

Article

Condition-Dependent Open Circuit Voltage Behavior in Vanadium Redox Flow Batteries and Implications for State-of-Charge Estimation

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Abstract

Accurate state-of-charge (SOC) estimation is essential for reliable operation of vanadium redox flow batteries (VRFBs), yet many model-based methods treat the open-circuit-voltage (OCV)-SOC relationship as a fixed calibration curve. This study experimentally investigates condition-dependent SOC-OCV behavior using a laboratory-scale VRFB equipped with a bypass OCV cell. The bypass OCV method was validated against an intermittent discharge–rest method, with OCV differences below 5 mV. SOC-OCV characteristics were then examined under different electrolyte flow rates, cycling histories, electrolyte/component refreshing conditions, and a dynamic stress test profile. The results show that the SOC-OCV curve varies with cycling history and flow rate, while electrolyte/component refreshing and dynamic operation further modify the measured OCV response. Fixed-curve-based SOC inversion confirms that calibration mismatch can introduce substantial SOC estimation errors, with a case-specific maximum error of 11.36% observed when the initial post-preconditioning constant-current curve was applied to the cell after 50 cycles under the tested 96 mL min^{−1} DST condition. These findings highlight the need for adaptive OCV correction and condition-dependent SOC-OCV mapping in practical VRFB SOC estimation.

Keywords: vanadium redox flow battery; state-of-charge estimation; SOC-OCV relationship; bypass OCV measurement; condition-dependent OCV behavior; electrolyte flow rate; cycling history; electrolyte imbalance

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1. Introduction

With the accelerated transition of the global energy system toward low-carbon and renewable generation, energy storage technologies have become essential for mitigating the intermittency of wind and photovoltaic power and supporting peak shaving, frequency regulation, and long-duration grid storage [1–3]. Among various energy storage technologies, VRFBs are regarded as a promising solution for large-scale energy storage owing to their decoupled power and energy ratings, intrinsic safety, long cycle life, and flexible scalability [4,5]. Nevertheless, practical VRFB systems still suffer from electrolyte imbalance, capacity fading, and efficiency degradation during long-term operation, which directly affect the available capacity, energy efficiency, and service life of the battery sys-

tem [6–9]. Therefore, accurate SOC estimation is a critical function of the battery management system, as it provides essential information for charge–discharge control, operating-range regulation, overcharge/overdischarge prevention, and electrolyte-capacity utilization [10,11].

Unlike conventional closed-cell batteries, the SOC of a VRFB is intrinsically related to the concentration distribution of vanadium species with different valence states in the positive and negative electrolytes. Under ideal conditions, where the two half-cell electrolytes remain balanced in concentration and capacity, the SOC can be evaluated by Coulomb counting or inferred from the SOC-OCV relationship derived from the Nernst equation. A generalized electrochemical framework developed by Di Noto et al. further relates the overall VRFB OCV to the positive- and negative-half-cell potentials, ion activities, and electrolyte valence imbalance [12]. This framework indicates that changes in the two electrolyte states can produce SOC-dependent and nonuniform variations in the full-cell voltage even though the underlying Nernst relations remain valid. In practical operation, however, the SOC is affected by coupled electrochemical and transport processes, including vanadium ion crossover, water migration, side reactions, temperature variation, flow-rate-dependent mass transport, and capacity fading [13–16]. Temperature is another important operating condition that may influence the measured SOC-OCV relationship. Thermodynamically, temperature affects the equilibrium potential through the Nernst equation, while it also modifies electrolyte properties, reaction kinetics, and membrane transport. Previous studies have shown that temperature gradients can alter ion transport and electrochemical behavior in VRFBs [17]. Consequently, together with ion crossover, water migration, electrolyte imbalance, flow-dependent mass transport, and capacity fading, temperature may contribute to condition-dependent variations in the measured SOC-OCV relationship.

Accordingly, various SOC estimation methods have been proposed for VRFBs, which can generally be classified into direct measurement methods, model-based estimation methods, and data-driven methods. The principles, characteristics, advantages, and limitations of these methods are summarized in Table 1.

Table 1. Comparison of Common SOC Estimation Methods for VRFB.

Category	Representative Methods	Main Feature	Advantages	Limitations	Typical Applications
Direct measurement	Coulomb counting [18]	SOC is calculated by integrating the charge/discharge current and comparing it with the rated or theoretical capacity.	Simple principle, easy implementation, suitable for online use.	Dependent on initial SOC and capacity; sensor errors accumulate over time.	Short-term operation, auxiliary estimation, SOC initialization.
	OCV method [18]	SOC is inferred from the SOC-OCV relationship derived from the Nernst equation or experimental calibration.	Clear physical meaning, relatively high accuracy, useful as a reference.	Requires rest or low-polarization conditions; affected by temperature, electrolyte state, and SOC-OCV curve shift.	Offline calibration, rest-state correction, model reference.
	Concentration/property measurement [19–27]	SOC is obtained from electrolyte states measured by titration, spectroscopy, conductivity, density, viscosity, or acoustic methods.	Directly reflects active-species concentration and electrolyte condition.	Complex instrumentation, high cost, limited online practicality.	Experimental validation, SOC calibration, high-accuracy diagnostics.

Model-based estimation	Electrochemical model (EM) [28,29]	SOC dynamics are described using mass balance, charge balance, transport, thermal behavior, and membrane crossover mechanisms.	Strong physical interpretability; can capture flow-rate, temperature, and crossover effects.	Numerous parameters, complex modeling, and high computational burden.	Mechanism analysis, system simulation, factor-sensitivity studies.
	Equivalent circuit model (ECM) [30–32]	Terminal-voltage dynamics and polarization behavior are represented by resistors, capacitors, and voltage sources.	Simple structure, easy parameter identification, suitable for engineering applications.	Limited physical interpretability; parameters vary with operating conditions and aging.	Online BMS estimation, parameter identification, voltage prediction.
	Filtering/observer methods [33–38]	SOC is recursively estimated by combining EM or ECM with EKF, UKF, RLS, H^∞ , sliding-mode observers, etc.	Capable of online correction of model errors and measurement noise; generally high accuracy.	Dependent on model fidelity; tuning of parameters and noise covariance is relatively complex.	Online SOC estimation, dynamic profiles, complex operating conditions.
Data-driven estimation	Neural networks/machine learning [39–42]	A nonlinear mapping between measurable inputs, such as voltage, current, temperature, and flow rate, and SOC is learned from data.	No need for an accurate physical model; strong nonlinear fitting capability.	Requires large high-quality datasets; limited generalization and interpretability.	Data-rich modeling, nonlinear systems, auxiliary SOC estimation.

As shown in Table 1, direct measurement methods are physically intuitive but are limited by accumulated integration errors, rest requirements, or additional measurement devices. Data-driven methods exhibit strong nonlinear mapping capability, but their performance depends strongly on the quality and coverage of training data, and their interpretability remains limited. In comparison, model-based estimation methods, especially those based on equivalent circuit models or simplified electrochemical models, can recursively correct the SOC using measurable electrical signals and identified model parameters. Owing to their favorable balance among estimation accuracy, physical interpretability, and engineering feasibility, model-based methods have been widely investigated for online SOC estimation in VRFBs. In these methods, the SOC-OCV relationship plays a fundamental role because it provides the thermodynamic equilibrium potential in the terminal-voltage model and is commonly used for SOC initialization, correction, and parameter identification. Representative model-based studies have employed an experimentally calibrated OCV-SOC relationship or a predefined equilibrium-voltage function within equivalent-circuit models, extended Kalman filters, unscented Kalman filters, particle filters, and multi-timescale estimators [32–35]. For example, Mohamed et al. represented the open-circuit cell potential as an intrinsic function of SOC in an equivalent-circuit model and subsequently used an extended Kalman filter for online SOC estimation [33]. Wei et al. developed multi-timescale and adaptive estimators in which model parameters, SOC, and capacity were updated online, while the equilibrium-voltage relationship remained an embedded model function [32]. More recent UKF- and hybrid-filter-based studies have similarly focused on improving state estimation, capacity tracking, parameter adaptation, or filter robustness on the basis of a predefined battery voltage model [34,35]. In such formulations, the estimator states, model parameters, covariance matrices, or noise statistics may be updated recursively, whereas the underlying SOC-OCV relationship is generally calibrated in advance and retained as a fixed or nominal model prior. This treatment is reasonable when the calibration and application conditions remain consistent, but it may

introduce systematic model bias if the actual SOC-OCV relationship evolves with flow rate, cycling history, electrolyte balance, component state, or operating profile.

