text{Diag},\#15} = 16.4$  Wh

Listing 1 shows the MATLAB<sup>®</sup> script to calculate *E* and  $E_{dis}$  using the commands cumtrapz and trapz, which were also used to calculate *Q* and  $Q_{dis}$ . Using the command plot (E, V), the measured voltage is plotted as a function of extracted energy *E* at each diagnostic test in Fig. 6. The zoomed-in window shows that the intersection of the voltage with the *x*-axis corresponds to the discharged energy  $E_{dis}$ , which helps to visualize energy fade during battery aging. The fresh cell discharged energy is  $E_{dis,Diag,\#1} = 17.9$  Wh whereas the aged cell discharged energy at the last diagnostic test is  $E_{dis,Diag,\#15} = 16.4$  Wh.

#### Capacity fade and energy fade calculations

Battery aging can be quantified in the form of capacity fade  $(Q_{fade})$  or energy fade  $(E_{fade})$  and calculated as

$$Q_{fade,\text{Diag},\#N} = \left(1 - \frac{Q_{dis,\text{Diag},\#N}}{Q_{dis,\text{Diag},\#1}}\right) \times 100 \quad [\%], \qquad N = 1, 2, ..., N_{tot}$$
(5)

$$E_{fade,\text{Diag},\#N} = \left(1 - \frac{E_{dis,\text{Diag},\#N}}{E_{dis,\text{Diag},\#1}}\right) \times 100 \quad [\%], \qquad N = 1, 2, ..., N_{tot}$$
(6)

where  $Q_{dis,\text{Diag},\#N}$  and  $E_{dis,\text{Diag},\#N}$  are calculated using Eqs. (2) and (4), respectively. The subscript Diag.#N refers to the diagnostic test at  $N = 1, 2, ..., N_{tot}$ , where  $N_{tot}$  is the final diagnostic test performed for the specific cell under analysis. The calculated  $Q_{fade}$  and  $E_{fade}$  are plotted in Fig. 7 as a function of cycle number wherein each data point corresponds to a diagnostic test.

As observed from Fig. 7, the  $Q_{fade}$  and  $E_{fade}$  trends are highly correlated with battery aging. We note that a rapid increase in capacity and energy fade is observed between Diag.#4 and 7 (around cycles 130–150) as labeled in the

<sup>&</sup>lt;sup>6</sup> If the capacity test is conducted at different C-rates, the Ragone plot can be created, a widely adopted method to compare energy storage technologies. The Ragone plot is constructed using the specific energy (Wh/kg) and specific power (W/kg), both of which are derived from the discharged energy  $E_{dis}$  calculated from the capacity test. For more information, refer to Catenaro et al. [21].



**Fig. 7** Capacity fade  $Q_{fade}$  and energy fade  $E_{fade}$  versus cycle number for cell W8.  $Q_{fade}$  and  $E_{fade}$  exhibit similar aging trends. The accelerated aging between Diag.#4 and 7 is highlighted in the dashed box, which could be a result of scheduling issues that forced the battery to be held at 4 V (high SOC) for long periods of time

dashed box. We hypothesize that this behavior could be associated with the battery not being cycled consistently because of scheduling issues (the exit condition of Step 4 in Table 3 shown in Appendix 2 was not met, and the battery was held at 4 V for a long period of time). Storing the battery at high SOC exacerbates battery aging, causing accelerated capacity fade and resistance increase [22]. The Arbin schedule was resumed after Diag.#7 (around cycle 150).

#### Module 2: State-of-Charge (SOC) and State-of-Energy (SOE)

#### SOC calculation

SOC is an internal state of the battery that characterizes the amount of capacity available at a given moment in time. Coulomb counting is commonly used to calculate the SOC by integrating the current from a known initial SOC state such as

$$SOC(t) = SOC(t_0) - \frac{\frac{1}{3600} \int_{t_0}^t I(\tau) d\tau}{Q_n} \times 100 \quad [\%]$$
(7)

where SOC( $t_0$ ) refers to the initial SOC in percent, SOC(t) is the SOC calculated from initial time  $t_0$  to a specific point in time t,  $I(\tau)$  is the applied current in ampere (A) (positive current for discharging) at time  $\tau$ , and  $Q_n$  is the nominal capacity. The nominal capacity is typically specified in the manufacturer's datasheet at a specific C-rate and temperature. For the INR21700-M50T cells, the nominal capacity is 4.85 Ah under conditions of a C/20 discharge rate and a temperature of 25 °C as shown in Table 1 in Appendix 2 [21, 23].

Although coulomb counting is a straightforward method for calculating SOC from experimental data, its implementation in real-world applications, such as in the BMS for EVs, presents several challenges. Due to sensor noise in the BMS, noisy current data will be integrated into the SOC calculation, leading to the accumulation of error over time and potentially inaccurate SOC estimates. In contrast, battery cyclers used in laboratory settings, such as the Arbin equipment, have high-precision sensors that allow users to use coulomb counting to calculate SOC. Another concern is the often unknown initial SOC,  $SOC(t_0)$ , in an EV battery. When an EV is parked and the battery remains at rest, the relationship between OCV and SOC can be leveraged to extract  $SOC(t_0)$ before the vehicle is put into operation again [4]. However, this method faces difficulties when applied to batteries that lack a clear one-to-one relationship between OCV and SOC, such as cells with the lithium iron phosphate (LFP) positive electrode, which exhibits a flat OCV curve as a function of SOC. To address these challenges, SOC estimation in realworld settings necessitates the development of sophisticated BMS models and algorithms. Adaptive filtering methods such as Kalman filters are widely used to perform closedloop SOC estimation during battery operation [4].

Listing 2 soc soe	<pre>function [SOC,SOE]=soc_soe_calculations(time, I, V, Q_dis, E_dis, SOC_</pre>	t0,1
calculations.m	SOE_tO	
	% INPUTS:	2
	% t = current and voltage acquisition time vector [s]	3
	% I = current vector applied to the cell [A]	4
	% (+I: discharging, -I: charging)	5
	% V = measured voltage vector [V]	6
	$% Q_{dis} = discharged capacity from the most recent capacity test [Ah]$	7
	% E_dis = discharged energy from the most recent capacity test [Ah]	8
	% SOC_t0 = initial SOC value [%]	9
	% SOE_tO = initial SOE value [%]	1(
	% OUTPUTS:	17
	<pre>% SOC = calculated state-of-charge vector [%]</pre>	15
	% SOE = calculated state-of-energy vector [%]	13
	%	14
		18
	% Calculate SOC at each point in time	10
	$SOC = SOC_{t0} - cumtrapz(time, I/3600)./Q_dis*100;$	17
	% Calculate SOE at each point in time	18
	SOE = SOE_t0 - cumtrapz(time, I.*V/3600)./E_dis*100;	15
	end	20

Listing 2 shows a MATLAB<sup>®</sup> script to calculate the SOC given the current and time data, initial SOC, and nominal capacity. In this calculation, the nominal capacity  $Q_n$  is taken as the discharged capacity  $Q_{dis}$  extracted from the most recent C/20 capacity test for a given cell, which is computed using Eq. (2). Refer to Fig. 11c to see the SOC calculation during the HPPC test at Diag.#1 for cell W8, calculated using the  $Q_{dis}$  extracted from the C/20 capacity test at Diag.#1 for cell W8, calculated using the  $Q_{dis}$  extracted from the C/20 capacity test at Diag.#1 from the same cell. For the capacity and HPPC tests, the initial SOC is given as SOC( $t_0$ ) = 100% since the initial voltage  $V(t_0)$  corresponds to the upper cutoff voltage  $V(t_0) = V_{max} = 4.2$  V. In cases when  $V(t_0) \neq V_{max}$ , an alternative approach can be used. This method is demonstrated in the "Calculating Initial SOC and SOE" section using the first current pulse sequence in the HPPC test as an example.

