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Directional DC Charge-Transfer Resistance on an Electrode–Electrolyte Interface in an AC Nyquist Curve on Lead-Acid Battery

Wubin Wang ¹, Wenxi Yao ¹, Wei Chen ², Dong Chen ², Zhen Ma ³ and Zhengyu Lu ^{1,*}

- ¹ College of Electrical Engineering, Zhejiang University, Hangzhou 310027, China; wubinwangzju@163.com (W.W.); ywxi@zju.edu.cn (W.Y.)
- ² Zhejiang Narada Power Source Co., Ltd., Hangzhou 310030, China; chw@narada.biz (W.C.); chendong0127@126.com (D.C.)
- ³ Shanghai Institute of Space Power-sources, Shanghai 200245, China; mazhen810615@126.com
- * Correspondence: eeluzy@cee.zju.edu.cn; Tel.: +86-571-879-52664

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Featured Application: Battery management system design on lead-acid batteries with electrochemical impedance spectroscopy and first principle linear circuit model.

Abstract: Both the frequency domain Nyquist curve of electrochemical impedance spectroscopy (EIS) and time domain simulation of DC equivalent first principle linear circuit ($FPLC_{DCequ}$) are some of the fundamentals of lead-acid batteries management system design. The Nyquist curve is used to evaluate batteries' state of health (SoH), but the curve does not distinguish charging/discharging impedances on electrode–electrolyte interfaces in the frequency domain. $FPLC_{DCequ}$ is used to simulate batteries' terminal electrical variables, and the circuit distinguishes charging/discharging impedances on electrode–electrolyte interfaces in the time domain. Therefore, there is no direct physical relationship between Nyquist and $FPLC_{DCequ}$ This paper proposes an AC equivalent first principle linear circuit ($FPLC_{ACequ}$) by average switch modeling, and the novel circuit distinguishes charging/discharging impedances on electrode–electrolyte interfaces in $PPLC_{DCequ}$ for lead-acid batteries management system design.

Keywords: state of health; state of charge; lead-acid battery; electrochemical impedance spectroscopy; battery management system; charge-transfer resistance; double-layer capacitance; first principle circuit; behavioral circuit; power electronics; average switch modeling

1. Introduction

Lead-acid batteries are widely used as a backup in power systems, e.g., in telecommunication stations and power plants. On lead-acid batteries, both the frequency domain Nyquist curve of EIS [1] and time domain simulation of DC equivalent first principle linear circuit ($FPLC_{DCequ}$) [2] are widely used in battery management system (BMS) design. In BMS design, linear electrical circuits, including AC and DC equivalent circuits, are more competitive than nonlinear electrochemical circuits. Firstly, linear electrical circuits, with electrical equivalent lumped elements, are intuitive for electrical engineers to understand the physical and electrochemical characteristics of batteries [3]. Batteries' physical and electrochemical parameters are mapped to electrical lumped elements, which are used to estimate batteries' state of health (SoH) or state of charge (SoC) [4]. Secondly, linear impedances are more convenient for simulating batteries' terminal electrical variables in software. Advanced digital signal processing requires that elements should be linear functions of frequency [5], and electrical lumped

impedances are nature linear functions of frequency. However, lumped electrochemical impedances are nonlinear functions of frequency [6], and are not convenient for programming. Unless special mention is given, the following circuits in this paper only refer to linear electrical circuits.

Elements in a circuit, fitting for EIS, are simplified from governing equations [7,8] in lead-acid battery and have clear physical/electrochemical meanings; so, they are the first principle and basis of classic threshold-based BMS design. Charge-transfer resistance and double-layer capacitance are related to non-cohesion of active mass of electrodes; contacting resistances represent the existence of stratification and corrosion of electrodes; nonlinear diffusion impedances characterize sulfating of electrodes [4,9]. Multi-scale SoC/SoH judgment based on EIS is an extension of threshold-based management [10,11]; circuits elements are nonlinearly influenced by various factors, e.g., SoC, charging or discharging, superimposed DC current [12]; other form signals, such as short step response, can take place of sinusoidal excitation to demonstrate dominant aging mechanisms on battery capacity [8]. The leading edge of BMS to forecast and optimize batteries' SoC/SoH is usually based on time domain simulation [13,14]; therefore, extracting directional DC charge-transfer resistances from an AC Nyquist curve is significant in time domain research on BMS.

The Nyquist curve, describing AC steady-state volt-ampere characteristics of batteries, is used to evaluate SoH [1], and AC equivalent behavioral linear circuit ($BHLC_{ACequ}$) is used for the curve fitting [15]. In certain frequency bands of Nyquist, impedances on electrode–electrolyte interfaces dominate curve shape [1,3]; at a certain frequency point of Nyquist, $BHLC_{ACequ}$ has a corresponding time domain waveform to approach the measurement point. Then, the behavioral relationship between $BHLC_{ACequ}$ and Nyquist is established.

*BHLC*_{ACequ} is an interpretation basis of the Nyquist curve [16]. The physical and electrochemical meanings of contacting resistor (R_c), stray inductor (L_s) and electrolyte bulk capacitor (C_{bulk}) in *BHLC*_{ACequ} are relatively clear [3]. Individual elements in *BHLC*_{ACequ} rely on the first principle [17], simplified from governing equations [7,8], but the elements' combination does not consider the first principle. Linear impedance on positive (or negative) electrode–electrolyte interfaces is generally modeled by a charge-transfer resistor (R_{ct}) and a double-layer capacitor (C_{dl}) [3,18]. The R_{ct} describes the DC steady-state volt-ampere characteristics of an electrode–electrolyte interface according to Tafel law [19]; the C_{dl} describes the DC transient-state volt-ampere characteristics of an electrode–electrolyte interface according to spatial anisotropy [19]. Both C_{dl} and R_{ct} in *BHLC*_{ACequ} do not distinguish charging/discharging, too [15,18,20]. The impedance, on a single (positive or negative) electrode–electrolyte interface, consisting of one R_{ct} and one C_{dl} , characterizes both charging and discharging at the same time. The authors of [21] also suggest that the long-chain series of an $R_{ct} \parallel C_{dl}$ circuit can approximate the Nyquist curve as close as possible, but long-chain series elements do not have practical physical and electrochemical meanings, and cannot distinguish charging/discharging impedances either.

 $FPLC_{DCequ}$, describing DC steady-state and transient-state volt-ampere characteristics of batteries, typically includes L_S , R_C , C_{bulk} and impedances on electrode–electrolyte interfaces (z_{eei}) [20]. z_{eei} distinguishes R_{ct} into charging ($R_{ct,pc}$ and $R_{ct,nc}$)/discharging ($R_{ct,pd}$ and $R_{ct,nd}$) [2,20,22]. $R_{ct,pc}$, $R_{ct,nc}$, $R_{ct,pd}$ and $R_{ct,nd}$ in $FPLC_{DCeq}$ are a function of the surface area of the solid electrolyte [2,3,22]. Surface areas of charging and discharging for electrochemical processes are mutually exclusive and collectively exhaustive [2,3,22]. Generally, they are different; therefore, charging ($R_{ct,pc}$ and $R_{ct,nc}$) and discharging ($R_{ct,pd}$ and $R_{ct,nd}$) charge-transfer resistors are different. However, C_{dl} in $FPLC_{DCequ}$ does not distinguish charging/discharging [3,20], and only one capacitor ($C_{dl,p}$ or $C_{dl,n}$) combines both charging and discharging and discharging characteristics of each electrode. C_{dl} is generated on a solid electrolyte interface and always in parallel with R_{ct} in $FPLC_{DCequ}$ [3,20]. Therefore, charging ($C_{dl,pc}$ or $C_{dl,nc}$) and discharging ($C_{dl,pd}$ or $C_{dl,nd}$) double-layer capacitors should depend on their individual electrochemical reaction surface areas, and they should be different in general.