However, the accuracy of these methods depends not only on the estimator structure but also on the validity of the embedded SOC-OCV mapping. Most improvements reported in model-based VRFB SOC estimation have focused on filter design, covariance adaptation, observer robustness, equivalent-circuit parameter identification, or voltage-residual correction, while the predefined SOC-OCV relationship itself is often assumed to remain valid after calibration. Consequently, a systematic change in this mapping may persist as a model-structure bias even when the estimator is well tuned. Comparatively less attention has been devoted to experimentally determining whether the SOC-OCV relationship remains invariant across different electrolyte flow rates, cycling histories, electrolyte/component states, and dynamic operating profiles. This issue is particularly important for VRFBs because the continuously circulating electrolytes and evolving physicochemical states can change the correspondence between normalized SOC, electrolyte composition, and the measured OCV. For VRFBs, this assumption may be restrictive because the continuously circulating electrolytes and evolving physicochemical states can alter the correspondence between the measured OCV and the average thermodynamic state of the battery. Ion crossover, self-discharge, water transfer, gas evolution, vanadium precipitation, and changes in membrane or electrode conditions may gradually modify the electrolyte balance and active-species distribution. Membrane structure and ion-transport selectivity are particularly important because they govern the trade-off between proton conductivity and the suppression of vanadium-species crossover. Previous membrane-optimization studies have shown that bilayer Nafion/ WO_3 structures and WO_3 -doped SPEEK membranes can suppress vanadium-ion permeation while maintaining adequate proton transport [43,44]. More recently, Li et al. demonstrated that incorporating hydrophilic ZrO_2 nanoparticles into a SPEEK matrix can enhance water uptake and proton conductivity while reducing vanadium-ion permeability and improving ion selectivity [45]. These studies illustrate that membrane composition, microstructure, and hydrophilicity jointly regulate proton conduction and vanadium-species crossover. Improved membrane selectivity can therefore mitigate cross-contamination, self-discharge, positive/negative electrolyte imbalance, and cycling-induced capacity decay, thereby reducing one potential source of long-term SOC-OCV evolution. In addition to these bulk-electrolyte effects, the surface state of porous electrodes may influence the measured voltage response. Changes in surface functional groups, wettability, electrochemically active area, and adsorbed species can modify the kinetics of the $\text{V}^{2+}/\text{V}^{3+}$ and $\text{VO}^{2+}/\text{VO}_2^+$ redox reactions and the rate at which the electrode/electrolyte interface approaches equilibrium. Chen et al. demonstrated that modification of graphite-felt surface properties can significantly regulate vanadium redox kinetics and polarization behavior [46]. More recently, Huang et al. showed that controlling the morphology and network structure of carbon nanotubes grown on thermally oxidized carbon cloth can regulate positive-electrode redox activity, conductive-network formation, and electrolyte-flow uniformity in VRFBs [47]. These studies demonstrate that electrode microstructure and interfacial properties can jointly influence redox kinetics and mass transport. Therefore, electrode-interface evolution may contribute to the measured or apparent OCV response under finite equilibration and continuous-flow conditions, although it does not necessarily alter the ideal thermodynamic equilibrium potential directly. In addition, electrolyte flow rate affects mixing, mass transport, concentration polarization, and the response consistency between the main battery and the OCV measurement path. Temperature may further alter the equilibrium potential, electrolyte properties, reaction kinetics, and membrane transport. Therefore, for VRFBs operating under varying cycling histories, flow conditions, thermal states, and bat-

tery conditions, the SOC-OCV relationship may deviate from a single fixed calibration curve and should be examined as a condition-dependent characteristic.

Motivated by this gap, the present study experimentally examines the validity of the fixed SOC-OCV assumption in SOC estimation of VRFB. The main contributions are summarized as follows. First, a bypass OCV measurement configuration is validated against an intermittent discharge–rest reference, enabling continuous characterization of the measured SOC-OCV relationship without interrupting main-cell operation. Second, a unified experimental matrix is used to quantify the dependence of the SOC-OCV relationship on electrolyte flow rate, the initial post-preconditioning and 50-cycle states, electrolyte-only and electrolyte-plus-component refreshing, and CC and DST operating profiles. The resulting curve shifts, intersection locations, and integral absolute OCV deviations are compared to reveal the condition dependence of the measured mapping. Third, the experimentally observed SOC-OCV deviations are propagated through fixed-curve SOC inversion to quantify the resulting estimation errors under selected calibration–application mismatch cases. This analysis demonstrates that SOC-OCV mismatch is not merely a measurement-noise issue, but a potential source of systematic model bias in SOC correction, voltage prediction, parameter identification, and capacity estimation. Accordingly, the objective of this study is not to propose a new filtering algorithm, but to experimentally evaluate the validity of a commonly embedded model assumption and to clarify the estimation consequences when the calibration and operating conditions are mismatched.

2. Experimental Setup and Methodology

2.1. VRFB Test Platform with Bypass OCV Measurement Configuration

The experimental platform used in this study was a laboratory-scale VRFB system equipped with a bypass OCV measurement unit, which was jointly designed and developed by the authors and Wuhan Zhisheng New Energy Co., Ltd. (Wuhan, Hubei Province, China). As shown in Figure 1, the platform mainly consists of a main test cell, a bypass OCV cell, positive and negative electrolyte reservoirs, circulation pumps, a battery cycler, and a host computer. The main test cell was used for charge–discharge operation and terminal-voltage measurement, whereas the bypass OCV cell was introduced into the electrolyte circulation loop to provide an external voltage reference associated with the sampled circulating-electrolyte state.

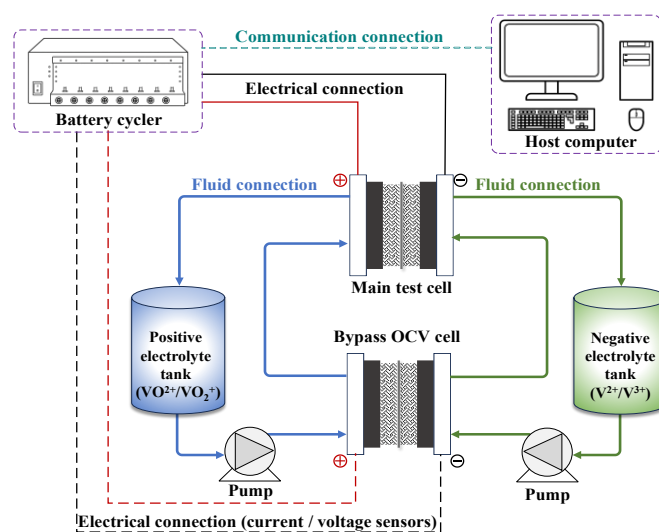


Figure 1. Schematic diagram of the VRFB test platform with a bypass OCV measurement cell.

Both the main test cell and the bypass OCV cell were single cells with an active area of $2\text{ cm} \times 2\text{ cm}$ and a rated current density of 160 mA cm^{-2} . Nafion 212 was used as the ion-exchange membrane. Before the experiment, 30 mL of electrolyte with an average vanadium valence of 3.5 was added to each of the positive and negative electrolyte reservoirs. The electrolyte consisted of 1.7 M vanadium ions and 4.2 M sulfuric acid. During the initial charging process, the 3.5-valence electrolyte was converted into the corresponding positive and negative redox couples, i.e., $\text{VO}^{2+}/\text{VO}_2^{+}$ in the positive electrolyte and $\text{V}^{2+}/\text{V}^{3+}$ in the negative electrolyte. Prior to testing, the negative electrolyte reservoir was purged with nitrogen to remove residual air and suppress the oxidation of V^{2+} species. Magnetic stirring was used in the positive and negative electrolyte tanks to accelerate electrolyte mixing.

During operation, the positive and negative electrolytes were circulated through the main test cell and the bypass OCV cell by pumps at the specified flow rates. The bypass OCV cell shared the same electrolyte streams with the main test cell but was electrically isolated from the charge–discharge circuit. Therefore, its measured voltage was used to characterize the OCV associated with the electrolyte composition arriving at the bypass measurement path. This configuration enabled continuous OCV monitoring without interrupting the operation of the main test cell, thereby providing a basis for constructing and analyzing the SOC-OCV relationship under different operating conditions. It should be noted that the bypass cell measures the voltage response of the sampled circulating electrolyte rather than the instantaneous local equilibrium potential inside the porous electrodes of the main cell. Consequently, the representativeness of the measured bypass OCV may depend on electrolyte mixing, hydraulic transport, residence time, and concentration redistribution along the circulation loop. Under dynamic operating conditions, the bypass OCV response may exhibit a transport-related delay relative to the instantaneous electrochemical state inside the main cell. The magnitude of this delay depends on the circulation-loop volume, electrolyte flow rate, and local mixing behavior. However, a quantitative transport time was not directly measured in the present experiment. Moreover, the effective flow-path volume and residence-time distribution, including the effects of tubing, junctions, mixing, and flow dispersion, were not independently characterized. Therefore, a reliable single time constant cannot be reconstructed retrospectively from the available data. The bypass OCV should consequently be interpreted as a continuously measured voltage reference associated with the circulating electrolyte state rather than an exact instantaneous equilibrium potential at the electrode interface.

Charge–discharge tests were carried out using a battery cycler (CT-4008Tn-5V6A-S1-F, NEWARE, Shenzhen, China). The voltage and current measurement accuracies of the cycler were both $\pm 0.05\%$ of full scale. The battery cycler was connected to a host computer for real-time control and data acquisition. The terminal voltage and current of the main test cell, together with the voltage of the bypass OCV cell, were recorded during the experiments. The collected data were subsequently used for SOC calculation, SOC-OCV curve construction, and evaluation of SOC-OCV deviations under different flow-rate and battery-state conditions.

2.2. SOC-OCV Characterization Methods

The SOC-OCV characteristics of the VRFB were obtained using the bypass OCV measurement method and the intermittent discharge-rest method. Before each formal experimental sequence, the cell was subjected to one low-current preconditioning cycle at 60 mA cm^{-2} (0.24 A). This procedure was performed before the subsequent CC-CV cycling or other prescribed experimental profiles. Its primary purpose was to convert the initial 3.5-valence electrolyte into the corresponding positive and negative vanadium redox couples and to establish a common and reproducible initial condition for the following tests.