We highlight the dependence of SOC on its normalizing factor, the nominal capacity, by showcasing the SOC calculations on C/20 and C/40 capacity tests conducted on a fresh cell. Figure 8a shows the voltage curves from the C/20 and C/40 capacity tests as a function of extracted capacity Q, which is calculated using Listing 1. From the zoomedin window in Fig. 8a, it is apparent that the  $Q_{dis}$  at C/40  $(Q_{dis,C/40} = 4.87 \text{ Ah})$  is slightly higher than that of C/20  $(Q_{dis,C/20} = 4.83 \text{ Ah})$ .<sup>7</sup> Figure 8b illustrates the voltage curves for the C/20 and C/40 capacity tests plotted against SOC, which is calculated using Listing 2. In this figure, the nominal capacity is taken as  $Q_{dis,C/20}$  to calculate the SOC during C/20 capacity test (SOC<sub>C/20</sub>) and as  $Q_{dis,C/40}$  for the SOC calculation during C/40 capacity test (SOC<sub>C/40</sub>). Because the SOC is calculated with respect to the extracted capacity from its corresponding capacity test, the zoomed-in window shows SOC reaching 0% at  $V = V_{min} = 2.5$  V for both C/20 and C/40 curves. In Fig. 8c, the voltage of the C/20 capacity test is plotted as a function of SOC, with the nominal capacity taken as  $Q_{dis,C/40}$ . The zoomed-in window in Fig. 8c shows that the SOC<sub>C/20</sub> = 0.734% at  $V = V_{min}$ , which greater than 0% since  $Q_{dis,C/40} = 4.87$  Ah is greater than  $Q_{dis,C/20} = 4.83$ Ah. If SOC<sub>C/40</sub> is calculated using  $Q_{dis,C/20}$ , the SOC at  $V = V_{min}$  would be less than 0%, which is not consistent with the definition of SOC. As illustrated, the calculation of SOC relies on the nominal capacity. Therefore, SOCs should be interpreted in conjunction with the nominal capacity that was employed to compute the SOC values.

#### SOE calculation

Similar to coulomb counting to calculate SOC, the SOE can be calculated as



**Fig. 8 a** Voltage from C/20 and C/40 capacity tests versus extracted capacity *Q*. Zoomed-in window highlights the extracted discharged capacity values:  $Q_{dis,C/20} = 4.83$  Ah and  $Q_{dis,C/40} = 4.87$  Ah. **b** Voltage from C/20 and C/40 capacity tests versus SOC. The SOC<sub>C/20</sub> calculated with  $Q_n = Q_{dis,C/20}$  and the SOC<sub>C/40</sub> calculated with  $Q_n = Q_{dis,C/20}$  and the SOC is 0% at  $V = V_{min} = 2.5$  V for both C/20 and C/40 curves. **c** Voltage from C/20 capacity test versus SOC, with SOC<sub>C/20</sub> calculated using  $Q_n = Q_{dis,C/40}$ . Since the SOC at  $V = V_{min} = 2.5$  V for both C/20 and C/40 curves. **c** Voltage from C/20 capacity test versus SOC, with SOC<sub>C/20</sub> calculated using  $Q_n = Q_{dis,C/40}$ . Since  $Q_{dis,C/40} > Q_{dis,C/20}$ , the SOC at  $V = V_{min} = 2.5$  V is greater than zero: SOC<sub>C/20</sub> = 0.734%

$$SOE(t) = SOE(t_0) - \frac{\frac{1}{3600} \int_{t_0}^t V(\tau) I(\tau) d\tau}{E_n} \times 100 \quad [\%]$$
(8a)

$$= \text{SOE}(t_0) - \frac{\frac{1}{3600} \int_{t_0}^t P(\tau) d\tau}{E_n} \times 100 \quad [\%]$$
(8b)

where SOE( $t_0$ ) is the initial SOE in percent, SOE(t) is the SOE calculated from initial time  $t_0$  to a specific point in time t,  $V(\tau)$  is the measured terminal voltage in volts (V) at time  $\tau$ ,  $P(\tau)$  is the measured power in watts (W) at time  $\tau$ , and  $E_n$  is the nominal energy<sup>8</sup> in Wh. For the INR21700-M50T

<sup>&</sup>lt;sup>7</sup> The total extracted capacity increases with decreasing discharge C-rate according to Peukert's equation [24].

<sup>&</sup>lt;sup>8</sup> If  $E_n$  is not provided in the manufacturer's datasheet, it can be calculated by multiplying the nominal capacity  $Q_n$  and nominal voltage  $V_n$ , which are typically reported in the datasheet.



Fig.9 SOC and SOE versus time during the C/20 capacity test at Diag.#1 for cell W8

cells, the nominal energy is  $E_n = 17.6$  Wh under conditions of a C/20 discharge rate and a temperature of 25 °C, which was calculated by multiplying the nominal capacity  $Q_n$  and nominal voltage  $V_n$  shown in Table 1 in Appendix 2 [21, 23]. Listing 2 shows a script to calculate SOE. Similar to the SOC calculation, the nominal energy  $E_n$  is taken as the discharged energy  $E_{dis}$  extracted from the most recent C/20 capacity test for a given cell, which is computed using Eq. (4). For the capacity and HPPC tests, the initial SOE is given as  $SOE(t_0) = 100\%$  since the voltage at  $t_0$  corresponds to the upper cutoff voltage  $V(t_0) = V_{max} = 4.2$  V.

Although SOC is commonly used for characterizing the amount of charge stored in a cell, in certain applications such as in grid storage where power measurements are provided, it is more practical to use SOE than SOC [25]. In such cases, Eq. (8b) can be used to calculate SOE. To show the distinction between SOC and SOE, Fig. 9 plots the calculated SOC and SOE during the C/20 capacity test

Fig. 10 a HPPC current profile and voltage response for cell W8 at Diag.#1. On the time axis, the initial time  $\hat{t}_0$  is labeled, which is needed to calculate  $SOE(\tilde{t_0})$ . **b** Zoomed-in view of the 1st pulse sequence and its initial voltage  $V_0$  at time  $\tilde{t_0}$  indicated with the red dot. The initial and final time during the 1st pulse sequence are denoted as  $t_0$  and  $t_f$ , respectively. **c** Pseudo- $OCV_{dchg}$  curve obtained from C/20 capacity test (more information in Module 3). SOC is determined when pseudo- $OCV_{dchg} = V_0$ , resulting in SOC = 93.45%, which is equivalent to  $SOC(\tilde{t_0})$ . d SOC and SOE calculation during the 1st pulse sequence. Initial SOC and initial SOE are calculated and labeled accordingly,  $SOC(\tilde{t_0}) = 93.45\%$  and  $SOE(\tilde{t_0}) = 89.35\%$ 



at Diag.#1 for cell W8. The SOC and SOE were calculated using the  $Q_{dis}$  and  $E_{dis}$  obtained from the C/20 capacity test at Diag.#1 for cell W8, respectively.

#### **Calculating initial SOC and SOE**

For the capacity and HPPC tests, the initial SOC and SOE are given as  $SOC(t_0) = SOE(t_0) = 100\%$  since the initial voltage  $V(t_0)$  corresponds to the upper cutoff voltage  $V(t_0) = V_{max} = 4.2$  V. However, when the initial voltage does not match  $V_{max}$ , a different method needs to be used to determine the initial SOC and SOE.

In this regard, we provide an illustrative example by calculating the initial SOC and SOE for the 1st pulse sequence in the HPPC test. Figure 10a shows the HPPC current profile and voltage response for cell W8 at Diag.#1 with  $\hat{t}_0$  denoting the time at the beginning of the HPPC test. Figure 10b provides a closer look at the 1st pulse sequence, with its initial time denoted as  $\tilde{t}_0$  and final time as  $\tilde{t}_f$ . The goal is to show this 1st pulse sequence's initial SOC, SOC( $\tilde{t}_0$ ), and initial SOE, SOE( $\tilde{t}_0$ ), calculations.

To compute SOC( $\tilde{t_0}$ ), the initial voltage  $V_0$  from the voltage response of the 1st pulse sequence at time  $\tilde{t_0}$  is extracted ( $V_0 = 4.089$  V) and marked with a red circle, as shown in Fig. 10b. Then, the psuedo- $OCV_{dchg}$  curve obtained from the C/20 capacity test is used to determine the SOC value when pseduo- $OCV_{dchg}$  equals the extracted initial voltage  $V_0$ . Refer to Module 3 for more information on the pseudo- $OCV_{dchg}$  curve (Fig. 12). Figure 10c shows the SOC value when pseudo- $OCV_{dchg} = V_0 = 4.089$  V, labeled with a black dot on the x-axis as SOC = 93.45% and equal to the initial SOC of the 1st pulse sequence, SOC( $\tilde{t_0}$ ).<sup>9</sup> Figure 10d shows the SOC calculation of the 1st pulse sequence using Eq. 7 with SOC( $\tilde{t_0}$ ) = 93.45% and the nominal capacity equal to the discharged capacity extracted from the C/20 capacity test at Diag.#1, such that  $Q_n = Q_{dis.Diag.#1}$ .