Existing $BHLC_{ACequ}$ does not distinguish charging impedances ($R_{ct,pc}$, $C_{dl,pc}$, $R_{ct,nc}$ and $C_{dl,nc}$) from discharging impedances ($R_{ct,pd}$, $C_{dl,pd}$, $R_{ct,nd}$ and $C_{dl,nd}$) on electrode–electrolyte interfaces. Therefore, there is no physical relationship between the EIS Nyquist curve and $FPLC_{DCequ}$.

This paper proposes AC equivalent first principle linear circuit ($FPLC_{ACequ}$) by average switch modeling [23]. $FPLC_{ACequ}$ accurately models the steady-state AC fundamental response as the same as $FPLC_{DCequ}$, and average switch modeling calculates steady-state DC static response as the same as $FPLC_{DCequ}$. $FPLC_{ACequ}$ bridges the physical relationship between Nyquist and $FPLC_{DCequ}$. $FPLC_{ACequ}$. $FPLC_$

2. AC Equivalent First Principle Linear Circuit and Experiments

2.1. Requirements of FPLC_{ACequ}

The $FPLC_{ACequ}$ must meet three requirements: Firstly, elements in $FPLC_{ACequ}$ should be AC equivalent linear, and voltage responses in circuit simulation should not contain a steady-state DC static component. Secondly, charging impedances ($R_{ct,pc}$, $C_{dl,pc}$, $R_{ct,nc}$ and $C_{dl,nc}$) and discharging impedances ($R_{ct,pd}$, $C_{dl,pd}$, $R_{ct,nd}$ and $C_{dl,nd}$) on electrode–electrolyte interfaces in $FPLC_{ACequ}$ should be distinguished. Thirdly, steady-state AC fundamental responses in $FPLC_{ACequ}$ should be consistent with steady-state AC fundamental responses in $FPLC_{ACequ}$.

2.2. Analysis of AC Equivalent Impedances on Electrode–Electrolyte Interfaces by Average Switch Modeling

Directional linear impedances on electrode–electrolyte interfaces of $FPLC_{DCequ}$ are solid in theory [2,3], and its transient-state and steady-state responses under DC-input have also been experimentally verified [2,3]. Furthermore, in this paper, average switch modeling is proposed to explore responses of $FPLC_{DCequ}$ under pure AC-input and to analyze AC equivalent linear impedances on electrode–electrolyte interfaces.

2.2.1. Vector Analysis of Responses of Electrode–Electrolyte Interfaces by Average Switch Modeling

Assuming that amplitudes of sinusoidal currents excited from the electrochemical workstation are small enough, voltage responses of batteries' terminals are also trigonometric waveforms as the same frequency as excitation currents [24]. At any certain frequency, internal impedances of batteries are equivalent to linear-constant-time-invariant impedances, and impedances on electrode–electrolyte interfaces of both positive and negative electrodes are also considered as linear-constant-time-invariant [1,3].

Analysis of Steady-State DC Static Responses by Tafel law

Under stable AC current injection, steady-state DC static responses of impedances on electrode–electrolyte interfaces should be zero in EIS operation. If there are any steady-state DC static voltage responses of batteries' terminals, there should exist non-zero steady-state DC static current injections through batteries' terminals according to Tafel law [25]. This is contradictory to EIS practice.

Vector Analysis of Steady-State AC Fundamental Voltage Response by average switch modeling

Firstly, linear decomposition of equivalent steady-state AC fundamental response vector on electrode–electrolyte interfaces exists. According to the electrical vector analysis principle [26], space vector is regarded as a static vector in rotating the coordinate as the same rotating frequency as stable excitation, and each space vector (V_O) has a clear amplitude and phase in the rotating coordinate. In the rotating coordinate, the target vector can be equivalent to two vectors (V_1 and V_2) by linear superposition. As shown in Figure 1a, amplitudes and phases of the two vectors can be different,

and there are infinite sets of two vectors (V_{1i} and V_{2i}) equivalent to the target space vector (V_O). In the following sections, the target vector is set as steady-state AC fundamental voltage response of impedances on electrode–electrolyte interfaces of both positive and negative electrodes.



Figure 1. Vector analysis of steady-state AC fundamental voltage responses: (**a**) there are infinite sets of two vectors (V_{1i} and V_{2i}) equivalent to target vector (V_O) in rotating coordinate; (**b**) the target vector (V_{eei}) is equivalent to the sum of new charging ($0.5V_{Cha}$) and discharging ($0.5V_{Dis}$) vectors by linear superposition.

Secondly, the linear decomposition of steady-state AC fundamental voltage response vector on electrode–electrolyte interfaces is unique. When stable AC current injections flow through charging impedances on electrode–electrolyte interfaces of both positive and negative electrodes, the charging vector of steady-state the AC voltage fundamental response (V_{Cha}) is obtained as Equation (1), so be discharging vector of steady-state AC voltage fundamental responses (V_{Dis}), as Equation (2). During one period of stable AC current injections, both charging and discharging vectors appear for exactly half a period, and their available time is mutually exclusive and collectively exhaustive. According to average switch modeling [23,26], a new charging vector (V'_{Cha}), as Equation (3), is exactly half an amplitude and the same phase of charging vector in the coordinate plane. So be new discharging vectors (V'_{Dis}), as Equation (4) because, during stable AC excitation, both charging and discharging vectors (V'_{Dis}), as Equation (5) and Figure 1b. Figure 2 is an AC equivalent impedance ($Z_{eei}e^{j\theta_{eei}}$) similar to Equation (6) by removing the current ($I_{EIS}e^{j\theta_{EIS}}$) from Equation (5). The physical meanings of elements in the above equations are explained in Table A1 of the Appendix A.

$$V_{Cha} = \left(I_{EIS}e^{j\theta_{EIS}}\right) \left(Z_{Cha}e^{j\theta_{Cha}}\right),\tag{1}$$

$$V_{Dis} = (I_{EIS}e^{j\theta_{EIS}})(Z_{Dis}e^{j\theta_{Dis}}),$$
⁽²⁾

$$V_{Cha}' = 0.5 \times (I_{EIS} e^{j\theta_{EIS}}) (Z_{Cha} e^{j\theta_{Cha}}), \tag{3}$$

$$V'_{Dis} = 0.5 \times (I_{EIS} e^{j\theta_{EIS}}) (Z_{Dis} e^{j\theta_{Dis}}), \tag{4}$$

$$V_{eei} = V'_{Cha} + V'_{Dis'} \tag{5}$$

$$Z_{eei}e^{j\theta_{eei}} = 0.5 \times \left(Z_{Cha}e^{j\theta_{Cha}} \right) + 0.5 \times \left(Z_{Dis}e^{j\theta_{Dis}} \right), \tag{6}$$



Figure 2. AC equivalent first principle impedances ($Z_{eei}e^{j\theta_{eei}}$) on electrode–electrolyte interfaces.