It was not intended to demonstrate that all electrochemical performance indicators had reached a fully stabilized long-term state. In this manuscript, the term “fresh cell” therefore refers to the initial post-preconditioning state, i.e., the experimental baseline after the low-current preconditioning process and before the subsequent 50-cycle test. Thus, “fresh” does not denote a completely unused cell or a fully stabilized long-term operating state.

For each SOC-OCV characterization test, the cell was first charged at the rated current density until the terminal voltage reached 1.6 V, followed by a constant-voltage stage at 1.6 V until the current decreased to 0.05 A. The state at the end of the CC-CV charging process was defined as 100% SOC. The cell was then discharged at the rated current density to 0.8 V, which was defined as 0% SOC. To account for capacity variations under different operating conditions, the actual charge capacity and discharge capacity of each test were used to normalize the SOC during the corresponding charge and discharge processes, respectively.

In the bypass OCV method, the main test cell was operated under the prescribed charge–discharge process, while the bypass OCV cell shared the same circulating electrolytes and remained electrically isolated from the charge–discharge circuit. Therefore, the bypass-cell voltage was used as an external OCV reference associated with the time-varying sampled circulating-electrolyte state, subject to the hydraulic transport and mixing effects described in Section 2.1. The current, terminal voltage of the main cell, and bypass OCV were recorded simultaneously with a sampling interval of 1 s.

The intermittent discharge-rest method was used to obtain discrete SOC-OCV points for comparison. In this method, the fully charged cell was discharged at the rated current density for 5 min and then rested for 10 min to reduce the influence of polarization. The terminal voltage at the end of each rest period was taken as the OCV at the corresponding SOC. This process was repeated until the terminal voltage reached 0.8 V.

All experiments were conducted in an air-conditioned laboratory. According to the laboratory air-conditioning records, the ambient temperature was maintained approximately within 25 ± 1 °C during the test period. In addition, the external surface temperatures of the main cell and electrolyte reservoirs were checked periodically using an infrared thermometer to avoid large temperature differences among the comparative experiments. No obvious abnormal temperature rise was observed during these intermittent inspections. However, neither the cell nor the circulating electrolytes were actively temperature-controlled, and the internal electrolyte temperature was not continuously or precisely recorded. The infrared measurements provided only approximate surface-temperature checks and could not resolve short-term fluctuations or spatial temperature gradients within the cell, reservoirs, and circulation loop. Temperature was therefore not treated as an independent experimental variable in the present test matrix, which was designed primarily to investigate electrolyte flow rate, cycling history, renewal condition, and operating profile. Although the common ambient-temperature range and periodic inspections reduced large thermal differences among the comparative tests, a residual temperature contribution to the measured OCV response cannot be completely excluded.

2.3. Experimental Protocols

The experimental protocols were designed to investigate the SOC-OCV characteristics of the VRFB under different flow-rate conditions, cycling histories, cell states, and operating profiles. The cell in its initial post-preconditioning state, hereafter referred to as the “fresh cell,” was first tested as the baseline condition. SOC-OCV characterization tests were conducted at four electrolyte flow rates, i.e., 36, 60, 96, and 120 mL min^{−1}, using the CC-CV charge/CC discharge profile combined with bypass OCV measurement. In addition, the intermittent discharge-rest method was performed for the fresh cell at selected flow rates to validate the bypass OCV measurement method.

After the baseline tests, the cell was subjected to 50 charge–discharge cycles at the rated current density using CC–CV charging and CC discharging. The charge and discharge capacities of each cycle were recorded to evaluate the capacity evolution during cycling. The capacity retention after 50 cycles was calculated relative to the initial post-preconditioning reference capacity. The SOC–OCV characterization tests were then repeated at 36, 60, 96, and 120 mL min^{−1} to evaluate the cycling-induced deviation of the SOC–OCV relationship. After cycling, two sequential renewal conditions were examined. In both cases, the electrolyte reservoirs were emptied and rinsed with distilled water and fresh electrolyte, while the circulation tubing was not separately rinsed. In the electrolyte-only case, the original membrane and electrodes were retained without additional rinsing or soaking; in the electrolyte-and-component case, both were replaced with new components. Therefore, a small amount of cycled electrolyte may have remained in the tubing and, for the electrolyte-only case, within the original membrane and porous electrodes. The same low-current preconditioning procedure was applied after each renewal before SOC–OCV characterization. The additional recovery relative to the electrolyte-only case was used to examine whether the membrane and/or electrode state contributed further to the measured SOC–OCV deviation. These experiments were designed as a stepwise diagnostic comparison. However, because separate membrane-only and electrode-only replacement groups were not included, the individual contributions of the membrane and electrodes could not be independently quantified.

To examine the influence of dynamic operating profiles, a dynamic stress test (DST) discharge experiment was further conducted at a flow rate of 96 mL min^{−1} for the cycled cell. Before the DST discharge test, the cell was charged using the same CC–CV protocol. The bypass OCV was recorded during the DST discharge process to analyze the OCV response under dynamic current excitation.

Each test was repeated twice to ensure repeatability. If a relatively large deviation was observed between the two repeated tests, an additional test was conducted. The low-current preconditioning process was not included in the reported cycling history. The experimental matrix, including the test conditions, cycling history, flow-rate settings, operating profiles, and main purposes, is summarized in Table 2.

Table 2. Experimental matrix for SOC–OCV characterization.

Test Group	Condition	Cycling History	Flow Rate (mL min ^{−1})	Profile	Purpose
T1	Fresh cell	0	36, 60, 96, 120	CC–CV/CC + bypass OCV	Baseline and flow-rate effect
T2	Fresh cell	0	36, 96	Intermittent discharge–rest	Bypass OCV validation
T3	Cycled cell	50 cycles	36, 60, 96, 120	CC–CV/CC + bypass OCV	Cycling-induced deviation
T4	Cycled cell with refreshed electrolyte	50 cycles before electrolyte replacement	36, 60	CC–CV/CC + bypass OCV	Electrolyte-state effect
T5	Cycled cell with refreshed electrolyte and components	50 cycles before electrolyte and components replacement	60	CC–CV/CC + bypass OCV	Component replacement effect
T6	Cycled cell	50 cycles	96	CC–CV/DST + bypass OCV	Dynamic-condition effect

Note: “Fresh cell” refers to the initial post-preconditioning state after completion of the low-current conversion procedure. The preconditioning cycle is not included in the reported cycling history; therefore, a cycling history of 0 indicates the experimental baseline immediately after preconditioning and before the subsequent 50-cycle test. The same low-current preconditioning procedure was repeated after electrolyte or component replacement before the corresponding SOC–OCV characterization tests.

2.4. Data Processing and Evaluation Metrics

The measured current, terminal voltage, bypass OCV, and time data were processed to construct the SOC-OCV curves. For each charge or discharge process, the SOC was calculated by Coulomb counting and normalized using the actual charge or discharge capacity of the corresponding test. To quantify the capacity evolution during the 50-cycle test, the discharge-capacity retention was calculated as:

$$R_Q = \frac{Q_{\text{cycled_cell}}}{Q_{\text{fresh_cell}}} \times 100\% \quad (1)$$

where $Q_{\text{fresh_cell}}$ is the discharge capacity measured under the initial post-preconditioning reference condition and $Q_{\text{cycled_cell}}$ is the discharge capacity after 50 cycles.

All SOC-OCV curves were interpolated onto a common SOC grid. The charge and discharge OCV curves obtained under the same condition were then averaged at identical SOC points to obtain the representative SOC-OCV curve.

Different evaluation metrics were used for different analysis purposes. To validate the bypass OCV measurement method, the OCV values obtained by the bypass OCV method were compared with the discrete OCV points obtained by the intermittent discharge-rest method at the same SOC values. The mean absolute error (MAE), root mean square error (RMSE), and maximum absolute error were used to quantify the consistency between the two OCV acquisition methods.

For the comparison of SOC-OCV curves under different battery states or flow-rate conditions, the OCV difference was calculated at the same SOC points. The sign of the OCV difference was used to identify the direction of the curve shift, while the integral area of the absolute OCV difference was used to quantify the overall curve deviation over the full SOC range. This metric was mainly used to evaluate the accumulated SOC-OCV deviation among the fresh cell, the cycled cell, the refreshed-electrolyte cell, and the refreshed-electrolyte-and-component cell. In addition, the intersection points between different curves were identified to analyze the SOC regions where the OCV deviation changed direction.

To provide a clearer overview of the experimental evidence and its implications for SOC estimation, the overall analytical framework of this study is illustrated in Figure 2. As shown in Figure 2, the experimental results in Section 3 are organized from bypass OCV validation to flow-rate, cycling, refreshing, and dynamic-operating-condition analyses, and are then linked to the SOC estimation error analysis and model-based estimation implications discussed in Section 4.