To calculate the initial SOE, we utilize the HPPC current profile and voltage response shown in Fig. 10a. First, the current and voltage are integrated from the very beginning of the HPPC test at time  $\hat{t}_0$  up to just before the 1st pulse sequence is applied at time  $\tilde{t}_0$  to find the extracted energy from  $\hat{t}_0$  to  $\tilde{t}_0$ . To calculate SOE( $\tilde{t}_0$ ), Eq. 8a is used with the following substitutions:  $E_n = E_{dis,\text{Diag.#1}} = 17.9$ Wh (discharged energy extracted from C/20 capacity test at Diag.#1),  $t_0 = \hat{t}_0$ , and  $t_f = \tilde{t}_0$ . With these substitutions, Eq. 8a is rewritten as

$$SOE(\tilde{t}_0) = \overbrace{SOE(\tilde{t}_0)}^{100\%} - \frac{\frac{1}{3600} \int_{\tilde{t}_0}^{\tilde{t}_0} V(\tau) I(\tau) d\tau}{E_{dis, \text{Diag}, \#1}} \times 100 \quad [\%]$$
<sup>(9)</sup>

where SOE( $\hat{t_0}$ ) equals 100% since  $\hat{t_0}$  refers to the beginning of the HPPC test when  $V = V_{max} = 4.2$  V. This equation yields SOE( $\tilde{t_0}$ ) = 89.35%. Figure 10d shows the SOE calculation using Eq. (8a) with SOE( $\tilde{t_0}$ ) = 89.35% and taking the nominal energy as  $E_n = E_{dis,Diag,\#1}$ .

#### Module 3: Open-Circuit Voltage (OCV) curve

The OCV is defined as the measured terminal voltage when no current flows through the battery [26]. The OCV curve is typically represented as a function of SOC and used in various BMS models to estimate the internal battery states [4, 27, 28]. In this section, we demonstrate two methods to extract the OCV curve, denoted as  $OCV_{dchg}$ , from the HPPC and capacity tests. We distinguish the OCV extracted in charging and discharging due to the inherent hysteresis behavior in LIBs [29, 30]. Since the capacity and HPPC tests in this dataset are performed during battery discharging, we use the subscript "dchg" in  $OCV_{dchg}$  to indicate that the OCV curve is extracted during discharging.

#### Method 1: OCV<sub>dchg</sub> estimation from HPPC test

In the HPPC test, a 1-h rest period is implemented before the application of each current pulse sequence. During this 1-h rest interval, the voltage gradually relaxes to a steadystate value. Given that nine sets of pulse sequences are applied in this HPPC dataset, nine voltage relaxation points are extracted as indicated by the red circles in Fig. 11a. Figure 11b provides a closer look at the voltage relaxation during the 1-h rest period before the 2nd pulse sequence is applied. The voltage relaxation point before the 1st pulse sequence application is labeled as  $V_{0,p1}$ , and the voltage relaxation point before the 2nd pulse sequence application is labeled as  $V_{0,p2}$ . Nine voltage relaxation points, denoted as  $V_{0,pM}$  where M = 1, 2, ..., 9, are extracted for the estimation of the  $OCV_{dchg}$  curve. The SOC during the HPPC test is calculated using Eq. (7) and plotted as a function of time in Fig. 11c, with the red circles corresponding to the SOC values at each extracted  $V_{0,pM}$  point.

Method 2: pseudo- $OCV_{dchg}$  calculation from capacity test Given a capacity test, the voltage can be plotted as a function of SOC, as shown in Fig. 8b. This voltage versus SOC plot is used to approximate the OCV curve and commonly referred to as the pseudo-OCV or the quasi-stationary OCV curve, since the system is not at complete equilibrium due to the low current administered during the capacity test [12, 31]. We denote the pseudo-OCV curve obtained from the capacity test as pseudo- $OCV_{dchg}$ . While we used C/20, a lower C-rate such as C/40 or C/50 can be used to better mimic the zero current condition and minimize ohmic losses at the cost of a longer experiment duration.

<sup>&</sup>lt;sup>9</sup> This method works if the data's initial current is zero  $I(t_0) = 0$ , signifying the OCV condition.

**Fig. 11** Extracted voltage relaxation points from HPPC test for cell W8 at Diag.#1. **a** HPPC current profile and voltage response with the equilibrium voltages indicated with red circles. **b** Zoomed-in plot of **a**, showing the equilibrium voltages  $V_{0,p1}$  and  $V_{0,p2}$  for the 1st and 2nd pulse sequences. **c** SOC calculated during the HPPC test using  $Q_n = Q_{dis,Diag.#1}$  with red circles indicating the SOC values at the voltage relaxation points shown in **a** 



Figure 12 shows the  $OCV_{dchg}$  and pseudo- $OCV_{dchg}$  curves obtained from the HPPC and capacity tests, respectively. The extracted  $V_{0,p1}, V_{0,p2}, ..., V_{0,p9}$  HPPC points are shown in red circles while the pseudo- $OCV_{dchg}$  calculated from the capacity test is represented by the solid line. As one can see, similar results are obtained from the two  $OCV_{dchg}$  estimation methods. It is worth noting that if more current pulses are applied at smaller SOC increments during the HPPC test,



**Fig. 12**  $OCV_{dchg}$  curve is estimated from the C/20 capacity and HPPC tests for cell W8 at Diag.#1. The red dots indicate the extracted HPPC voltage relaxation points, and the solid line refers to the pseudo- $OCV_{dchg}$  obtained from the capacity test

additional  $V_0$  points can be obtained to improve the accuracy of the  $OCV_{dchg}$  curve construction. However, each extracted  $V_0$  point in the HPPC test necessitates a 1-h rest period. As a result, the HPPC experimental time will increase linearly with the increasing number of desired  $V_0$  values at different SOC points.

#### Module 4: resistance and power

### Hybrid Pulse Power Characterization (HPPC) test: internal resistance calculation

In this module, the internal resistance and power are extracted at every instance a current pulse sequence is applied during the HPPC test. The current pulses are applied in discharge and charge at every 10% SOC increments, where the first pulse occurs at 90% SOC and the last pulse (9th pulse) occurs at 10% SOC as shown in Fig. 11a and c.

Figure 13a shows the current pulse sequence and the voltage response at the 1st pulse. A pictorial representation of the voltage response due to a discharge current

pulse is shown in Fig. 13b: (1) instantaneous voltage drop (purple line) indicates the high-frequency DC resistance in discharge, also called discharge ohmic resistance ( $R_{0,dchg}$ ), resulting from electric and electrolyte ionic resistance; (2) nonlinear voltage drop (orange line) arises from the chargetransfer resistance ( $R_{ct}$ ) at the electrolyte and solid particle interface; and (3) linear voltage drop (green line) is from the polarization resistance ( $R_p$ ) which originates from the lithium diffusion in the solid active material particles [32]. Barai et al. [32] reported that the onset of  $R_p$  occurs around 5 s after the current pulse is applied. In this paper, we extract the high-frequency DC resistance in discharge,  $R_{0,dchg}$ , and in charge,  $R_{0,chg}$ . Readers can refer to Barai et al. [32] to learn more about extracting  $R_{ct}$  and  $R_p$  from the HPPC test.

The HPPC discharge ohmic resistance  $(R_{0,dchg})$  and charge ohmic resistance  $(R_{0,chg})$  are calculated as

$$R_{0,dchg,pM} = \frac{|V_{1,pM} - V_{0,pM}|}{|I_{1,pM} - I_{0,pM}|} = \frac{|\Delta V_{dchg,pM}|}{|\Delta I_{dchg,pM}|}, \quad M = 1, 2, \dots, 9$$
(10a)

$$R_{0,chg,pM} = \frac{|V_{4,pM} - V_{3,pM}|}{|\underbrace{I_{4,pM} - I_{3,pM}}_{I_{4,pM}}|} = \frac{|\Delta V_{chg,pM}|}{|\Delta I_{chg,pM}|}, \quad M = 1, 2, \dots, 9$$

where the subscript *pM* refers to the *M*th pulse sequence with M = 1, 2, ..., 9 since there are nine pulse sequences in the HPPC test. Figure 13a shows the 1st pulse sequence and the labels for  $V_{0,p1}$ ,  $V_{1,p1}$ ,  $V_{3,p1}$ ,  $V_{4,p1}$ ,  $I_{0,p1}$ ,  $I_{1,p1}$ ,  $I_{3,p1}$ , and  $I_{4,p1}$ . As the equation shows, the discharge pulse current  $\Delta I_{dchg,pM}$ is equal to  $I_{1,pM}$  since  $I_{0,pM} = 0$ , and the charge pulse current  $\Delta I_{chg,pM}$  is equal to  $I_{4,pM}$  due to  $I_{3,pM} = 0$ . Since the  $R_{0,dchg,pM}$ and  $R_{0,chg,pM}$  calculations depend on  $\Delta V_{dchg,pM}$  and  $\Delta V_{chg,pM}$ respectively, we recommend using a sampling rate of 0.1 s or smaller to obtain an accurate estimation of the ohmic resistances.