Time Domain Simulation of FPLC_{ACequ} Impedances

During charging, the voltage response of impedances on electrode–electrolyte interfaces of both positive and negative electrodes is regarded as a linear transfer function [3,20], and positive half-wave sinusoidal current excites the transfer function in its charging half-cycle. So be during discharging. Two linear transfer functions responses are linearly superposed to simulate a one-cycle voltage response of impedances on electrode–electrolyte interfaces.

Vector analysis has a strict time-sharing requirement; the sinusoidal current excitation is naturally divided into positive and negative half. Amplitude superposition is carried out by linearly adding up charging and discharging voltage responses. Figure 3 is an $FPLC_{DCequ}$ [3,20] for steady-state simulation with divided half-wave sinusoidal currents, and is intuitive compared with Figure 2.



Figure 3. DC equivalent first principle impedances on electrode-electrolyte interfaces.

However, in *FPLC*_{DCequ} simulation, steady-state DC static voltage response of impedances on electrode–electrolyte interfaces appear in Figure 4. Under positive half-wave sinusoidal current injection, periodic voltage responses of charging impedances on electrode–electrolyte interfaces are excited; According to average switch modeling principles, an equivalent DC positive response $\langle v_{Cha} \rangle$ is on electrode–electrolyte interfaces, as Equation (7). Similarly, an equivalent DC negative response $\langle v_{Dis} \rangle$ is on electrode–electrolyte interfaces, as Equation (8). Then equivalent DC response V_{DC} on electrode–electrolyte interfaces is the sum of $\langle v_{Cha} \rangle$ and $\langle v_{Dis} \rangle$, as Equation (9). Steady-state DC static voltage responses are shown in *FPLC*_{DCequ} simulation under DC-input [2,3,20], but do not exist in experiments under AC-input. The physical meanings of elements in the above equations are explained in Table A1 of the Appendix A.

$$\langle v_{Cha} \rangle = \frac{1}{T} \int_0^T v_{Cha} dt, \tag{7}$$

$$\langle v_{Dis} \rangle = \frac{1}{T} \int_0^1 v_{Dis} dt, \tag{8}$$

$$V_{DC} = \langle v_{Cha} \rangle + \langle v_{Dis} \rangle, \tag{9}$$

Linear superposition of terminal transient voltage responses in $FPLC_{DCequ}$, excited by time-division input, has been verified on physical-electrochemical derivation, numerical calculations and experiments under DC-input [20]; linear sub-models are switched by a low-pass filter and hysteresis relay [20]. In Figure 4, the black solid line is the output of transient voltage responses in $FPLC_{DCequ}$ simulation under AC-input. The black dashed line cancels the steady-state DC voltage response from the black solid line, and the DC component is exactly equal to Equation (9). The blue dotted line filters the steady-state AC fundamental voltage response out of the black solid line by Equation (10), and the blue dotted line is very close to the black dashed line, which has a little distortion from higher harmonics. The pink dot-dash line is the steady-state AC voltage response in the $FPLC_{ACequ}$ simulation. The physical meanings of elements in the above equations are explained in Table A1 of the Appendix A.

$$TF_{filter} = \frac{\frac{\omega}{Q}s}{s^2 + \frac{\omega}{Q}s + \omega^2}, \ Q = 10,$$
(10)

In Figure 4, the steady-state AC fundamental voltage response of both $FPLC_{ACequ}$ and $FPLC_{DCequ}$ in the simulation are equal, and electrode–electrolyte interface impedances in $FPLC_{ACequ}$ and $FPLC_{DCequ}$ are one-to-one equivalent. The equivalent relationship is unique, and equivalent results in vector analysis are available for both steady and transient states in electrical circuits [27]. The possibility of distinguishing charging/discharging impedances is lost in $BHLC_{ACequ}$ because $BHLC_{ACequ}$ obtains a steady-state AC fundamental voltage response by filtering out DC responses in $FPLC_{DCequ}$ as the blue dotted line. Therefore, the composition of steady-state AC fundamental voltage is not studied in $BHLC_{ACequ}$, but research on the composition of DC components is necessary to study $FPLC_{DCequ}$ and $FPLC_{ACequ}$.



Figure 4. Steady-state AC fundamental voltage responses of both DC equivalent first principle linear circuit ($FPLC_{DCequ}$) and AC equivalent first principle linear circuit ($FPLC_{ACequ}$) are equal in simulations: (a) 5A rms current injections at 0.5 Hz; (b) 5A rms current injections at 1.0 Hz.

2.2.2. AC Equivalent Frist Principle Impedances on Electrode–Electrolyte Interfaces

Equation (6) implies that equivalent AC impedances on electrode–electrolyte interfaces is equal to half of the sum of charging and discharging impedances on electrode–electrolyte interfaces of both positive and negative electrodes.

Each element in AC equivalent first principle impedances is non-directional and totally linear. This advantage simplifies the simulation, and it does not need to determine the direction of excitation in advance, nor does it need auxiliary circuits to switch sub-models in simulations [20]. Further, the charging impedances ($Z_{Cha}e^{j\theta_{Cha}}$) are strictly separated from discharging impedances ($Z_{Dis}e^{j\theta_{Dis}}$). Equations (11) to (13) expand the impedances ($Z_{Cha}e^{j\theta_{Cha}}$, $Z_{Dis}e^{j\theta_{Dis}}$, $Z_{eei}e^{j\theta_{eei}}$) to charge-transfer resistors ($R_{ct,pc}$, $R_{ct,nc}$, $R_{ct,pd}$ and $R_{ct,nd}$) and double-layer capacitors ($C_{dl,pc}$, $C_{dl,pd}$ and $C_{dl,nd}$); Equation (14) is an equivalent transformation for the Nyquist fitting. The physical meanings of elements in the above equations are explained in Table A1 of the Appendix A.

$$Z_{Cha}e^{j\theta_{Cha}} = \frac{R_{ct,pc}}{1+jR_{ct,pc}\omega C_{dl,pc}} + \frac{R_{ct,nc}}{1+jR_{ct,nc}\omega C_{dl,nc}},$$
(11)

$$Z_{Dis}e^{j\theta_{Dis}} = \frac{R_{ct,pd}}{1 + jR_{ct,pd}\omega C_{dl,pd}} + \frac{R_{ct,nd}}{1 + jR_{ct,nd}\omega C_{dl,nd}},$$
(12)

$$Z_{eei}e^{j\theta_{eei}} = 0.5 \times \left(\frac{R_{ct,pc}}{1 + jR_{ct,pc}\omega C_{dl,pc}} + \frac{R_{ct,nc}}{1 + jR_{ct,nc}\omega C_{dl,nc}} + \frac{R_{ct,pd}}{1 + jR_{ct,pd}\omega C_{dl,pd}} + \frac{R_{ct,nd}}{1 + jR_{ct,nd}\omega C_{dl,nd}} \right),$$
(13)

$$Z_{eei}e^{j\theta_{eei}} = \frac{0.5R_{ct,pc}}{1+j(0.5R_{ct,pc})\omega(2C_{dl,pc})} + \frac{0.5R_{ct,nc}}{1+j(0.5R_{ct,pc})\omega(2C_{dl,nc})} + \frac{0.5R_{ct,pd}}{1+j(0.5R_{ct,pd})\omega(2C_{dl,pd})} + \frac{0.5R_{ct,nd}}{1+j(0.5R_{ct,pd})\omega(2C_{dl,nd})}, \quad (14)$$

2.3. AC Equivalent First Principle Linear Elements on Batteries

 R_C , L_S and C_{bulk} are typical equivalent first principle linear elements on batteries [3,20]. Under AC current injections, steady-state DC static and AC fundamental voltage responses of each element are formulated in Equations (15)–(20). These equivalent elements only have AC fundamental voltage responses, and do not have DC static voltage responses; therefore, it is not necessary to determine the direction of excitation in advance, nor does it need to switch sub-models in simulations. The physical meanings of elements in the above equations are explained in Table A1 of the Appendix A.