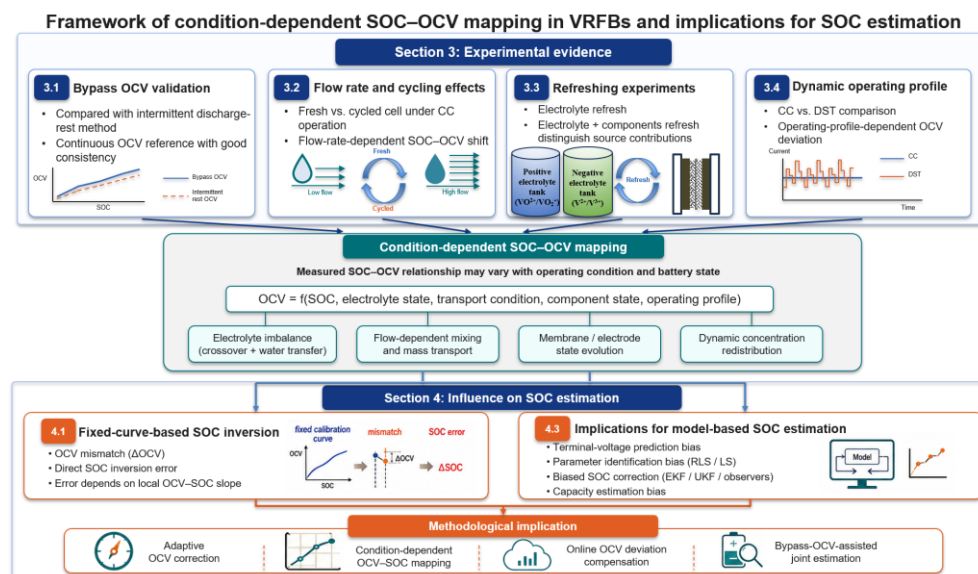


Figure 2. Overall framework of the condition-dependent SOC-OCV mapping in VRFBs and its implications for SOC estimation.

3. Experimental Results and Analysis

3.1. Validation of the Bypass OCV Measurement Method

To verify the reliability of the bypass OCV measurement method, the SOC-OCV curves obtained from the bypass OCV cell were compared with the discrete OCV points measured by the intermittent discharge-rest method. The intermittent discharge-rest method was used as a reference because the rest period can reduce the influence of polarization, and the terminal voltage at the end of each rest stage can be regarded as an approximate equilibrium OCV. Therefore, the consistency between these two methods was used to evaluate whether the bypass OCV cell could effectively track the electrolyte-state-dependent OCV during battery operation.

For quantitative comparison, the OCV deviation between the two methods at the same SOC point was defined as:

$$\Delta OCV_{method} = OCV_{bypass} - OCV_{rest} \quad (2)$$

where OCV_{bypass} and OCV_{rest} are the OCV values measured by bypass OCV method and the intermittent discharge-rest method, respectively. The mean absolute error (MAE), maximum absolute error (MAX) and root mean square error (RMSE) were adopted to quantify the curve deviation:

$$MAE = \frac{1}{N} \sum_{k=1}^N |\Delta OCV_k| \quad (3)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{k=1}^N \Delta OCV_k^2} \quad (4)$$

$$MAX = \max |\Delta OCV_k| \quad (5)$$

where k is the number of compared SOC points.

Figure 3 compares the SOC-OCV curves obtained by the bypass OCV method and the intermittent discharge-rest method at flow rates of 36 and 96 mL min⁻¹. The bypass OCV curves agree well with the discrete rest-voltage points over the full SOC range. Both methods show almost identical nonlinear OCV variation trends, including the rapid volt-

age change near high and low SOC regions and the relatively smooth voltage variation in the middle SOC range. This indicates that the bypass OCV cell can effectively track the voltage response associated with the sampled circulating-electrolyte state under the tested conditions.

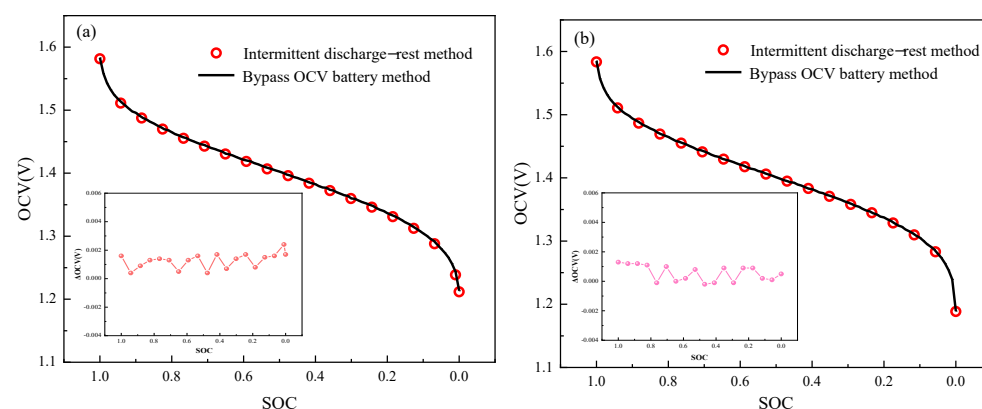


Figure 3. Comparison of SOC-OCV curves obtained by the bypass OCV method and the intermittent discharge-rest method under different flow rates: (a) 36 mL min^{−1}; (b) 96 mL min^{−1}.

The inset plots in Figure 3 and Table 3 further show the OCV difference between the two methods. At each stationary measurement point, the difference in OCV obtained by the two methods was less than 5 mV. Considering that the voltage measurement accuracy of the battery testing system is ± 2.5 mV, this deviation is within an acceptable range of measurement uncertainty. Meanwhile, the results also show that for test systems without an external bypass OCV cell, the intermittent discharge-resting method can still obtain relatively accurate SOC-OCV relationships. This method does not require an additional bypass device, is relatively simple to implement experimentally, and has good engineering applicability. However, compared with the continuous SOC-OCV data obtained by the bypass OCV cell method, the intermittent resting method can only obtain discrete OCV data points, and the test time is longer, thus still having certain limitations in terms of continuous dynamic characterization capabilities.

Table 3. Error comparison between the bypass OCV method and the intermittent discharge-rest method.

Flow Rate (mL min ^{−1})	MAE (mV)	RMSE (mV)	MAX (mV)
36	1.274	1.374	2.400
96	0.600	0.755	1.300

The smaller error observed at 96 mL min^{−1} suggests that increasing the electrolyte flow rate improves the consistency between the bypass OCV method and the intermittent discharge-rest reference. At the higher flow rate, stronger convection and circulation can reduce axial concentration gradients in the flow channels, improve electrolyte penetration and renewal within the porous electrodes, and enhance mixing in the reservoirs and connecting pipelines. The electrolyte reaching the bypass cell is therefore more likely to represent the average composition of the circulating electrolyte, while the transport delay between the main cell, reservoirs, and bypass path is reduced. In contrast, at 36 mL min^{−1}, concentration boundary layers and intraporous concentration gradients may become more pronounced, and the residence time of the electrolyte in the cell and connecting pipelines becomes longer. Under these conditions, the electrolyte composition at the main-cell reaction interface, the main-cell outlet, the reservoirs, and the bypass-cell inlet may not be fully synchronized. The bypass cell may therefore measure a spatially aver-

aged or delayed electrolyte state that differs slightly from the local composition near the working-electrode interface, resulting in the larger deviation from the intermittent discharge–rest reference. Although the bypass cell is electrically isolated and therefore does not experience the load-current polarization of the main cell, its measured voltage may still be affected by finite interfacial equilibration, electrolyte transport delay, and spatial concentration nonuniformity. These effects should be distinguished from the conventional ohmic, activation, and concentration polarization contained in the loaded terminal voltage of the main cell. Accordingly, the bypass OCV should be interpreted as a flow-dependent external voltage reference associated with the sampled circulating electrolyte. The lower error at 96 mL min^{−1} indicates improved consistency and representativeness of the bypass measurement under stronger circulation, rather than proving that the bypass voltage is identical to the instantaneous local equilibrium potential throughout the main cell.

Overall, the comparison demonstrates that the bypass OCV measurement method provides a reliable external OCV reference for the VRFB system. Compared with the intermittent discharge–rest method, the bypass OCV method can continuously acquire SOC-OCV data without interrupting the charge–discharge operation of the main test cell. Therefore, it is suitable for the subsequent analysis of SOC-OCV characteristics under different flow rates, cycling histories, and battery states.

3.2. Effect of Electrolyte Flow Rate and Cycling on SOC-OCV Characteristics

To evaluate the coupled influence of cycling history and electrolyte flow rate under quasi-static CC operation, the SOC-OCV curves of the cell in the initial post-preconditioning state (“fresh cell”) and after 50 cycles (“cycled cell”) were compared at flow rates of 36, 60, 96, and 120 mL min^{−1}. For each flow-rate condition, the charge and discharge OCV curves were first averaged at the same SOC points, and the resulting representative SOC-OCV curves were used for comparison. The OCV deviation between the cycled cell and the fresh cell was defined as:

$$\Delta ocv_k = ocv_{fresh_cell,k} - ocv_{cycled_cell,k} \quad (6)$$

where $ocv_{fresh_cell,k}$ and $ocv_{cycled_cell,k}$ are the OCV values of the fresh and cycled cells at the same SOC point k , respectively. The intersection point was determined by:

$$\Delta ocv(soc_{int}) = 0 \quad (7)$$

where soc_{int} denotes the SOC at which the OCV deviation changes sign. To quantify the overall difference between the two SOC-OCV curves over the full SOC range, the integral area of the absolute OCV difference was calculated as:

$$A = \int_0^1 |\Delta ocv| dsoc \quad (8)$$

Before comparing the SOC-OCV curves, the discharge-capacity evolution during the 50-cycle test was evaluated. The discharge capacity of fresh cell, cycled cell, and the corresponding capacity retention were shown in Table 4.