Listing 3 shows a MATLAB<sup>®</sup> script to calculate  $R_{0,dchg,pM}$  and  $R_{0,chg,pM}$  at all the pulses M = 1, 2, ..., 9. The script outputs two vectors, R0\_dchg and R0\_chg, such that each element in the vectors represents the ohmic resistance at each pulse sequence.

Figure 14 shows the calculated  $R_{0,dchg}$  from the 1st to 9th pulse for cell W8 at every diagnostic test. Since the  $R_{0,chg}$  plot exhibits similar resistance values and aging behavior as  $R_{0,dchg}$ , the figure is omitted here for brevity. Although  $R_{0,dchg}$  is commonly expressed as a function of SOC (Fig. 14a), plotting  $R_{0,dchg}$  against the voltage just before the discharge current is applied ( $V_{0,pM}$ ) can be particularly useful for BMS applications wherein voltage measurements are used to infer or estimate internal states in the battery (Fig. 14b). The gradual upward shift



**Fig. 13 a** HPPC discharge and charge current pulse profiles and the voltage response at the 1st pulse. **b** Schematic of the voltage response corresponding to different electrochemical processes due to the discharge current pulse [32]. The instantaneous voltage drop (purple line) indicates the discharge ohmic resistance  $R_{0,dchg}$ , the nonlinear voltage drop (orange line) originates from the charge-transfer resistance  $R_{ct}$ , and the linear voltage drop (green line) is from the polarization resistance  $R_n$  [32]

observed in the curves indicates an increase in internal resistance across the entire SOC range due to aging.

To highlight the effect of aging at different SOCs, the  $R_{0,dchg}$  calculated at each pulse number is plotted as a function of cycle number as shown in Fig. 15. Not only is the resistance higher at low SOC but also the rate of resistance increase is higher as indicated by the larger slope of the 9th pulse.

We define the relative resistance increase  $(R_{0,increase})$  as

$$R_{0,increase,pM,\text{Diag},\#N} = \left(\frac{R_{0,dchg,pM,\text{Diag},\#N}}{R_{0,dchg,pM,\text{Diag},\#1}} - 1\right) \times 100 \quad [\%], \qquad \begin{cases} N = 1, 2, \dots, N_{tot} \\ M = 1, 2, \dots, 9 \\ (11) \end{cases}$$

where  $R_{0,dchg,pM,\text{Diag},\#N}$  refers to the calculated discharge resistance at a given pulse number M and diagnostic test Diag.#N, where  $N_{tot}$  refers to the total number of HPPC diagnostic tests conducted for the specific cell under analysis. In this dataset,  $R_{0,increase,p1,\text{Diag},\#N}$  refers to the relative resistance increase at SOC = 90%,  $R_{0,increase,p2,\text{Diag},\#N}$  at SOC = 80%, and so forth till  $R_{0,increase,p9,\text{Diag},\#N}$  at SOC = 10% for a given diagnostic test Diag.#N. Listing 3 hppc\_R0\_
calculations.m

```
function [R0_dchg, R0_chg]=hppc_R0_calculations(t,I,V)
% INPUTS:----
                                                                           2
%
 time = current and voltage aquisition time vector in HPPC test [s]
                                                                           3
% I = applied current vector in HPPC test [A]
                                                                           4
% (negative I: charging, positive I: discharging)
                                                                           5
% V = measured voltage vector in HPPC test [V]
                                                                           6
% OUTPUTS:------
                                                                           7
 R0_dchg = discharge ohmic resistance [Ohms]
%
                                                                           8
% R0_chg = charge ohmic resistance [Ohms]
                                                                           9
%
% Calculate change in current (delta_I) at every time step
                                                                           12
delta_I = I(2:end) - I(1:(end - 1));
                                                                           13
% Extract indices of large discharge and charge pulses
                                                                           14
tol = 0.01; % conservative tolerance
delta_I_pos_ind = find(delta_I>tol);
delta_I_neg_ind = find(delta_I<-tol);</pre>
                                                                           17
                                                                           18
% Extract indices when I_dchg are applied
                                                                           19
I_dchg_ind = delta_I_pos_ind(2:3:end);
                                                                           20
% Reasoning for (2:3:end):-----
                                                                           21
% 1. delta_I_pos_ind(1) refers to the rising edge of the
                                                                           22
% first 1C discharge pulse applied to reach 90% SOC,
                                                                           23
% so it is neglected.
                                                                           24
 2. Every 3 elements are extracted since the trailing edge of
%
                                                                           25
%
 I_chg pulses and rising edge of the 1C discharge pulses
                                                                           26
% produce positive delta_I.
                                                                           27
%
                                                                           28
% Extract indices when I_chg are applied
                                                                           29
I_chg_ind = delta_I_neg_ind(3:3:end);
                                                                           30
% Reasoning for (3:3:end):-----
                                                                           31
% 1. delta_I_pos_ind(1) refers to the trailing edge of the
                                                                           32
% first 1C discharge pulse applied to reach 90% SOC,
                                                                           33
%
 and delta_I_pos_ind(2) refers to the trailing edge of
                                                                           34
% the first I_dchg pulse, so they are neglected.
                                                                           35
% 2. Every 3 elements are extracted since the trailing edge
                                                                           36
\% of the 1C discharge pulses and the trailing edge of the I_dchg
                                                                           37
% pulses produce positive delta_I.
                                                                           38
                                                                           30
% Find I_dchg and I_chg
                                                                           40
I_dchg = delta_I(I_dchg_ind);
                                                                           41
I_chg = delta_I(I_chg_ind);
                                                                           42
% Find V0,V1 to calculate R0_dchg
                                                                           43
VO = V(I_dchg_ind);
                                                                           44
V1 = V(I_dchg_ind+1);
                                                                           45
% Find V3,V4 to calculate R0_chg
                                                                           46
V3 = V(I_dchg_ind);
                                                                           47
V4 = V(I_dchg_ind+1);
                                                                           48
% Calculate R_dchg
                                                                           49
R0_dchg = abs(V1-V0)./abs(I_dchg);
                                                                           50
% Calculate R_chg
                                                                           51
R0_chg = abs(V4-V3)./abs(I_chg);
end
```

**Fig. 14** Discharge resistance  $R_{0,dchg}$  plotted as a function of **a** SOC and **b** voltage.  $R_{0,dchg}$  calculated at every instance the discharge current pulses (1–9) are applied during the HPPC tests for cell W8. The light-to-dark grayscale colors indicate progressive aging in the form of resistance increase from Diag.#1 to Diag.#15





**Fig. 15** Discharge resistance  $R_{0,dchg}$  at each pulse number versus cycle number for cell W8. Resistance is not only higher at low SOC but also the rate of resistance increase is higher (9th pulse)

In Fig. 16, the relative resistance increase at 50% SOC,  $R_{0,increase,p5}$ , is plotted as a function of cycle number with each point corresponding to a diagnostic test from Diag.#1 to Diag.#15. Capacity fade  $Q_{fade}$  is plotted in the same figure, showing the resemblance in their aging trends. This is congruent with some results reported in the literature that found a correlation between the increase in resistance and reduction in capacity due to certain degradation mechanisms [11]. Figure 16 offers insight into the potential use of internal resistance as a predictor for capacity or energy, which are generally more challenging to estimate compared to internal resistance<sup>10</sup>.

#### Hybrid Pulse Power Characterization (HPPC) test: Power calculation

The discharge power  $(P_{dchg})$  quantifies the maximum available power within the cutoff voltage limits of the battery [9] and is calculated as

$$P_{dchg,pM} = \frac{V_{min} \times (V_{0,pM} - V_{min})}{R_{0,dchg,pM}}, \quad M = 1, 2, \dots, 9 \quad (12)$$



**Fig. 16** Relative resistance increase of the discharge resistance at the 5th pulse (50% SOC)  $R_{0,increase,p5}$  and capacity fade  $Q_{fade}$  as a function of cycle number for cell W8. The 5th pulse is chosen as a demonstration, but any pulse number can be chosen from the HPPC test. The  $R_{0,increase,p5}$  and  $Q_{fade}$  exhibit similar trends during battery aging

where  $V_{min}$  is the lower cutoff voltage (2.5 V),  $R_{0,dchg,pM}$  is the discharge resistance calculated using Eq. (10a),  $V_{0,pM}$ corresponds to the equilibrium voltage used to calculate  $R_{0,dchg,pM}$ , and  $P_{dchg,pM}$  is the discharge power at the *M*th pulse. The charge power can be calculated similarly if the HPPC test in charge is available [9].