Linear C_{bulk} , replacing the nonlinear Warburg impedance ($z_{Warburg}$) in Equation (21), represents the diffusion process of electrolyte. $z_{Warburg}$ usually characterizes the diffusion process of electrolyte [19], so researchers [28] propose to connect $z_{Warburg}$ with impedances on electrode–electrolyte interfaces in series to simplify the equivalent circuit. Warburg impedances of both negative and positive electrodes are combined as one equivalent $z_{Warburg}$. In this paper, this equivalent $z_{Warburg}$ is replaced by one C_{bulk} . Firstly, linear C_{bulk} has a clear electrochemical meaning under small-signal EIS operation [20]; secondly, linear C_{bulk} is a special nonlinear Constant Phase Element (z_{CPE}) with P equal to one in Equation (22).

$$V_C = \left(I_{EIS} e^{j\theta_{EIS}}\right) \left(R_C e^{j0}\right),\tag{15}$$

$$\langle v_C \rangle = \frac{1}{T} \int_0^T v_C dt = 0, \tag{16}$$

$$V_{StrayInd} = \left(I_{EIS}e^{j\theta_{EIS}}\right) \left(L_{S}e^{j\frac{\pi}{2}}\right),\tag{17}$$

$$\langle v_{StrayInd} \rangle = \frac{1}{T} \int_0^T v_{StrayInd} dt = 0, \tag{18}$$

$$V_{BulkCap} = \left(I_{EIS}e^{j\theta_{EIS}}\right) \left(C_{bulk}e^{j\left(-\frac{\pi}{2}\right)}\right),\tag{19}$$

$$\langle v_{BulkCap} \rangle = \frac{1}{T} \int_0^T v_{BulkCap} dt = 0,$$
⁽²⁰⁾

$$z_{Warburg} = \frac{R}{\left(jwT_{Warburg}\right)^{P}} \tanh\left(jwT_{Warburg}\right)^{P},\tag{21}$$

$$z_{CPE} = \frac{T_{CPE}^{-1}}{\left(j\omega\right)^{P}},\tag{22}$$

2.4. Experiment of Steady-state DC static Voltage Responses on Battery Terminals

The purpose of the experiment is to clarify that there are no steady-state DC static voltage responses on batteries' terminals under stable AC sinusoidal current excitation. Nowadays, board-level BMS is used to operate at frequencies as low as 0.5 Hz or 1.0 Hz. So, the electrochemical workstation (Solartron ModulabXM) sends high-precision pure trigonometric (sinusoidal) current-source excitations (5A rms) to the tested battery at two fixed frequencies, 0.5 Hz and 1.0 Hz. The tested battery, manufactured by Zhejiang Narada Power Source Co., Ltd., as shown in Figure 5, is a 500 Ah lead-acid cell with model name GFM-500R and number E-08#. The detection circuit, in Figure 6, is designed to sample battery terminal voltage and to amplify errors between terminal voltage and reference voltage (2.132 V) with DC gain (40.14). The overall configuration of the experimental platform is in Figure 7. AC current injections of the electrochemical workstation are intermittently closed and open, and the outputs of the detection circuit are measured by a digital multimeter (UNI-T UT33A+). When AC current injection is closed, the multimeter display is read at a fixed time delay; when AC current injection is open, the multimeter display is read at the same fixed time delay. After measuring two cycles by the same time delay, length of the next time delay is increased by 30 s.



Figure 5. Tested battery E-08#.



Figure 6. Detection circuit of steady-state DC static over-potentials on batteries' terminals.



Figure 7. Experimental platform.

2.5. Experiment of Steady-State AC fundamental Voltage Responses on Battery Terminals

Voltage response in the frequency domain reflects the steady-state amplitude and phase electrical characteristic of batteries' terminals. The experimental platform is set as Figure 7, but excludes the detection circuit.

2.6. Experiment of Extracting Directional Charge-Transfer Resistance in AC Nyquist Curve

Four batteries were paralleled in 70 °C accelerated aging tests for seven months, part of the twelve batteries stack multi-objective experiments in Figure 8. All batteries were designed and manufactured by Zhejiang Narada Power Source Co., Ltd. with model name GFM-500R; these four samples were numbered as E-52#, E-11#, E-02# and E-20#. After float charging with regulated terminal voltage (N*2.23 V, N is the number of testing batteries in the stack) at 70 °C for a month, the batteries stack was discharged for checking capacities and recharged for capacities recovering at room temperature. Twenty-four hours after recharging, each battery was individually scanned by the electrochemical workstation (Solartron ModulabXM) with 5A rms pure sinusoidal currents excitation and frequencies bands were from 1 MHz to 1 kHz. After EIS scanning, batteries were put back into a high-temperature container for the next test round. Battery capacities checking are plotted in Figure 9a and Nyquist curves of EIS are displayed in Figure 9b–e. Only even-numbered round experiments are shown to avoid crossing in Figure 9b–e.



Figure 8. Twelve batteries stack.





Figure 9. Capacities and EIS plots of batteries in accelerated aging tests: (**a**) batteries' capacities of tests rounds; (**b**) EIS of E-52#; (**c**) EIS of E-11#; (**d**) EIS of E-02#; (**e**) EIS of E-20#.

3. Results and Discussion

3.1. Results of Steady-State DC Static Voltage Responses on Battery Terminals

All measurement points are shown in Table 1. Some points data, before closed AC injection, are off records because they are almost the same as the last check point. The time domain outputs of the detection circuit are shown in Figure 10. Procedures of pulse and step were used to reduce sampling points and to act as low-pass filtering. In Figure 10, outputs are mainly in the transient process at the beginning, and gradually approaching to 660 mV after one hour. Then, the outputs are nearly stable around 660–670 mV, and the maximum voltage fluctuation, 10 mV in the secondary side, will not exceed 0.25 mV in the primary side, which is significantly less than the magnitude (3.2 mV in the primary side) obtained by $FPLC_{DCequ}$ simulation in Figure 4. Therefore, the experiment can prove that steady-state DC static overpotential on electrode–electrolyte interfaces is indeed zero under fixed frequency AC current inputs.