Table 4. The discharge capacity and capacity retention under different flow rate.

Flow Rate (mL min ^{−1})	Q_{fresh_cell} (Ah)	Q_{cycled_cell} (Ah)	R_Q (%)
36	1.2277	1.0431	84.96
60	1.2382	1.0624	85.80
96	1.2435	1.0675	85.85
120	1.2509	1.0778	86.16

The measured capacity retention after 50 cycles ranged from 84.96% to 86.16% across the four flow-rate conditions and therefore remained above 80% in all cases. This capacity change confirms that the electrochemical state of the battery evolved during cycling. However, the SOC-OCV curves were normalized using the actual capacity measured in each corresponding test. Therefore, the following comparison is made at the same normalized SOC rather than at the same absolute discharged charge.

Figure 4 compares the SOC-OCV curves of the fresh and cycled cells under different electrolyte flow rates. A clear flow-rate-dependent deviation can be observed after 50 cycles. At each flow rate, the SOC-OCV curves of the fresh and cycled cells intersect once. In the high-SOC region above the intersection point, the OCV of the cycled cell is lower than that of the fresh cell. In contrast, in the low-SOC region below the intersection point, the cycled cell exhibits a higher OCV than the fresh cell. This indicates that cycling does not simply cause a uniform upward or downward shift in the SOC-OCV curve, but induces a SOC-dependent redistribution of OCV deviation.

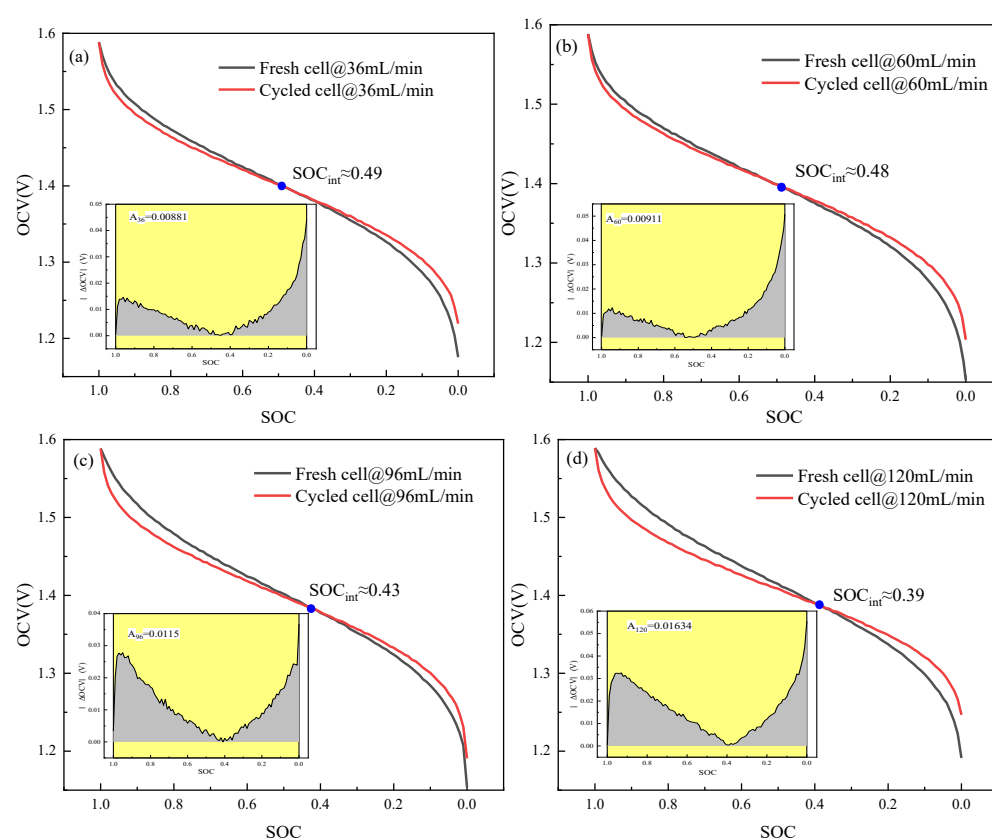


Figure 4. Comparison of SOC-OCV curves between the fresh cell and the cycled cell under different flow rates: (a) 36 mL min^{−1}; (b) 60 mL min^{−1}; (c) 96 mL min^{−1}; (d) 120 mL min^{−1}.

The SOC position of the intersection point gradually shifts toward lower SOC values as the flow rate increases. Specifically, the intersection SOC decreases from approximately 0.49 at 36 mL min^{−1} to 0.48, 0.43, and 0.39 at 60, 96, and 120 mL min^{−1}, respectively. This result suggests that, at higher flow rates, the SOC region in which the cycled-cell OCV remains lower than the fresh-cell OCV becomes wider. Meanwhile, the positive OCV deviation of the cycled cell is mainly concentrated in the low-SOC region.

To the best of our knowledge, explicit discussion of the intersection between two SOC-OCV curves has received limited attention in previous VRFB studies. In the present work, the intersection SOC is introduced as a descriptive indicator rather than an intrinsic electrochemical parameter. It indicates that the cycling-induced SOC-OCV deviation cannot be represented by a constant voltage offset but changes sign along the SOC axis. Such

behavior suggests that the influences of electrolyte imbalance, vanadium crossover, water transfer, species redistribution, and active-material utilization vary with SOC, resulting in different OCV deviations in different SOC regions. Consequently, the intersection should be interpreted as a characteristic of the observed curve redistribution under the tested conditions, rather than as a universal property of VRFBs. From a half-cell-potential perspective, the full-cell OCV is determined by the difference between the positive- and negative-electrolyte equilibrium potentials. This interpretation is consistent with the generalized electrochemical framework of Di Noto et al. [12], in which the full-cell OCV is governed by the coupled positive- and negative-half-cell potentials, electrolyte activities, and valence balance. Cycling-induced crossover, water transfer, and side reactions do not necessarily change the ion activities and valence balance of the two electrolytes in an identical or SOC-independent manner. At some SOC levels, the resulting changes in the two half-cell potentials may partially compensate each other, whereas at other SOC levels they may reinforce each other. Consequently, the net full-cell OCV deviation can change sign across the SOC range, producing an intersection rather than a uniform translation. Electrode kinetic evolution may additionally affect the finite-time apparent voltage through local concentration gradients and incomplete interfacial equilibration, but it does not by itself establish a unique thermodynamic shift. Because the present study did not measure the individual half-cell potentials, vanadium valence distributions, or electrolyte activities, the observed crossover cannot be uniquely assigned to one degradation mechanism. It is more appropriately interpreted as the combined SOC-dependent consequence of electrolyte imbalance, species redistribution, and finite-time interfacial response.

The absolute OCV difference integral area further confirms the increasing deviation with flow rate. As shown in Figure 5, increases from 0.00881 at 36 mL min⁻¹ to 0.00911, 0.0115, and 0.01634 at 60, 96, and 120 mL min⁻¹, respectively. This monotonic increase indicates that the accumulated SOC-OCV deviation between the fresh and cycled cells becomes more pronounced at higher electrolyte flow rates. Compared with the point-wise OCV deviation, the integral area provides a more comprehensive measure of the overall curve difference because it accounts for the deviation over the entire SOC range.

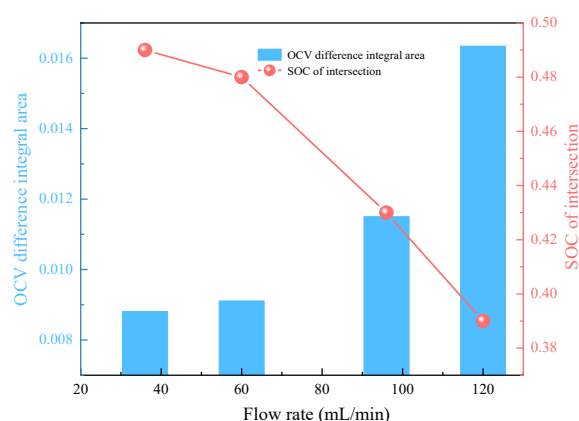


Figure 5. Variation in the absolute OCV difference integral area and intersection SOC with electrolyte flow rate.

The above phenomena may be associated with the coupled effects of electrolyte transport, mixing, cycling-induced electrolyte imbalance, and component-state evolution. During repeated charge–discharge cycling, vanadium-ion crossover, water migration, and side reactions can change the electrolyte volume, concentration, and valence balance between the two half-cells. The electrolyte flow rate affects the mass-transfer and mixing processes among the main cell, electrolyte reservoirs, and bypass OCV cell, thereby changing the measured OCV response. In addition, repeated cycling may alter the surface state

of the porous graphite-felt electrodes. Possible changes include variations in surface functional groups, wettability, electrochemically active area, pore accessibility, and adsorbed vanadium-containing species. These changes may modify the exchange-current density and the kinetics of the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ reactions. Chen et al. showed that modification of graphite-felt interfacial properties can significantly regulate negative-electrode reaction kinetics and polarization behavior [46], supporting the view that electrode-interface evolution can influence the measured voltage response. It should be noted that such surface-state changes do not necessarily alter the ideal Nernst equilibrium potential at a prescribed uniform electrolyte composition. Instead, they may affect local concentration distributions, the rate of interfacial equilibration, residual mixed-potential behavior, and the finite-time apparent OCV measured by the continuously flowing bypass cell.