The discharge power  $P_{dchg}$  at every HPPC pulse is plotted in Fig. 17 as a function of SOC and voltage at each diagnostic test. As the battery ages, the power capability decreases, which is evident from the downward shift of the power curve across the entire SOC range. This trend is expected, as aging is associated with an increase in discharge resistance  $R_{0,dchg}$ , and there is a direct inverse relationship between  $R_{0,dchg}$  and  $P_{dchg}$  as shown in Eq. (12).

#### Power fade calculation

To determine power fade, we first need to calculate the available power ( $P_{avail}$ ) at every diagnostic test. A detailed methodology is provided here to calculate  $P_{avail}$ , which requires the discharge power  $P_{dchg}$  calculated from the discharge current pulses in the HPPC test and the extracted energy *E* from the C/20 capacity test.

Figure 18 demonstrates how to extract  $P_{avail}$  at Diag.#1 ( $P_{avail,Diag,\#1}$ ) for cell W8. Figure 18a displays the discharge power  $P_{dchg}$  versus SOC plot, which is extracted from the Diag.#1 curve in Fig. 17a. Figure 18b illustrates the extracted energy *E* on the *y*-axis, calculated from the C/20 capacity test at Diag.#1 using Eq. (3a), and SOC on the *x*-axis, calculated during the C/20 capacity test at Diag.#1 using Eq. (7). In Fig. 18a, each  $P_{dchg}$  is associated with a SOC value, which is used to determine the extracted energy *E* value at the same SOC value in Fig. 18b and labeled

<sup>&</sup>lt;sup>10</sup> To calculate internal resistance, a short discharge or charge current pulse can be applied when the battery is at rest and the voltage response can be measured. Then, the instantaneous  $R_{0,dchg}$  or  $R_{0,chg}$ can be calculated at the SOC when the pulse was applied using Eq. (10a) or Eq. (10b). This process provides a relatively quick way to assess internal resistance at a certain SOC. In contrast, to extract discharged capacity  $Q_{dis}$  or discharged energy  $E_{dis}$ , a capacity test needs to be conducted by fully discharging the battery from 100% SOC to 0% SOC with a slow C-rate, which takes multiple hours to conduct (C/3 or C/20 C-rates are commonly used in the capacity test, taking 3 h and 20 h respectively) [33]. These tests are time-consuming compared to the relatively rapid assessment of internal resistance using short current pulses.

**Fig. 17** Discharge power  $P_{dchg}$  plotted against **a** SOC and **b** voltage.  $P_{dchg}$  calculated using the discharge resistance  $R_{0,dchg}$  extracted from the HPPC tests conducted on cell W8. With battery aging, the power curve shifts downwards, indicating a decrease in power capability across the entire SOC range



with color-coded circles on the y-axis. Using the extracted energy E values that correspond to each  $P_{dchg}$ , Fig. 18c is constructed by plotting the  $P_{dchg}$  against the extracted energy E values determined in Fig. 18b. In Fig. 18c, the star label on the x-axis denotes the energy target ( $E_{target}$ ), which is a metric used to evaluate whether a battery meets specific manufacturer or vendor requirements. According to the DOE battery manual [9], a battery is considered to have reached its end-of-life (EOL) when it can no longer provide the specified energy target. In this paper, we define  $E_{target}$  to be 70%<sup>11</sup> of the discharged energy at Diag.#1

$$E_{target} = E_{dis,\text{Diag},\#1} \times 70\% \tag{13}$$

such that  $E_{target}$  is defined for a fresh cell at the beginning-oflife (BOL) and stays constant throughout battery aging [9]. For cell W8, the discharged energy at Diag.#1 was determined to be  $E_{dis,\text{Diag},\#1} = 17.9$  Wh as shown in Fig. 6 of Module 1. Therefore, the  $E_{target} = 70\% \times 17.9$  Wh = 12.5 Wh. Finally,  $P_{avail,\text{Diag},\#1}$  can be determined by finding the  $P_{dchg}$ value that corresponds to the  $E_{target}$  as shown in Fig. 18c.

Following the steps provided in Fig. 18, Fig. 19 is constructed by plotting  $P_{dchg}$  as a function of extracted energy *E* for all the diagnostic tests. The vertical dashed line in Fig. 19 corresponds to the energy target ( $E_{target} = 12.5$  Wh), and the  $P_{dchg}$  value that intersects with the dashed line is equal to the available power  $P_{avail,Diag,\#N}$  at a given diagnostic test *N*. To provide a clear visual, Fig. 19 highlights the extraction of  $P_{avail,Diag,\#1}$  and  $P_{avail,Diag,\#15}$ .



**Fig. 18 a** Discharge power  $P_{dchg}$  versus SOC at Diag.#1 for cell W8.  $P_{dchg}$  is extracted from the discharge current pulses applied at evenly spaced SOC intervals in the HPPC test. **b** Extracted energy *E* versus SOC, calculated from C/20 capacity test for cell W8 at Diag.#1. As shown in **a**, each  $P_{dchg}$  is associated with a SOC. The extracted energy values at these SOC points are extracted and marked with color-coded circles on the *y*-axis. The total discharged energy from the C/20 capacity test is labeled in purple as  $E_{dis,\text{Diag},\#1}$ . **c** Discharge power  $P_{dchg}$  versus extracted energy *E* points from **b**. The star label on the *x*-axis corresponds to the energy target  $E_{target} = 12.5$  Wh, which equals 70% of the  $E_{dis,\text{Diag},\#1} = 17.9$  Wh. The available power  $P_{avail,\text{Diag},\#1}$ , which is the  $P_{dchg}$  value at  $E_{target}$ , is marked on the *y*-axis with a gray dot

<sup>&</sup>lt;sup>11</sup> A commonly used criterion for reaching EOL in EV applications is capacity reaching 80% of the initial cell capacity. However, this criterion was proposed by USABC in 1996 [34] when most EVs were based on nickel batteries with much lower energy and power densities than LIBs. Since then, the "80%" metric has been deemed outdated for EVs today, and a lower threshold, such as 70%, is now commonly used to better represent the EV battery retirement criterion [35].



**Fig. 19** Discharge power  $P_{dchg}$  and extracted energy E plot at all the diagnostic tests for cell W8. The available power  $P_{avail,\text{Diag},\#N}$  at a given diagnostic test N is extracted by locating the  $P_{dchg}$  value that intersects with the vertical dashed line, the energy target  $E_{target}$  value (70% of  $E_{dis,\text{Diag},\#1}$ ). Extraction of  $P_{avail,\text{Diag},\#1}$  and  $P_{avail,\text{Diag},\#15}$  is shown with labels on the y-axis



**Fig. 20** Power fade  $P_{fade}$  and energy fade  $E_{fade}$  versus cycle number for cell W8. Although the absolute values of  $P_{fade}$  and  $E_{fade}$  differ, their trends exhibit similar behavior



**Fig. 21** Schematic of EIS impedance plot, which is characterized by frequency ranges that correspond to different physical meanings: high frequency (300 Hz <  $\omega$ ) for ohmic effect, mid-frequency (1 Hz <  $\omega$  < 300 Hz) for charge-transfer effect, and low frequency for diffusion effects ( $\omega$  < 1 Hz)