No.	Pulse Procedures	Timing (s)	Output (mV)
1	Before 0.5 Hz/5 A injection	740	451
2	150 s after 0.5 Hz/5 A injection close	880	484
3	150 s after 0.5 Hz/5 A injection open	1070	512
4	Before 0.5 Hz/5 A injection	1160	521
5	150 s after 0.5 Hz/5 A injection close	1310	546
6	150 s after 0.5 Hz/5 A injection open	1490	560
7	Before 0.5 Hz/5 A injection	1580	566
8	180 s after 0.5 Hz/5 A injection close	1760	577
9	180 s after 0.5 Hz/5 A injection open	1950	586
10	Before 0.5 Hz/5 A injection	2000	Missing
11	180 s after 0.5 Hz/5 A injection close	2180	597
12	180 s after 0.5 Hz/5 A injection open	2370	611
13	Before 0.5 Hz/5 A injection	2420	613
14	210 s after 0.5 Hz/5 A injection close	2630	619
15	210 s after 0.5 Hz/5 A injection open	2870	633
16	Before 0.5 Hz/5 A injection	3000	627
17	210 s after 0.5 Hz/5 A injection close	3210	636
18	210 s after 0.5 Hz/5 A injection open	3450	637
19	Before 0.5 Hz/5 A injection	3680	645
20	240 s after 0.5 Hz/5 A injection close	3920	644
21	240 s after 0.5 Hz/5 A injection open	4210	653
22	Before 0.5 Hz/5 A injection	4280	648

Table	1.	Measurement	timings	and	results
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No.	Pulse Procedures	Timing (s)	Output (mV)
23	240 s after 0.5 Hz/5 A injection close	4520	654
24	240 s after 0.5 Hz/5 A injection open	4815	663
25	Before 1.0 Hz/5 A injection	5970	663
26	150 s after 1.0 Hz/5 A injection close	6110	676
27	150 s after 1.0 Hz/5 A injection open	6340	668
28	Before 1.0 Hz/5 A injection		
29	150 s after 1.0 Hz/5 A injection close	6490	660
30	150 s after 1.0 Hz/5 A injection open	6720	668
31	Before 1.0 Hz/5 A injection		
32	180 s after 1.0 Hz/5 A injection close	6900	663
33	180 s after 1.0 Hz/5 A injection open	7130	674
34	Before 1.0 Hz/5 A injection		
35	180 s after 1.0 Hz/5 A injection close	7310	670
36	180 s after 1.0 Hz/5 A injection open	7535	665
37	Before 1.0 Hz/5 A injection		
38	210 s after 1.0 Hz/5 A injection close	7745	674
39	210 s after 1.0 Hz/5 A injection open	7990	669
40	Before 1.0 Hz/5 A injection		
41	210 s after 1.0 Hz/5 A injection close	8200	669
42	210 s after 1.0 Hz/5 A injection open	8450	661

Table 1. Measurement timings and results.



Figure 10. Time series of outputs of detection circuit.

Under sinusoidal AC current injections, steady-state DC static voltage responses on electrode–electrolyte interfaces are nearly zero in this detection experiment. Results of the detection circuit are almost ideal; some small errors can be tolerated and may be caused by ambient temperature fluctuations and battery self-heating by injection currents. Maybe a little steady-state DC static voltage response does appear on battery terminals, although it does not affect $FPLC_{ACequ}$ in engineering applications.

3.2. Results of Steady-State AC Fundamental Voltage Responses on Battery Terminals

Figure 11a is $FPLC_{ACequ}$ on battery, and Figure 11b is $BHLC_{ACequ}$ on battery. $FPLC_{ACequ}$ is shown in Equation (23) and $BHLC_{ACequ}$ is shown in Equation (24). The Nyquist curve from the EIS of the same 500 Ah battery (E-08#) is plotted with diagonal cross points in Figure 12. In Figure 12, the fitting curve of $FPLC_{ACequ}$ is plotted with cross points, and the fitting curve of $BHLC_{ACequ}$ is plotted with dot

points. The physical meanings of elements in the above equations are explained in Table A1 of the Appendix A.

$$z_{FPLC_{ACequ}} = R_{CFP} + j\omega L_{SFP} + \frac{1}{j\omega C_{bulkFP}} + \frac{0.5R_{ct,pc}}{1 + j(0.5R_{ct,pc})\omega(2C_{dl,pc})} + \frac{0.5R_{ct,nc}}{1 + j(0.5R_{ct,nc})\omega(2C_{dl,nc})} + \frac{0.5R_{ct,nc}}{1 + j(0.5R_{ct,nd})\omega(2C_{dl,nd})} + \frac{0.5R_{ct,nd}}{1 + j(0.5R_{ct,nd})\omega(2C_{dl,nd})},$$
(23)

$$z_{BHLC_{ACequ}} = R_{CBH} + j\omega L_{SBH} + \frac{1}{j\omega C_{bulkBH}} + \frac{R_{ct,p}}{1 + jR_{ct,p}\omega C_{dl,p}} + \frac{R_{ct,n}}{1 + jR_{ct,n}\omega C_{dl,n}},$$
(24)



Figure 11. Circuits fitting for EIS and Bode plots: (a) *FPLC*_{ACequ}; (b) behavioral linear circuit (*BHLC*_{ACequ}).



Figure 12. Experiment Nyquist curve is fitted by *FPLC*_{ACequ} and *BHLC*_{ACequ}.

The Nyquist curve is fitted by $FPLC_{ACequ}$ and $BHLC_{ACequ}$ through software Zview, and element values in circuits are compared in Table 2. According to test conditions, SoC on batteries are nearly 100%; charge-transfer resistances ($R_{ct,pc}$ and $R_{ct,nc}$) for charging of $FPLC_{ACequ}$, are much higher than charge-transfer resistances ($R_{ct,pd}$ and $R_{ct,nd}$) for discharging [3,20]. Charge-transfer resistors and double-layer capacitors are directional different. In Figure 4, elements values for simulation are also from Table 2.

Elements in First Principle Circuit	Values	Error	Error%	Elements in Behavioral Circuit	Values	Error	Error%
R _{CFP}	604.4 μΩ	10.9 μΩ	1.8	R _{CBH}	628.2 μΩ	8.1 μΩ	1.3
L_{SFP}	185.9 nH	4.9 nH	2.6	L _{SBH}	182.5 nH	5.2 nH	2.9
C_{bulkFP}	12,300.0 F	754.9 F	6.1	C _{bulkBH}	11,855.0 F	737.5 F	6.2
R _{ct,nd}	116.2 μΩ	59.452 μΩ	51.1	R _{ct} ,n	410.0 μΩ	24.6 μΩ	6.0
$R_{ct,nc}$	467.6 μΩ	147.8 μΩ	31.6	R _{ct} ,p	978.5 μΩ	42.1 μΩ	4.3
$R_{ct,pd}$	643.2 μΩ	153.6 μΩ	23.9	C _{dl,n}	125.2 F	10.8 F	8.7
$R_{ct,pc}$	1711.6 μΩ	153.9 μΩ	9.0	C _{dl,p}	1272.0 F	111.8 F	8.8
$C_{dl,nd}$	34.5 F	19.2 F	55.7	1			
$C_{dl.nc}$	83.9 F	25.7 F	30.7				
$C_{dl,pd}$	358.0 F	196.9 F	55.0				
$C_{dl,pc}$	1036.0 F	227.0 F	31.6				
Chi-squared	0.011			Chi-squared	0.013		
Weighted sum of squares	0.98			Weighted sum of squares	1.27		

Table 2. Values of elements in *FPLC*_{ACequ} and *BHLC*_{ACequ} for E-08#.

3.3. Results of Extraction Directional Charge-Transfer Resistance in AC Nyquist Curve

In Figure 13c,d, both magnitude and phase bode plots have obvious fitting errors at low frequencies. The errors are mainly due to C_{bulk} . $z_{Warburg}$ is supposed to reduce these errors, but is not convenient for BMS design.