The influence of flow rate on the measured SOC-OCV relationship should be interpreted by distinguishing the local electrolyte state inside the main cell from the electrolyte state sampled by the bypass measurement path. At higher flow rates, stronger forced convection reduces concentration gradients along the flow channels and within the porous electrodes, improves electrolyte renewal, and enhances mixing between the cell outlets, reservoirs, and pipelines. As a result, the electrolyte entering the bypass cell more closely represents the average circulating-electrolyte composition. If cycling has produced a persistent imbalance between the positive and negative electrolytes, stronger circulation may allow this average imbalance to be reflected more consistently in the bypass OCV response, which may partly explain the larger accumulated fresh-cycled curve deviation observed at higher flow rates. At lower flow rates, concentration boundary layers and local species gradients inside the porous electrodes may become more pronounced. The local electrolyte composition governing the main-cell interfacial reaction may therefore differ from the composition transported to the reservoirs and subsequently sampled by the bypass cell. In this case, hydraulic transport delay, incomplete reservoir mixing, and local concentration redistribution may smooth or delay part of the cycling-induced voltage difference measured by the bypass path. Thus, the smaller accumulated curve deviation at low flow rate does not necessarily indicate that the underlying electrolyte imbalance is weaker; it may also reflect reduced synchronization between the local main-cell state and the sampled bypass-electrolyte state. Therefore, the flow-rate dependence observed in Figures 4 and 5 contains two coupled effects: a physical effect of flow rate on concentration distribution and mass transfer within the VRFB, and a measurement-path effect associated with how accurately the bypass electrolyte represents the average circulating state. Because the present experiment did not include spatially resolved concentration measurements or a hydraulic residence-time model, these two contributions cannot be quantitatively separated. Because the SOC axis of each curve was normalized by its own measured discharge capacity, a reduction in available capacity mainly changes the relationship between absolute discharged charge and normalized SOC. It does not, by itself, necessarily produce the observed sign-changing OCV deviation at the same normalized SOC. The single intersection and the opposite deviation directions in the high- and low-SOC regions suggest that the cycling effect involves a redistribution of electrolyte composition, activity, or utilization rather than a simple uniform shift caused by capacity loss.

These results suggest that, under the tested conditions, the SOC-OCV relationship of the VRFB exhibits dependence on both cycling history and electrolyte flow rate, rather than remaining identical to the fresh-cell calibration curve. Consequently, relying solely on a calibration curve derived from a new battery may lead to SOC estimation errors when the actual flow rate or electrolyte state differs from the calibration condition. Therefore, practical applications may benefit from online correction of the SOC-OCV curve or from ensuring that calibration conditions are consistent with actual operating flow rates and electrolyte states.

3.3. Effect of Electrolyte and Component Refreshing on SOC-OCV Characteristics

To further examine the possible sources of the cycling-induced SOC-OCV deviation, refreshing experiments were conducted at a flow rate of 60 mL min⁻¹. The tested states were analyzed as a stepwise diagnostic sequence, including the initial post-preconditioning state, the state after 50 cycles before refreshing, the electrolyte-refreshed state, and the electrolyte-and-component-refreshed state. Figure 6 compares the corresponding SOC-OCV curves and their absolute deviations relative to the initial post-preconditioning reference. This comparison was used to evaluate the recovery associated with electrolyte replacement and the additional recovery associated with replacement of the membrane and electrodes.

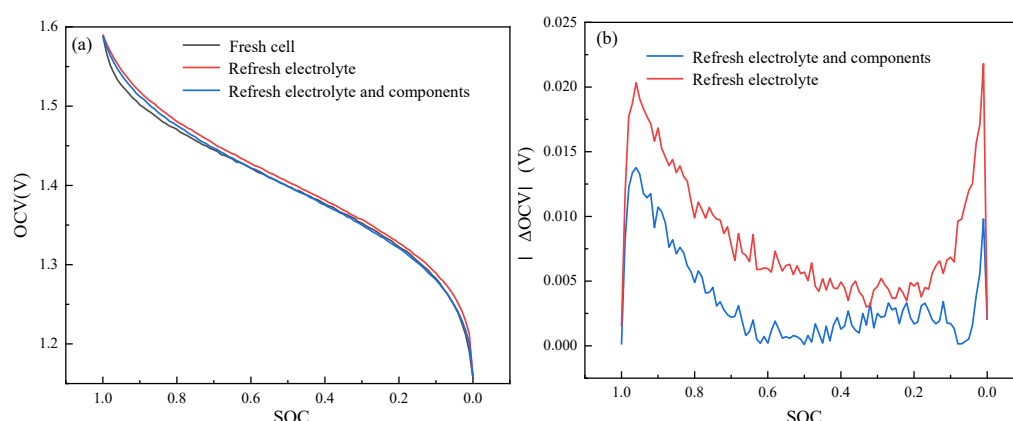


Figure 6. Stepwise SOC–OCV comparison under different renewal conditions at 60 mL min⁻¹: (a) SOC–OCV curves; (b) absolute OCV deviations relative to the initial post-preconditioning reference.

Figure 6 compares the SOC-OCV curves obtained under the initial post-preconditioning condition, after electrolyte replacement, and after simultaneous replacement of the electrolyte and cell components. The corresponding absolute OCV deviations relative to the initial post-preconditioning curve are also presented. As shown in Figure 6a, replacing the electrolyte alone shifted the SOC-OCV curve only slightly toward the initial reference. The electrolyte-refreshed curve remained higher than the reference over most of the SOC range, indicating that restoration of the bulk electrolyte alone was insufficient to recover the initial SOC-OCV characteristics completely. In contrast, after simultaneous replacement of the electrolyte, membrane, and electrodes, the SOC-OCV curve moved substantially closer to the initial post-preconditioning reference. As shown in Figure 6b, the absolute OCV deviation of the electrolyte-and-component-refreshed case was lower than that of the electrolyte-only-refreshed case over most of the SOC range. The difference between the two refreshing conditions was particularly evident in the high- and low-SOC regions, whereas the deviations were relatively close in the middle-SOC region.

To quantify the stepwise recovery, the accumulated SOC-OCV deviation of each state relative to the initial post-preconditioning reference was defined as:

$$A_j = \int_0^1 |OCV_j - OCV_{fresh_cell}| dSOC \quad (9)$$

where the subscript j denotes the cycled state before refreshing (A_1), the electrolyte-refreshed state (A_2), or the electrolyte-and-component-refreshed state (A_3), and OCV_{fresh_cell} represents the SOC-OCV curve of the initial post-preconditioning cell. The integral area of the absolute SOC-OCV difference under different states are summarized in Table 5.

Table 5. Comparison of the accumulated SOC-OCV deviation under different refreshing conditions at 60 mL min^{−1}.

State	Integral Absolute OCV Deviation
Fresh cell	0
Cycled cell (A ₁)	0.00911
Cycled cell with refreshed electrolyte (A ₂)	0.00838
Cycled cell with refreshed electrolyte and components (A ₃)	0.00352

As summarized in Table 5, electrolyte replacement reduced the accumulated SOC-OCV deviation from 0.00911 to 0.00838 V, corresponding to a decrease of only 0.00073 V. By comparison, simultaneous replacement of the electrolyte, membrane, and electrodes further reduced the deviation from 0.00838 to 0.00352 V, corresponding to an additional decrease of 0.00486 V. Therefore, the reduction observed after the second refreshing procedure was substantially larger than that obtained after electrolyte replacement alone. This result indicates that the adopted electrolyte-renewal procedure alone did not fully recover the cycling-induced SOC-OCV deviation under the tested condition. Electrolyte-related processes, including vanadium-species crossover, water transfer, side reactions, active-species loss, and changes in the positive and negative electrolyte volumes or valence balance, may alter the activities of the redox species and thereby affect the equilibrium voltage. The relatively small reduction after the adopted electrolyte-renewal procedure indicates that this procedure was insufficient to reproduce the initial measured SOC-OCV response. Because the original membrane and porous electrodes were retained and the circulation tubing was not separately rinsed, a small amount of cycled electrolyte may have remained in these regions and subsequently mixed with the refreshed electrolyte. Consequently, the reduction from A₁ to A₂ should not be interpreted as a direct quantitative measure of the independent contribution of the electrolyte itself and may represent a conservative estimate of the recovery achievable through more complete electrolyte displacement.