The power fade  $(P_{fade})$  is defined as the decrease in available power  $P_{avail}$  during battery aging and is calculated as

$$P_{fade,\text{Diag},\#N} = \left(1 - \frac{P_{avail,\text{Diag},\#N}}{P_{avail,\text{Diag},\#1}}\right)$$

$$\times 100 \quad [\%], \qquad N = 1, 2, ..., N_{tot}$$
(14)

where  $P_{avail,\text{Diag},\#N}$  and  $P_{fade,\text{Diag},\#N}$  refer to the available power and power fade at the *N*th diagnostic test, respectively. In Fig. 20,  $P_{fade}$  and  $E_{fade}$  are plotted as a function of cycle number for cell W8, with each point referring to a diagnostic test from Diag.#1 to Diag.#15. Although their absolute values differ, their aging trends are similar, as noted by the

```
Listing 4 EIS R0 Rct
                             function [eis_R0, eis_Rct]=eis_R0_Rct_calculations(Z_Re, Z_Im)
                             % INPUTS:-
                                                                                                           2
calculations.m
                             %
                               Z Re = real impedance vector from EIS test [mOhm]
                                                                                                           3
                               Z_Im = imaginary impedance vector from EIS test [mOhm]
                             %
                                                                                                           4
                             %
                               OUTPUTS : -
                                                                                                           5
                             %
                               eis_R0 = R0 extracted from EIS test [m0hm]
                                                                                                           6
                             %
                               eis_Rct = Rct extracted from EIS test [mOhm]
                                                                                                           7
                             %
                                                                                                           8
                                                                                                           9
                             \% For better results, chop off majority of the data where -Im(Z) is
                                  negative
                             index = find(-Z_Im > 0);
                             Z_Im = Z_Im(index - 1: end);
                                                                                                           12
                             Z_Re = Z_Re(index - 1: end);
                                                                                                           14
                             % Calculate RO using linear interpolation
                             eis_R0 = interp1(-Z_Im(1:2), Z_Re(1:2), 0);
                                                                                                           17
                             % Calculate Rct by locating the local minimum of Z_Im
                                                                                                           18
                             index = islocalmin(-Z_Im);
                                                                                                           19
                             eis_Rct = Z_Re(index)-eis_R0;
                                                                                                           20
                             end
```



**Fig. 22** Internal resistances at 50% SOC for cell W8. Comparison of  $R_{0,dchg,p5}$  HPPC,  $R_0 + R_{ct}$  EIS, and  $R_0$  EIS with respect to number of cycles. HPPC and EIS resistances follow similar aging trends. However, the resistances differ by an offset of approximately 4 m $\Omega$  between  $R_{0,dchg,p5}$  HPPC and  $R_0$  EIS, and 1.5 m $\Omega$  between  $R_{0,dchg,p5}$  HPPC and  $R_0$  EIS, and 1.5 m $\Omega$  between  $R_{0,dchg,p5}$  HPPC and  $R_0$  EIS

shared nonlinear behavior observed around cycles 130–150. An empirical observation reveals that the  $P_{fade}$  values are roughly double the magnitude of the  $E_{fade}$  values. This implies that one can effectively estimate either  $E_{fade}$  or  $P_{fade}$  by relying on information from just one of these metrics.

### Electrochemical Impedance Spectroscopy (EIS): internal resistance calculation

Figure 21 shows a schematic of the Nyquist plot to visualize the dynamic behavior of the battery at different points along the impedance spectrum in the EIS. The high-frequency region (300 Hz <  $\omega$ ) represents the ohmic effect [36]. The ohmic resistance ( $R_0$ ) is extracted by locating the Re(Z) value at Im(Z) = 0. The mid-frequency region (1 Hz  $\leq \omega \leq$  300 Hz) corresponding to the semicircle portion represents the chargetransfer effect [36]. The local minimum of -Im(Z) is labeled as point A in Fig. 21. The difference between the Re(Z) value at point A and  $R_0$  corresponds to the charge-transfer resistance ( $R_{ct}$ ).<sup>12</sup> The low-frequency region ( $\omega < 1$  Hz) dictates the diffusion effects in the battery and is usually expressed by the Warburg impedance ( $Z_W$ ) [36]. In this paper, we provide analysis methods and code for extracting  $R_0$  and  $R_{ct}$  from the EIS data.

The  $R_0$  and  $R_{ct}$  are calculated from the EIS at each diagnostic test using the script in Listing 4. To calculate  $R_0$ , the code extracts the Re(Z) value at Im(Z) = 0 using the linear interpolation function interp1. To calculate  $R_{ct}$ , the Re(Z) value at point A, the local minimum of -Im(Z), is extracted using the islocalmin<sup>13</sup> function.



Fig. 23 Flowchart of IC-DV curve calculations using the voltage versus extracted capacity curve from the C/20 capacity test at Diag.#1 for cell W8

Figure 22 shows a comparison of the  $R_{0,dchg,p5}$  HPPC,  $R_0$  EIS, and  $R_0+R_{ct}$  EIS at 50% SOC as a function cycle number. The  $R_{0,dchg,p5}$  HPPC is approximately 4 m $\Omega$  greater (15% difference) than the  $R_0$  EIS. The discrepancy between HPPC  $R_{0,dchg,p5}$  and EIS  $R_0$  is comparable to the values reported in the literature [38, 39]. Some studies attributed this discrepancy to the inherent differences in how the tests are conducted. The HPPC is a dynamic test that involves the application of current pulses, resulting in the battery to display non-linear behavior, as described by Butler-Volmer kinetics [38, 39]. In contrast, the battery is at equilibrium during EIS, and a sinusoidal current with a small amplitude is applied, resulting in a more linear battery response, also in accordance with Butler-Volmer kinetics [38, 39].

<sup>&</sup>lt;sup>12</sup> Depending on the cell chemistry and SOH, two semicircles can be present in the mid-frequency region [16].

 $<sup>^{13}</sup>$  The islocalmin was introduced in MATLAB  $^{\odot}$  version R2017b [37]. To run this script, the MATLAB  $^{\odot}$  version should be R2017b or newer.

Listing 5 IC DV

calculations.m



We also speculate that the higher sampling rate that was used in this dataset (1 s, which is higher than the recommended 0.1 s) may have caused the  $R_{0,dchg,p5}$  HPPC measurement to include the effects of  $R_{ct}$ . This speculation is supported by the observation that the  $R_{0,dchg,p5}$  HPPC values (blue line) are closer to the  $R_0+R_{ct}$  EIS values (orange line) than the  $R_0$  EIS values (red line), as shown in Fig. 22. The difference between  $R_{0,dchg,p5}$  HPPC and EIS  $R_0$  is approximately 4 m $\Omega$  (15% difference), while the difference between  $R_{0,dchg,p5}$ HPPC and  $R_0+R_{ct}$  EIS is only about 1.5 m $\Omega$  (6% difference).

## Module 5: Incremental Capacity (IC) and Differential Voltage (DV)

IC-DV analysis is used to study the battery aging behavior by tracking changes in the voltage curves, which facilitates the analysis of degradation modes. We start with a discussion of the theoretical background of IC-DV curves, focusing on the physical significance of the voltage plateaus in the half-cell and full-cell OCV curves and how they relate to the IC peak and DV valley features. Subsequently, we provide detailed calculation procedures to obtain IC-DV curves from the capacity test. Due to inherent noise in the data, accurate IC-DV curves cannot be obtained without applying appropriate signal filtering methods. Despite being an important aspect of IC-DV analysis, the calculation techniques are often omitted in the existing literature [40–44]. A detailed IC-DV calculation methodology is developed in the section following the theoretical background of half-cell and full-cell IC-DV curves.

#### Theory behind half-cell and full-cell IC and DV curves

Half cells are commonly used to study the intrinsic thermodynamic properties of an active electrode material. In contrast to full cells that consist of two active electrodes, half cells incorporate a single active electrode alongside a counter lithium metal electrode. The lithium metal counter electrode serves as a stable reference potential, enabling the study of the electrochemical characteristics of the active electrode [45, 46].

The active electrode in a half cell is characterized by a unique OCV versus lithium concentration curve that depends on the material's crystallographic structure and phase transitions occurring during lithium intercalation or de-intercalation [47]. The voltage of a cell corresponds to the difference in chemical potential between the two electrodes, with the chemical potential defined as the derivative of the Gibbs free energy with respect to lithium concentration [26, 48]. When two phases coexist, there exists a common tangent with a constant slope connecting the two valleys of the single-phase Gibbs free energy curves [49]. As a result, the voltage curve exhibits a flat plateau in the two-phase regions [49]. For example, the graphite negative electrode undergoes at least five phase transitions from C to LiC<sub>6</sub> resulting in several voltage plateaus in the half-cell OCV curve, whereas the LFP positive electrode is characterized by a single two-phase region resulting in a predominantly flat half-cell OCV curve [46].