Figure 13. Linear circuits fitting for bode plots: (a) $FPLC_{ACequ}$ fitting in magnitude; (b) $BHLC_{ACequ}$ fitting in magnitude; (c) $FPLC_{ACequ}$ fitting in phase; (d) $BHLC_{ACequ}$ fitting in phase.

The sums of resistances in $FPLC_{ACequ}$ are shown in Equations (25)–(28), and their amplitudes in magnitude bode plots are marked in Figure 13a. Based on contacting resistance, each step is corresponding to one charge-transfer resistance, and $0.5R_{ct,nd}$, $0.5R_{ct,nc}$, $0.5R_{ct,pd}$ and $0.5R_{ct,pc}$ orderly add up. The sums of resistances in $BHLC_{ACequ}$ are shown in Equations (29)–(30), and $R_{ct,n}$ and $R_{ct,p}$ orderly add up. They are also marked in Figure 13b. In magnitude bode plots, the asymptotes which roughly outline measured and fitting curves are drawn according to poles and zeros points.

$$R_{1FP} = R_{CFP} + 0.5R_{ct.nd},$$
 (25)

$$R_{2FP} = R_{CFP} + 0.5R_{ct,nd} + 0.5R_{ct,nc},$$
(26)

$$R_{3FP} = R_{CFP} + 0.5R_{ct,nd} + 0.5R_{ct,nc} + 0.5R_{ct,pd},$$
(27)

$$R_{4FP} = R_{CFP} + 0.5R_{ct,nd} + 0.5R_{ct,nc} + 0.5R_{ct,pd} + 0.5R_{ct,pc},$$
(28)

$$R_{1BH} = R_{CBH} + R_{ct,n}, \tag{29}$$

$$R_{2BH} = R_{CBH} + R_{ct,n} + R_{ct,p},\tag{30}$$

In experiments, batteries' capacities are almost full-charging; Therefore, charge-transfer resistances for discharging ($R_{ct,pd}$ or $R_{ct,nd}$) are smaller than charge-transfer resistances for charging ($R_{ct,pc}$ or $R_{ct,nc}$). Furthermore, if batteries' SoH is good, $R_{ct,pd}$ or $R_{ct,nd}$ for discharging are less than $R_{ct,pc}$ or $R_{ct,nc}$ for charging across the broad SoC range; otherwise, when batteries begin to discharge, $R_{ct,pd}$ and $R_{ct,nd}$ are used to increase significantly, and the batteries' terminal voltages drop obviously. Extracting the DC directional charge-transfer resistance from the AC Nyquist curve has engineering significance. In Figure 14, charge-transfer resistances of both $FPLC_{ACequ}$ and $BHLC_{ACequ}$ fluctuate during accelerated aging tests.



Figure 14. Elements values in linear circuits fitting for EIS: (a) $R_{ct,pc}$; (b) $R_{ct,pd}$; (c) $R_{ct,nc}$; and (d) $R_{ct,nd}$ in *FPLC*_{*ACequ*}; (e) $R_{ct,p}$; and (f) $R_{ct,n}$ in *BHLC*_{*ACequ*}.

However, increasing the decibel value of the sum of internal resistances, including contacting resistance and charge-transfer resistances, is relatively stable. Each decibel value of each ascending step in the magnitude bode plot is related to one charge-transfer resistance and one asymptotic line configured by the pole–zero pair in Figure 13a,b. Bode plots change during accelerated aging tests, but orders of $FPLC_{ACequ}$ and $BHLC_{ACequ}$ are fixed. Therefore, the scale ratio of the decibel value of each ascending step should be stable. Three ratios of decibel value of ascending steps in $FPLC_{ACequ}$, as Equations (31)–(33), are stable between 0.2 and 2.5 in Figure 15; these three steps are different and the ratios decrease from $DelatdB_{FP1}$ to $DelatdB_{FP3}$. The ratio of decibel value of ascending steps in $BHLC_{ACequ}$, as Equation (34), is stable between one and two in Figure 15.

$$DelatdB_{FP1} = 20 \log_{10} \left(\frac{R_C + 0.5R_{ct,nd} + 0.5R_{ct,nc}}{R_C + 0.5R_{ct,nd}} \right),$$
(31)

$$DelatdB_{FP2} = 20 \log_{10} \left(\frac{R_C + 0.5R_{ct,nd} + 0.5R_{ct,nc} + 0.5R_{ct,pd}}{R_C + 0.5R_{ct,nd} + 0.5R_{ct,nc}} \right),$$
(32)

$$DelatdB_{FP3} = 20log_{10} \left(\frac{R_{C} + 0.5R_{ct,nd} + 0.5R_{ct,nc} + 0.5R_{ct,pd} + 0.5R_{ct,pc}}{R_{C} + 0.5R_{ct,nd} + 0.5R_{ct,nc} + 0.5R_{ct,pd}} \right),$$
(33)

$$DelatdB_{BH} = 20log_{10} \left(\frac{R_C + R_{ct,n} + R_{ct,p}}{R_C + R_{ct,n}} \right), \tag{34}$$



Figure 15. Ratio of decibel values of ascending steps of the sum of internal resistances: (**a**) E-52#; (**b**) E-11#; (**c**) E-02#; and (**d**) E-20#.

In magnitude bode plots of Figure 13, the curves drawing from northwest at low frequency to southeast at high frequency are roughly straight lines. Assuming there is a four-bit analog-to-digital

converter for ideal straight-line input, its interpretation steps should be defined as 2^0 : 2^1 : 2^2 : 2^3 . So does a two-bit analog-to-digital converter, as 2^0 : 2^1 . The scale ratios of adjacent steps are two to maximize the measurement range. However, the curves in magnitude bode plots are not ideal straight lines, so the scale ratio of adjacent sums of resistances is not as ideal as two. Figure 15 shows a similar law, as the numbers of steps are strictly limited by $FPLC_{ACequ}$ and $BHLC_{ACequ}$. From this perspective, expansions and contractions of magnitude bode plots are reflecting on the sum of internal resistances, and resistances obtained in Nyquist are viable to characterize batteries' SoH.

In Figure 16, contacting resistances and stray inductances of both $FPLC_{ACequ}$ and $BHLC_{ACequ}$ are very close. High frequency zero points, determined by contacting resistances and stray inductances as Equation (35), are very close in both $FPLC_{ACequ}$ and $BHLC_{ACequ}$.



Figure 16. Elements values in linear circuits fitting for EIS: (**a**) R_{CFP} in $FPLC_{ACequ}$; (**b**) R_{CBH} in $BHLC_{ACequ}$; (**c**) L_{SFP} in $FPLC_{ACequ}$; (**d**) L_{SBH} in $BHLC_{ACequ}$.