The substantially larger reduction observed after simultaneous replacement of the electrolyte, membrane, and electrodes suggests that component-related changes also played an important role in the measured SOC-OCV recovery. From the membrane perspective, changes in microstructure, ion-selective transport pathways, water uptake, swelling, fouling, and retained-species adsorption may alter both proton conduction and vanadium-ion permeability. The Nafion membrane reported in [43] was shown to suppress vanadium-ion permeation while maintaining proton conductivity, demonstrating that membrane structure can directly regulate the balance between ionic conduction and crossover resistance. Comparable inorganic-doping strategies have likewise been reported to improve the balance between proton transport and vanadium-ion blocking [44]. The ZrO₂-SPEEK hybrid membrane reported by Li et al. further demonstrated that membrane hydrophilicity, proton conductivity, and vanadium-ion selectivity can be jointly regulated through organic-inorganic hybridization [45]. Although this membrane chemistry differs from the Nafion 212 membrane used in the present experiments, it provides additional materials-level evidence that changes in membrane structure and transport properties can influence crossover and electrolyte-state evolution. Accordingly, changes in the transport properties of the cycled Nafion 212 membrane may have affected vanadium crossover, water transfer, and the subsequent concentration and valence balance of the two electrolytes, thereby contributing to the residual SOC-OCV deviation after electrolyte replacement. The cycled electrodes may also have undergone changes in surface functional groups, wettability, active-site distribution, pore accessibility, adsorbed vanadium species, and redox reaction kinetics. Chen et al. demonstrated that the interfacial

properties of graphite felt can substantially affect negative-electrode reaction kinetics and polarization behavior [46]. Huang et al. further showed that the morphology and network structure of CNT-modified carbon cloth can regulate positive-electrode activity and electrolyte transport in VRFBs [47]. Together, these studies provide a materials-level basis for interpreting the larger recovery observed after simultaneous component replacement and indicate that electrode microstructure may affect the finite-time interfacial voltage response. It should be emphasized that these electrode-related changes do not necessarily alter the ideal Nernst equilibrium potential directly. However, under continuous electrolyte circulation and finite measurement time, they may affect local concentration distributions, interfacial equilibration, residual mixed-potential behavior, and the measured or apparent OCV response of the bypass cell. Such electrode-surface evolution has also been associated with changes in charge-transfer resistance in previous VRFB studies. However, because electrochemical impedance spectroscopy (EIS) was not performed in the present work, the evolution of charge-transfer resistance could not be evaluated directly. Therefore, its possible contribution is discussed only as a literature-supported mechanistic interpretation rather than an experimentally verified conclusion.

It should be noted that the electrolyte-and-component renewal condition does not represent an identical reproduction of a completely new battery. Only the electrolyte, membrane, and electrodes were replaced, whereas other components of the test platform, including the bipolar plates, flow frames, sealing structure, electrolyte circulation loop, and measurement system, remained unchanged. Therefore, this condition should be interpreted as a reconstructed electrochemical reference state within the same experimental platform rather than as an independent new-cell configuration. The results therefore support a combined electrolyte-component interpretation. Electrolyte replacement produced only a limited recovery, whereas simultaneous replacement of the electrolyte, membrane, and electrodes resulted in a much larger reduction in the accumulated SOC-OCV deviation. Under the present experimental conditions, the larger recovery after membrane and electrode replacement suggests an important component-related contribution in addition to the effect of electrolyte renewal.

However, this interpretation should not be regarded as a strict quantitative decomposition of the individual physical contributions. In addition, incomplete removal of the cycled electrolyte from the circulation tubing, membrane, and electrode pores may have reduced the apparent recovery in the electrolyte-only case. In the second refreshing procedure, the electrolyte and the cell components were replaced simultaneously. Therefore, the reduction from A₂ to A₃ may include not only membrane- and electrode-related effects but also interactions between the newly installed components and the refreshed electrolyte. In addition, separate membrane-only and electrode-only replacement experiments were not conducted, and the electrolyte composition, membrane permeability, electrode surface properties, and impedance response were not directly characterized. Consequently, the present results demonstrate a sequential recovery trend but do not allow the independent contributions of the electrolyte, membrane, and electrodes to be quantified. Further component-specific replacement experiments and direct physicochemical and electrochemical characterization are required to verify the underlying mechanisms.

3.4. Effect of Dynamic Operating Conditions on SOC-OCV Characteristics

After examining the effects of cycling history, flow rate, and electrolyte/component refreshing, the applicability of the CC-based apparent bypass-voltage-SOC relationship under dynamic operating conditions was further evaluated. To examine this effect, the SOC-OCV curve of the cell after 50 cycles was compared under the CC discharge and DST discharge conditions at the same electrolyte flow rate of 96 mL min⁻¹. Before each dis-

charge test, the cell was charged using the same CC-CV protocol, and the bypass OCV was recorded during the subsequent discharge process.

As shown in Figure 7, the SOC-OCV curve obtained under the DST profile is lower than that obtained under the CC profile over most of the SOC range. The inset further confirms that the OCV difference, which defined as $\Delta OCV = OCV_{CC} - OCV_{DST}$, is positive in most regions, indicating a systematic downward shift in the DST-based OCV response relative to the CC-based curve. The difference is not a constant offset, but varies with SOC. It remains moderate in the middle SOC region and becomes more pronounced as the SOC decreases, suggesting that the measured OCV is more sensitive to operating-profile-induced electrolyte redistribution in the low-SOC region.

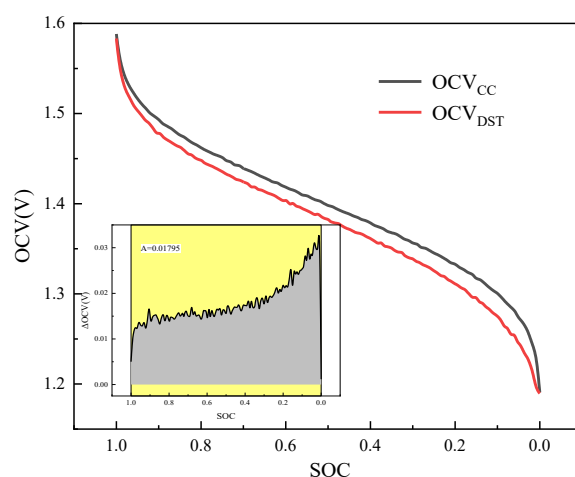


Figure 7. Comparison of SOC-OCV curves of the cycled cell under CC and DST discharge conditions at 96 mL min^{-1} .

However, the OCV difference does not continuously increase toward the end of discharge. As shown in the inset, the deviation decreases rapidly near the discharge end point, and the two curves converge to nearly the same value at SOC = 0. This behavior is mainly associated with the common discharge cut-off condition and the SOC normalization method used in this study. The SOC was normalized by the actual discharge capacity of each test, and SOC = 0 was defined at the end of discharge. Therefore, although CC and DST operation may lead to different transient concentration distributions during most of the discharge process, both curves are constrained to approach a similar terminal state near the cut-off condition. As a result, the operating-profile-induced OCV difference is reduced at the very end of discharge.

The integral area of the OCV difference is approximately 0.01788, confirming that the operating-profile-induced OCV deviation is non-negligible. A noteworthy observation is that the integral area between the CC- and DST-based SOC-OCV curves is larger than the OCV difference integral area between the fresh and cycled cells discussed in Figure 4c. In this comparison, the integral area between the CC- and DST-based SOC-OCV curves is larger than that between the fresh and cycled cells at the same flow-rate condition, suggesting that the operating profile may contribute substantially to the measured OCV deviation. In other words, the SOC-OCV deviation is not only a slow-varying effect associated with cycling history or electrolyte imbalance, but also depends on the instantaneous operating profile.

The difference between the CC- and DST-based SOC-OCV curves can be attributed to the distinct electrolyte utilization and concentration redistribution processes under the two operating profiles. Under CC discharge, the reaction rate is relatively stable, and the electrolyte concentration evolves more smoothly along the circulation loop. In contrast,

the DST profile introduces time-varying current excitation, which causes transient variations in reaction rate, local concentration gradients, and electrolyte mixing states. Although the bypass OCV cell is electrically isolated from the charge–discharge circuit, it shares the same circulating electrolytes with the main test cell. Therefore, its measured voltage still reflects the electrolyte state affected by dynamic operation, including concentration redistribution, mixing delay, and flow-path-dependent transport. Because no additional relaxation stage was introduced after each DST pulse, the electrolyte reaching the bypass cell may retain concentration gradients generated by the preceding current excitation. Moreover, hydraulic transport and mixing between the main-cell outlet and the bypass measurement path may smooth and delay the corresponding voltage response. Therefore, the DST-based bypass voltage should be interpreted as a delayed, mixed, and incompletely equilibrated apparent voltage response of the circulating electrolyte, rather than as the instantaneous thermodynamic equilibrium potential at the electrode interfaces of the main cell. If a sufficiently long relaxation period were provided after the dynamic current excitation, the transient concentration gradients would be expected to decay progressively, and the bypass voltage should approach a corresponding quasi-equilibrium level. It should also be noted that the relaxation characteristics of a VRFB are not directly equivalent to those of a lithium-ion battery. Continuous electrolyte circulation and reservoir mixing can promote relatively rapid homogenization of the liquid-phase species, whereas local concentration gradients within the porous electrodes and hydraulic transport delays may still require a finite relaxation period. Moreover, excessively long open-circuit rest may introduce additional changes through vanadium crossover and self-discharge. Therefore, the appropriate relaxation duration should balance sufficient concentration equilibration against the disturbance caused by prolonged open-circuit storage. The corresponding relaxation trajectory and appropriate rest duration were not directly investigated in the present DST experiment.