Oftentimes, the half-cell OCV versus lithium concentration curve is estimated with the half-cell capacity test voltage versus extracted capacity curve (V versus Q) conducted at a low C-rate, C/20 or lower. The voltage plateaus from the half-cell capacity test are transformed into sharp "peaks" in the IC curve ( $\Delta Q/\Delta V$  vs. V) and "valleys" in the DV curve ( $\Delta V/\Delta Q$  versus Q), highlighting the electrode thermodynamic signatures [12]. Wider voltage plateaus result in taller IC peaks and wider DV valleys. When LAM occurs in the active electrode, a reduction in lithiation sites occurs and the OCV curve shrinks with respect to lithium composition, causing the voltage plateaus to become narrower [50]. As a result, the IC peaks become shorter, and the DV valleys become narrower. When LLI occurs in the active Fig. 24 Capacity tests in charging and discharging at C/20 and C/40 of a fresh INR21700-M50T cell. Voltage plateaus and IC-DV features obtained from Ansean et al. [55]. a Voltage plateaus are labeled in black circles for the charging curves and in white circles for the discharging curves. b DV curves in charging and discharging at C/20 and C/40. DV "valleys" correspond to the voltage plateaus. c IC curves in charging and discharging at C/20 and C/40. IC "peaks" correspond to the voltage plateaus



electrode, the reduction in cyclable lithium leads to shifting of the OCV curve with respect to lithium composition, leading to horizontal movement of the IC peaks and DV valleys [50].

In a full cell, the overall cell OCV is obtained by subtracting the half-cell OCV curves of the positive and negative electrodes. This superposition of half-cell curves can result in overlapping IC and DV features from the positive and negative electrodes. This makes degradation mode analysis challenging as the merged features lose their physical meaning the peaks and valleys in the full-cell IC-DV curves may no longer correlate to the voltage plateaus of the active electrodes.

To address these challenges, algorithms have been developed to simulate changes in the full-cell IC-DV curves during battery aging [40–43]. These algorithms leverage fresh half-cell data from both positive and negative electrodes and simulate "stretching" or "shifting" of the half-cell curves to mimic the full-cell behavior when a particular degradation mode occurs [40–43]. Validation of such simulation results can be challenging, as it often requires post-mortem experiments to confirm the presence of the degradation mechanisms. the non-overlapping features in the full-cell IC-DV curves to identify the degradation modes. This method uses fresh halfcell data from each electrode to first identify the presence of non-overlapping features in the full-cell IC-DV curves. With the identified full-cell IC-DV non-overlapping features, only the full-cell IC-DV curves are required for degradation mode analysis since the contributions from each electrode can be distinguished [22, 31, 51–53]. However, it is important to note that this method has limitations, as not all cells may have non-overlapping features and not all degradation modes may not be distinguishable, such as LLI and LAM in the negative electrode [22, 31, 51–53].

Another method adopts a mechanistic approach by using

#### IC and DV calculations

To calculate the full-cell IC-DV curves, the C/20 capacity test data is used since it is an approximation of the OCV curve. The full-cell IC-DV curves are calculated using the measured voltage and extracted capacity Q from the capacity test. Since voltage measurements are usually noisy due to tolerance limitations of the battery cycler, a filtering method needs to be implemented. We outline the steps required to calculate IC and DV:

Step 1: Calculate DV by differentiating measured raw voltage  $V_{raw}$  with respect to extracted capacity Q

$$DV_{raw}(t_i) = \frac{V_{raw}(t_{i+1}) - V_{raw}(t_i)}{Q(t_{i+1}) - Q(t_i)}.$$
(15)

where  $DV_{raw}(t_i)$  refers to the unfiltered DV at time  $t_i$ , and  $Q(t_i)$  and  $Q(t_{i+1})$  refer to the extracted capacities at two consecutive discrete points in time,  $t_i$  and  $t_{i+1}$ . Similarly,  $V_{raw}(t_i)$  and  $V_{raw}(t_{i+1})$  are the measured voltages at two consecutive discrete points in time.

*Step 2:* Apply a filter to smooth  $DV_{raw}$ 

$$DV_{filtered} = G(z) \cdot DV_{raw}$$
(16)

where  $DV_{filtered}$  is the filtered DV and G(z) is a discrete time filter. One can use a low-pass filter or smoothing filter such as Savitzky-Golay [54].

Step 3: Calculate IC<sub>filtered</sub> by computing the inverse of  $DV_{filtered}^{14}$ 

$$IC_{filtered} = \frac{1}{DV_{filtered}}.$$
(17)

Figure 23 shows a flowchart summarizing the IC and DV calculations using C/20 capacity test data at Diag.#1 for cell W8. The MATLAB<sup>®</sup> script in Listing 5 calculates the IC and DV curves using the steps mentioned above. Readers can refer to our code [2] for more details on the sgolayfilt<sup>15</sup> implementation.

Figure 24 shows the voltage and calculated IC-DV curves from C/20 and C/40 capacity tests conducted on a fresh cell in charging and discharging. The voltage plateaus and the corresponding IC-DV feature labels are obtained from Ansean et al. [55] who reported data from cells with the same chemistry as those featured in this dataset (NMC811/Si-Gr). The voltage plateaus for the charging



**Fig. 25** IC-DV curves of cell W8 as the battery ages. The movement of the peaks and valleys are indicated with arrows or with an equal sign if no change occurs

curves<sup>16</sup> are labeled with black circles and with white circles for the discharging curves. The IC and DV features<sup>17</sup> originating from the voltage plateaus are labeled in Fig. 24c and b, respectively. The IC-DV features from the C/40 capacity test can be characterized by the C/20 data, indicating that the C/20 rate is sufficiently low enough to capture the thermodynamic characteristics. The slight deviations of the peak and valley locations between the charge and discharge IC-DV curves originate from inherent hysteresis behavior in the battery [56]. We note that INR21700-M50T cells are used in our experimental campaign, so

<sup>&</sup>lt;sup>14</sup> It is more robust to calculate IC<sub>*filtered*</sub> by taking the inverse of DV<sub>*filtered*</sub> rather than calculating IC directly from V<sub>raw</sub>. The  $\Delta V_{raw}$  values are usually very small, causing IC<sub>*raw*</sub> =  $\Delta Q/\Delta V_{raw}$  to become several orders of magnitude larger than its true value. For this reason it is difficult to calculate IC<sub>*filtered*</sub> by filtering IC<sub>*raw*</sub>.

 $<sup>^{15}</sup>$  To run sgolayfilt,  $MATLAB^{\circledast}\mbox{``s Signal Processing Toolbox is required.}$ 

<sup>&</sup>lt;sup>16</sup> In the context of capacity tests in charging, we employ the nomenclature "stored capacity," denoted as  $Q_{stored}$ , as opposed to "discharged capacity," Q. The calculation of  $Q_{stored}$  follows Eq. (1), which is identical to the formula for calculating Q, with a minor modification. In order to maintain positive values for  $Q_{stored}$ , we take the absolute value of the charging current, since the charging current is negative according to our sign convention.

<sup>&</sup>lt;sup>17</sup> In the literature, the voltage plateaus are commonly referred to as IC "peaks" and DV "valleys." This is true for the capacity test in charging, where the voltage plateaus (black circles) translate to "peaks" in IC and "valleys" in DV. However, in the capacity test in discharging, the voltage plateaus (white circles) translate to "valleys" in IC and "peaks" in DV. For consistent terminology, we refer to the IC features corresponding to the voltage plateaus as "peaks" and DV features as "valleys" in both the charging and discharging cases.

the peak and valley IC-DV features shown in Fig. 24 are unique to the NMC811/Si-Gr chemistry.

In Fig. 25, the peak and valley movements with battery aging are indicated with arrows or with an equal sign if no change occurs. To understand the physical meaning of the peak and valley movements, a degradation mode analysis can be conducted by tracking the changes in the characteristic capacity pertaining to a particular phase in the electrode [22, 31, 51–53].

#### Conclusions

In this paper, we provide an approachable guide to calculate and analyze LIB performance and health indicators from diagnostic tests such as the capacity test, HPPC test, and EIS. We demonstrate the analysis on a publicly available aging dataset generated from LG INR21700-M50T cylindrical cells [1] and provide MATLAB<sup>®</sup> scripts to perform the calculations discussed in the paper. From the capacity test, capacity and energy are extracted at each diagnostic test to quantify aging in terms of capacity fade and energy fade. We show how to calculate SOC and SOE, which are important internal states in the battery that quantify the amount of charge and energy stored in the cell, respectively. Such internal states are critical in BMS applications to understand the current state of the battery to make an informed decision about the battery operation. The OCV curves are estimated using the capacity test voltage curve and the HPPC test by extracting the HPPC equilibrium voltage points. The HPPC and EIS tests are used to calculate the internal resistance at various SOCs and quantify the increase in resistance as the battery ages. Furthermore, the internal resistance extracted from the HPPC is used to calculate the power capability, which is used to quantify the power fade due to battery aging. Lastly, we provide the theoretical background and calculation methods of IC-DV curves that can be used to track the thermodynamic changes in the voltage curve during aging. We anticipate that this paper can serve as a valuable reference for students, educators, and the general public interested in the practical aspects of battery electrochemical testing and performance and health metric calculations. Our aim is to provide a reference for those embarking on careers in model-based BMS design and battery aging and characterization analysis.