The $FPLC_{ACequ}$ provides DC directional charge-transfer resistances for charging and discharging. Characteristic charge-transfer resistances on the electrode–electrolyte interface are calculated in [29] by $FPLC_{ACequ}$. During the first four accelerated aging tests rounds, positive characteristic charge-transfer resistances of E-02# are always high, and positive characteristic charge-transfer resistances of E-20# are climbing up in Figure 17a [29]. The positive characteristic charge-transfer resistances of E-52# reach a maximum at the fifth test round in Figure 17a [29]. The increasing of positive characteristic charge-transfer resistances represents non-cohesion of active mass of the positive electrode [4]; all these changes are early warnings of subsequent capacity degradation in Figure 9a. These early warnings are not be interpreted in $BHLC_{ACequ}$; the positive/negative behavioral charge-transfer resistances and contacting resistances of E-20# and E-11# fluctuate close to each other in Figure 14e,f and Figure 16b. Charge-transfer resistances in $FPLC_{ACequ}$, compared in $BHLC_{ACequ}$, characterize inside physical and electrochemical changes.



Figure 17. Characteristic charge-transfer resistances in $FPLC_{ACequ}$: (**a**) $r_{ct,p}$ of positive electrode; (**b**) $r_{ct,n}$ of negative electrode. [29].

3.4. Boundary between First Principle Circuits on Batteries in Field Applications

The steady-state DC static voltage responses appear in experiments in the literature [2,3,20], and the steady-state DC static voltage response is nearly zero in experiments of this paper. In field applications, injections of battery terminals are generally constant DC or stable AC currents; engineering separation between $FPLC_{ACequ}$ and $FPLC_{DCequ}$ can mainly be determined by time constants of injection currents. Time constants of currents are compared with time constants of impedances on electrode–electrolyte interfaces, especially of positive electrodes. If the time constants of impedances are much larger than the time constants of currents, $FPLC_{ACequ}$ is suitable; if the time constants of impedances are much smaller than the time constants of currents [20], $FPLC_{DCequ}$ is more suitable.

The practical rule of the boundary is considered in perspective of limit, but not from the perspective of arbitrary injections. This practical rule of option between these two first principle circuits has not been mentioned before. Boundaries of separation between $FPLC_{ACequ}$ and $FPLC_{DCequ}$ may be gradual or abrupt, and the boundaries patterns still need further research.

The purpose of this article is to establish a one-to-one relationship between the Nyquist curve and $FPLC_{DCequ}$. The steady-state DC static voltage response in Nyquist is zero after software and hardware filtering. The $FPLC_{ACequ}$ satisfies requirements in Section 2.1 and matches experimental results.

3.5. Comparing with Nonlinear Models

Average switch modeling is proposed to obtain $FPLC_{ACequ}$, and circuit orders are increased to include directional charge-transfer resistances. Average switch modeling can be extended to nonlinear electrochemical circuits. Nonlinear electrochemical elements, such as the constant phase element and Warburg element, are totally nondirectional and frequency-dependent [1], and they mainly represent the electrolyte diffusion process [24]. So, linear charge-transfer resistances for charging/discharging in nonlinear electrochemical circuits are the same as in $FPLC_{ACequ}$.

Figure 18a is an AC equivalent first principle nonlinear circuit (*FPNLC*_{ACequ} in Equation (36)), and Figure 18b is an AC equivalent behavioral nonlinear circuit (*BHNLC*_{ACequ} in Equation (37)) on batteries. The Nyquist of the EIS from the same 500 Ah battery (model GFM-500R and number E-8#), is

plotted with diagonal cross points in Figure 19; in Figure 19, the fitting curve of $FPNLC_{ACequ}$ is plotted with cross points, and the fitting curve of $BHNLC_{ACequ}$ is plotted with dot points.



Figure 18. Nonlinear circuits fitting for EIS: (**a**) *FPNLC*_{ACequ}; (**b**) *BHNLC*_{ACequ}.



Figure 19. Experimental Nyquist curve is fitted by FPNLC_{ACequ} and BHNLC_{ACequ}.

The Nyquist is fitted by $FPNLC_{ACequ}$ and $BHNLC_{ACequ}$ through software Zview, and element values in circuits are compared in Table 3. In Figure 19, both nonlinear circuits have obvious fitting errors at low frequencies. The errors are mainly due to z_{CPE} , and $z_{Warburg}$ is supposed to reduce these errors, but this is not mainly a concern in this paper.

$$z_{FPNLC_{ACequ}} = R_{CFP} + j\omega L_{SFP} + \frac{T_{CPE}^{-1}}{(j\omega)^{P}} + \frac{0.5R_{ct,pc}}{1 + j(0.5R_{ct,pc})\omega(2C_{dl,pc})} + \frac{0.5R_{ct,nc}}{1 + j(0.5R_{ct,nc})\omega(2C_{dl,nc})} + \frac{0.5R_{ct,nc}}{1 + j(0.5R_{ct,nd})\omega(2C_{dl,nc})} + \frac{0.5R_{ct,nc}}{1 + j(0.5R_{ct,nc})\omega(2C_{dl,nc})} + \frac{0.5R_{ct,nc}}{1 + j(0.5R_{ct,nc})\omega(2C_{dl,nc})}$$

Elements in First Principle Circuit	Values	Error	Error%	Elements in Behavioral Circuit	Values	Error	Error%
R _{CFP}	613.2 μΩ	6.7 μΩ	1.1	R _{CBH}	668.5 μΩ	13.5 μΩ	2.0
L_{SFP}	184.9 nH	3.7 nH	2.0	L_{SBH}	179.3 nH	9.5 nH	5.3
T_{CPE}	2.9×10^{6}	4.4×10^5	15.3	T_{CPE}	2.9×10^{6}	7.9×10^5	27.3
Р	2.95	$4.8 imes 10^{-2}$	1.6	Р	3.1	$6.6 imes 10^{-2}$	2.1
R _{ct.nd}	283.2 μΩ	54.6 μΩ	19.3	R _{ct,n}	957.0 μΩ	44.8 μΩ	4.7
R _{ct,nc}	748.9 μΩ	65.4 μΩ	8.7	$R_{ct,p}$	$8.5 imes 10^{19}$ Ω	$1\times 10^{20}\;\Omega$	117.6
R _{ct.pd}	1702.2 μΩ	83.0 μΩ	4.9	$C_{dl,n}$	258.3 F	21.8 F	8.4
$R_{ct,pc}$	$2.0 imes 10^{20}$ Ω	$2.0 imes 10^{20}$ Ω	100	$C_{dl,p}$	5874.0 F	585.2 F	10.0
$C_{dl.nd}$	44.5 F	7.3 F	16.4				
$C_{dl.nc}$	148.3 F	27.5 F	18.6				
$C_{dl,pd}$	794.0 F	86.5 F	10.9				
$C_{dl.vc}$	3884.0 F	235.3 F	6.1				
Chi-squared	0.006			Chi-squared	0.047		
Weighted sum of squares	0.57			Weighted sum of squares	4.42		

Table 3. Values of elements in Figure 18.

4. Conclusions

Impedances on electrode–electrolyte interface of $FPLC_{ACequ}$, established by average switch modeling, have a one-to-one relationship with impedances on the electrode–electrolyte interface of $FPLC_{DCequ}$. Therefore, a unique physical bridge from AC Nyquist, fitting by $FPLC_{ACequ}$, to the directional DC charge-transfer resistance of $FPLC_{DCequ}$ is proposed. Steady-state AC fundamental responses of $FPLC_{ACequ}$ are verified by theoretically derived time domain simulation and experiments in this paper.

This novel method provides an opportunity to review previous conclusions between *BHLC*_{ACequ} and SoC/SoH with directional DC charge-transfer resistances, and this is going to be researched further by authors.