#### **Appendix 1. C-rate definition**

C-rate is the rate at which the battery is discharged or charged relative to its nominal capacity  $Q_n$ . The equation is given as

$$C-rate = \frac{|I|}{Q_n}$$
(18)

where |I| is the absolute value of the current applied to the battery in ampere (A) and the units of C-rate are in  $\frac{A}{Ah} = \frac{1}{h}$ . The absolute value of the current is used since C-rate is a positive value regardless of whether the battery is charged or discharged. As an example, the C-rate is calculated and written at different currents for a battery with  $Q_n = 10$  Ah:

$$C\text{-rate} = \frac{|I|}{Q_n} = \frac{5[A]}{10[Ah]} = \frac{1}{2} \left[ \frac{1}{h} \right]$$
  

$$\rightarrow C/2 (2 \text{ h to charge or discharge})$$
  

$$C\text{-rate} = \frac{|I|}{Q_n} = \frac{10[A]}{10[Ah]} = \frac{1}{1} \left[ \frac{1}{h} \right]$$
  

$$\rightarrow 1C (1 \text{ h to charge or discharge})$$
  

$$C\text{-rate} = \frac{|I|}{Q_n} = \frac{20[A]}{10[Ah]} = \frac{2}{10} \left[ \frac{1}{h} \right]$$
  
(19)

Therefore, the inverse of the C-rate is number of hours it takes to discharge or charge the battery.

#### Appendix 2. Designing cycling experiments

Battery aging is affected by cell temperature, rate of charge and discharge, and depth-of-discharge (DOD)<sup>18</sup> [57, 58]. In real-world applications, such as in EVs, eVTOL aircrafts, and grid energy storage systems, the battery experiences different discharging profiles that are specific to the application condition. For instance, the urban dynamometer driving schedule (UDDS) profile can be used to replicate the average driving profile in city conditions, characterized by deceleration and acceleration events [59]. In an eVTOL aircraft, the battery experiences constant loads during cruise and highpower loads during takeoff and landing [60]. In grid energy storage systems, batteries are subject to dispatch duty cycles in the form of power profiles [61].

In the dataset used in this paper [1], the aging test campaign was conducted on ten<sup>19</sup> INR21700-M50T cylindrical cells with NMC811 cathode and Si-Gr anode (Table 1). The cells were subjected to repeated instances of the experimental *Cycle*, a constant current (CC)-constant voltage (CV) charging protocol, and UDDS discharge driving profile used to replicate EV real-driving scenarios. The total number of

<sup>&</sup>lt;sup>18</sup> DOD represents the percentage of charge removed during discharging relative to the fully charged state.

<sup>&</sup>lt;sup>19</sup> It is recommended to test more than one cell for each experimental condition to gain insight into the statistical variability of the cell performance, usually arising from cell-to-cell variations due to factors outside of the users control (such as manufacturing defects) [62].

1	
Manufacturer	LG Chem
Model	INR21700-M50T
Positive electrode	NMC811 [63, 64]
Negative electrode	graphite and silicon [65]
Size (diameter×length)	21.44 mm × 70.80 mm
Weight	69.25 g
Nominal capacity $(Q_n)$	4.85 Ah
Nominal voltage $(V_n)$	3.63 V
Upper cutoff voltage $(V_{max})$	4.2 V
Lower cutoff voltage( $V_{min}$ )	2.5 V
Cutoff current	50 mA

Table 1	Technical	specifications	INR21700	-M50T	cells	[23]
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repeated *Cycle* instances at every diagnostic test is specified in Table 3, as well as the charging C-rate used for each cell.

Table 2 shows the six steps involved in the *Cycle*. Step 1 consists of a CC charge at the C-rate of C/4, C/2, 1C, or 3C, which is specified in the second column of Table 3. We vary the charging C-rate to study how charging speed affects battery degradation. Once 4 V is reached, Step 2 begins wherein the battery is under CV charge at 4 V until the current goes below 50 mA. Step 3 performs another CC charge at C/4 until the upper cutoff voltage of 4.2 V is reached. In Step 4, the battery is CV charged until the current goes below 50 mA and then rested for 30 min. Steps 1-4 exemplify a standard CC-CV charging protocol to charge lithium-ion batteries to 100% SOC. In Step 5, the battery is CC discharged from 100 to 80% SOC at C/4. Step 6 discharges the battery from 80 to 20% SOC using a series of concatenated UDDS profiles. The 80 to 20% SOC in Step 6 represents a typical driving SOC range in that most users will not always charge to 100% SOC before driving and will charge the vehicle well before 0% SOC is reached. Once Step 6 is completed, Step 1 will start again to repeat the Cycle until the desired number of cycles is reached. Figure 26 shows a visual representation of the cycling profile described in Table 2.



**Fig. 26** The experimental *Cycle* used in the aging campaign [1]. Positive current is for discharging, and negative current is for charging. Steps 1–4 correspond to a CC-CV charging protocol, and Steps 5–6 discharge the battery with a CC discharge followed by a series of concatenated UDDS profiles. Table 2 describes the steps in detail. Once Step 6 is completed, the *Cycle* resumes to Step 1 to repeat the steps. The number of *Cycles* associated with each diagnostic test is defined in Table 3

# Appendix 3. Ampere-hour throughput definition

The ampere-hour throughput  $(Ah_{throughput})$  measures the total current passed through the battery in both charging and discharging. It is calculated as

$$Ah_{throughput}(t) = \underbrace{\frac{1}{3600} \int_{t_0}^{t} |I(\tau)| d\tau}_{Ah}$$
(20)

where |I| is the absolute value of the current applied to the battery in ampere (A) and  $Ah_{throughput}(t)$  is the ampere-hour throughput in Ah calculated from an initial time instant  $t_0$ to a certain point in time t. Although cycle number is commonly used to track the number of times the battery has been cycled, a cycle does not contain information on the amount of current passed through the battery for a given cycle. In

Step	Action	Exit condition
1	CC charge at C-rate specified in the second column of Table 3	4 V is reached
2	CV charge	Current below 50 mA
3	CC charge at C/4	4.2 V is reached
4	CV charge followed by 30 min rest	Current below 50 mA
5	CC discharge at C/4	20% discharged capacity (80% SOC)
6	UDDS discharge	60% discharged capacity (20% SOC)

Table 2	Description of the
experim	ental Cycle [1]

Label	Charge C-rate	Environment	Diagnostic test (cycle)														
		(°C)															
			#1	#2	#3	#4	#5	#6	#7	<b>#8</b>	<b>#9</b>	#10	#11	#12	#13	#14	#15
W3	3C	23	0	25	75 <sup>a</sup>	-	-	-	-	-	-	-	-	-	-	-	-
W4	C/4	23	0	25	75	123	132	159	176	179	-	-	-	-	-	-	-
W5	C/2	23	0	25	75	125	159	167	187	194	219	244	269	294	319	344	369
W7	C/4	23	0	25	75	125	141 <sup>a</sup>	-	-	-	-	-	-	-	-	-	-
W8	C/2	23	0	25	75	125	148	150	151	157	185	222	247	272	297	322	347
W9	1C	23	0	25	75	122	144	145	146	150	179	216	241	266	291	316	341
W10	3C	23	0	25	75	122	146	148	151	159	188	225	250	275	300	325	350
G1	3C	23	0	25	30	37	62	87	112	137	162	187	212	-	-	-	-
V4	C/4	23	0	20	45	70	95	120	145	170	194	219	244	-	-	-	-
V5	1C	23	0	12	18	29	-	-	-	-	-	-	-	-	-	-	-

Table 3 Cells label, test charging condition, temperature, and diagnostic test number. For each diagnostic test, the number of cycles experienced by the cell is reported. All cells are tested at 23 °C

<sup>a</sup>The cell was dismissed, and the aging campaign was terminated

contrast, Ah<sub>throughput</sub> allows quantification of the amount of charge passed in and out of the battery and provides a more generalizable metric than cycle number. Figure 27 shows the discharged capacity  $Q_{dis}$  as a function of cycle number and Ah<sub>throughput</sub> for all ten cells. As expected, the  $Q_{dis}$  aging trajectory of a cell exhibits similar trends when plotted against cycle number and Ah<sub>throughput</sub>.

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**Fig. 27** Discharged capacity  $Q_{dis}$  as a function of **a** cycle number and **b** Ah<sub>throughput</sub> for all ten cells

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