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Appendix A

Item	Elements	Physical Meanings
1	EIS	electrochemical impedance spectroscopy
2	FPLC _{DCequ}	DC equivalent first principle linear circuit
3	SoH	state of health
4	<i>FPLC</i> _{ACequ}	AC equivalent first principle linear circuit
5	BMS	battery management system
6	SoC	state of charge
7	BHLC _{ACequ}	AC equivalent behavioral linear circuit
8	R _C	contacting resistor
9	L_S	stray inductor
10	C _{bulk}	electrolyte bulk capacitor
11	R _{ct}	charge-transfer resistor
12	C_{dl}	double-layer capacitor
13	Z _{eei}	impedance on electrode-electrolyte interface
14	R _{ct,pc}	charge-transfer resistor for charging on electrode–electrolyte interface of positive electrode
15	R _{ct,nc}	charge-transfer resistor for charging on electrode–electrolyte interface of negative electrode
16	R _{ct,pd}	charge-transfer resistor for discharging on electrode–electrolyte interface of positive electrode
17	R _{ct,nd}	charge-transfer resistor for discharging on electrode–electrolyte interface of negative electrode
18	$C_{dl,p}$	double-layer capacitor for both charging and discharging on electrode–electrolyte interface of positive electrode
19	$C_{dl,n}$	double-layer capacitor for both charging and discharging on electrode–electrolyte interface of negative electrode
20	C _{dl,pc}	double-layer capacitor for charging on electrode-electrolyte interface of positive electrode
21	C _{dl,nc}	double-layer capacitor for charging on electrode–electrolyte interface of negative electrode
22	$C_{dl,pd}$	double-layer capacitor for discharging on electrode–electrolyte interface of positive electrode
23	C _{dl,nd}	double-layer capacitor for discharging on electrode–electrolyte interface of negative electrode
24	$I_{EIS}e^{j\theta_{EIS}}$	fixed frequency sinusoidal current, excited from electrochemical workstation, I_{EIS} is the amplitude and θ_{EIS} is the static angle (rad) in rotating space vector plane
25	$Z_{Cha}e^{j\theta_{Cha}}$	linear impedances for charging on electrode–electrolyte interfaces of both positive and negative electrodes, Z_{Cha} is the amplitude and is the static angle (rad) in rotating space vector plane
26	$Z_{Dis}e^{j heta_{Dis}}$	linear impedances for discharging on electrode–electrolyte interfaces of both positive and negative electrodes, Z_{Dis} is the amplitude and θ_{Dis} is the static angle (rad) in rotating space vector plane

Table A1. The physical meanings of elements and abbreviations.

Item	Elements	Physical Meanings
27	$Z_{eei}e^{j\theta_{eei}}$	equivalent linear impedances on electrode–electrolyte interfaces of both positive and negative electrodes, Z_{eei} is the amplitude and θ_{eei} is the static angle (rad) in rotating space vector plane
28	V _{Cha}	charging voltage vector, steady-state AC fundamental response of linear impedances $Z_{Cha}e^{j\theta_{Cha}}$, in rotating space vector plane
29	V _{Dis}	discharging voltage vector, steady-state AC fundamental voltage response of linear impedances $Z_{Dis}e^{j\theta_{Dis}}$, in rotating space vector plane
30	V'_{Cha}	new charging voltage vector, half amplitude of V_{Cha} , in rotating space vector plane
31	V' _{Dis}	new discharging voltage vector, half amplitude of V_{Dis} , in rotating space vector plane
32	V _{eei}	target voltage vector, steady-state AC fundamental response of impedance $Z_{eei}e^{j\theta_{eei}}$, in rotating space vector plane
33	Т	fixed period of sinusoidal current, excited from electrochemical workstation
34	v _{Cha}	transient voltage responses of impedances for charging on electrode-electrolyte interfaces of both positive and negative electrodes
35	v_{Dis}	transient voltage responses of impedances for discharging on electrode-electrolyte interfaces of both positive and negative electrodes
36	$\langle v_{Cha} \rangle$	average voltage response of impedances for charging on electrode–electrolyte interfaces of both positive and negative electrodes during the period <i>T</i>
37	$\langle v_{Dis} \rangle$	average voltage response of impedances for discharging on electrode–electrolyte interfaces of both positive and negative electrodes during the period <i>T</i>
38	S	complex variable in transfer function
39	TF_{filter}	transfer function of band pass filter
40	Q	quality factor of band pass filter
41	ω	electrical angular velocity of sinusoidal current, excited from electrochemical workstation
42	$R_C e^{j0}$	linear contacting resistance, reflecting conductivity of path which currents flowing along terminals, cell connectors, plate connectors, electrodes, and electrolyte; R_C is the amplitude and 0 is the static angle (rad) in rotating space vector plane
43	$L_S e^{j\frac{\pi}{2}}$	linear stray inductance, in series with linear contacting resistance; L_S is the amplitude and $\frac{\pi}{2}$ is the static angle (rad) in rotating space vector plane
44	$C_{bulk}e^{j(-rac{\pi}{2})}$	linear electrolyte bulk capacitance, reflecting capacity characteristics of bulk electrolyte; C_{bulk} is the amplitude and $\left(-\frac{\pi}{2}\right)$ is the static angle (rad) in rotating space vector plane
45	V_C	contacting resistance voltage vector, steady-state AC fundamental responses on linear contacting resistance $R_C e^{j0}$
46	v_C	transient voltage responses of linear contacting resistance
47	$\langle v_C \rangle$	average voltage response of linear contacting resistance during the period <i>T</i>
48	V _{StrayInd}	inductance voltage vector, steady-state AC fundamental responses on linear stray inductance $L_S e^{j\frac{\pi}{2}}$

Table A1. Cont.

Item	Elements	Physical Meanings
49	v _{StrayInd}	transient voltage responses of linear stray inductance
50	$\langle v_{StrayInd} \rangle$	average voltage response of linear stray inductance during the period T
51	<i>V</i> _{BulkCap}	electrolyte bulk capacitance voltage vector, steady-state AC fundamental responses on linear electrolyte bulk capacitance $C_{bulk}e^{j(-\frac{\pi}{2})}$
52	v _{BulkCap}	transient voltage responses of linear electrolyte bulk capacitance
53	⟨v _{BulkCap} ⟩	average voltage response of linear electrolyte bulk capacitance during the period ${\cal T}$
54	z _{Warburg}	Warburg impedance
55	T _{Warburg}	diffusion constant of Warburg impedance
56	R	ohmic constant of Warburg impedance
57	z_{CPE}	Constant Phase Element
58	T _{CPE}	diffusion constant of Constant Phase Element
59	Р	constant of power function
60	R _{ct,p}	charge-transfer resistor for both charging and discharging on electrode–electrolyte interface of positive electrode
61	R _{ct,n}	charge-transfer resistor for both charging and discharging on electrode–electrolyte interface of negative electrode
62	R _{CFP}	linear contacting resistance of <i>FPLC</i> _{ACequ}
63	R _{CBH}	linear contacting resistance of BHLC _{ACequ}
64	L _{CFP}	linear stray inductance of <i>FPLC</i> _{ACequ}
65	L _{CBH}	linear stray inductance of BHLC _{ACequ}
66	<i>FPNLC</i> _{ACequ}	AC equivalent first principle nonlinear circuit
67	BHNLC _{ACequ}	AC equivalent behavioral nonlinear circuit

Table A1. Cont.

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