These results indicate that the apparent bypass-voltage–SOC response measured under the tested conditions depends not only on cycling history, electrolyte flow rate, and cell state, but also on the operating profile. Accordingly, a quasi-equilibrium SOC–OCV curve calibrated under CC or relaxed conditions may differ from the apparent voltage–SOC response measured during dynamic operation. This difference should be interpreted primarily as an operating-profile-dependent nonequilibrium and measurement-path effect, rather than as direct evidence that the intrinsic thermodynamic equilibrium potential has permanently changed. Such mismatch remains important for model-based SOC estimation because the measured or modeled voltage relationship is commonly used for SOC correction, initialization, parameter identification, and terminal-voltage prediction.

Overall, the results in Sections 3.1–3.4 show that the measured SOC–OCV relationship of the tested VRFB may vary with cycling history, electrolyte flow rate, electrolyte/component state, and operating profile. Therefore, the influence of such SOC–OCV deviations on SOC estimation is further analyzed in the following section.

4. Influence of SOC–OCV Deviation on SOC Estimation

4.1. SOC Estimation Error Caused by Fixed SOC–OCV Curves

Before presenting the inversion results, the error definition should be clarified. In this section, the SOC coordinates of the compared curves are obtained by Coulomb counting and normalized using the actual capacity measured in each corresponding test. The bypass-voltage-based SOC–OCV curves are then used as unified experimental reference mappings for fixed-curve inversion. Therefore, the reported SOC errors quantify the systematic deviation caused by applying a calibration curve obtained under one condition to data obtained under another condition. They should not be interpreted as absolute errors relative to an independently measured thermodynamic true SOC. The experimental re-

sults in Section 3 show that the SOC-OCV relationship of the VRFB varies with cycling history and operating profile. To further quantify the influence of such OCV deviation on SOC estimation, the SOC estimation error caused by using fixed SOC-OCV curves was analyzed. Three SOC-OCV curves obtained at 96 mL min⁻¹ under different cycling and operating conditions were used for comparison: the initial post-preconditioning cell under CC discharge, the cell after 50 cycles under CC discharge, and the cell after 50 cycles under DST discharge, designated as OCV_{fresh} , OCV_{CC} , and OCV_{DST} , respectively. Because each curve was constructed using the actual capacity of the corresponding test, the influence of an outdated nominal capacity was largely removed from the comparison. The resulting error should therefore be interpreted as a curve-to-curve SOC-inversion discrepancy designed to quantify SOC-OCV mapping inconsistency, rather than as a complete uncertainty budget for an online SOC estimator. To evaluate the OCV mismatch among different curves, three OCV deviation variables were defined as follows:

$$\Delta OCV_1(SOC_k) = OCV_{CC}(SOC_k) - OCV_{fresh}(SOC_k) \quad (10)$$

$$\Delta OCV_2(SOC_k) = OCV_{DST}(SOC_k) - OCV_{fresh}(SOC_k) \quad (11)$$

$$\Delta OCV_3(SOC_k) = OCV_{DST}(SOC_k) - OCV_{CC}(SOC_k) \quad (12)$$

where ΔOCV_1 represents the OCV deviation caused by cycling under CC operation, ΔOCV_2 represents the combined deviation caused by cycling and DST operation relative to the fresh-cell curve, and ΔOCV_3 represents the operating-profile-induced OCV deviation between DST and CC under the same cycling state. The accumulated OCV deviation over the full SOC range was quantified by the integral area of the absolute OCV difference:

$$A_i = \int_0^1 |\Delta OCV_i(SOC)| dSOC, \quad i = 1, 2, 3 \quad (13)$$

In the discrete form, the integral area was calculated as:

$$A_i \approx \sum_{k=1}^{N-1} \frac{|\Delta OCV_i(SOC_k)| + |\Delta OCV_i(SOC_{k+1})|}{2} (SOC_{k+1} - SOC_k) \quad (14)$$

where N is the number of SOC grid points.

For SOC inversion, a selected SOC-OCV curve was used as the fixed reference curve. Given the OCV value of the actual curve, the estimated SOC was obtained by inverse interpolation of the fixed reference curve:

$$SOC_{est} = f_{ref}^{-1}(OCV_{actual}) \quad (15)$$

where f_{ref} denotes the fixed reference SOC-OCV curve. The SOC estimation error was then calculated as:

$$e_{SOC}(SOC_k) = SOC_{est}(SOC_k) - SOC_{true}(SOC_k) \quad (16)$$

Three fixed-curve inversion cases were considered. First, the fresh-CC curve was used to estimate the SOC of the cycled-CC curve, denoted as $e_{SOC,1}$, which evaluates the SOC error caused by applying a fresh-cell calibration curve to a cycled cell. Second, the fresh-CC curve was used to estimate the SOC of the cycled-DST curve, denoted as $e_{SOC,2}$, which evaluates the combined influence of cycling history and dynamic operating profile. Third, the cycled-CC curve was used to estimate the SOC of the cycled-DST curve, denoted as $e_{SOC,3}$, which provides a controlled estimate of the additional SOC-inversion error associated with the operating-profile difference under the same cycling state and flow-rate condition.

Figure 8a compares the corresponding OCV deviations. The integral areas of ΔOCV_1 , ΔOCV_2 , and ΔOCV_3 are 0.011494 V, 0.021200 V, and 0.017945 V, respectively. The area of ΔOCV_2 is much larger than that of ΔOCV_1 , indicating that the OCV deviation becomes more significant when the cycled cell operates under the DST profile. Moreover, the area of ΔOCV_3 remains large even though the cycled-CC and cycled-DST curves correspond to the same cycling history and flow rate. This indicates that the operating profile itself can introduce a considerable OCV mismatch.

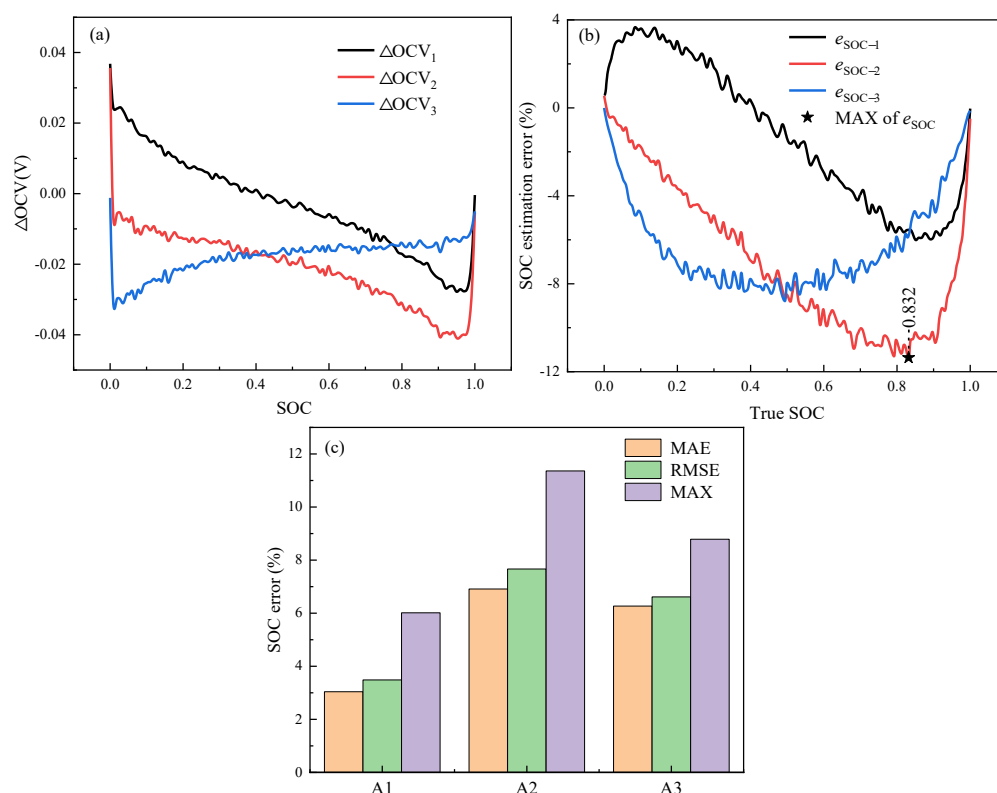


Figure 8. SOC estimation error caused by fixed SOC-OCV curves at 96 mL min⁻¹: (a) OCV deviations; (b) SOC estimation error curves; (c) MAE, RMSE, and MAX of SOC estimation errors. The marked point in (b) indicates the maximum absolute error.

The SOC estimation errors obtained by inverse interpolation are shown in Figure 8b, and the statistical indicators are summarized in Figure 8c. When the actual curve is the cycled-CC curve but the initial post-preconditioning CC curve is used for SOC inversion, the MAE, RMSE, and MAX are 3.04%, 3.48%, and 6.01%, respectively. This result shows that using an initial-state SOC-OCV curve for a cell after 50 cycles can introduce a non-negligible SOC bias. When the actual curve is the cycled-DST curve and the initial post-preconditioning CC curve is used as the fixed reference, the SOC estimation error increases significantly, with MAE, RMSE, and MAX reaching 6.91%, 7.66%, and 11.36%, respectively. The maximum absolute error occurs at a normalized SOC of approximately 0.832, within the high SOC region, and corresponds to a high-current pulse of the DST profile. Because the CC and DST tests have different discharge durations and current trajectories, the maximum-error location is identified using normalized SOC rather than absolute elapsed time. The large error at this point is associated with the combined effect of the local SOC-OCV curve mismatch and the sensitivity of the inverse mapping. In a relatively flat SOC-OCV region, a moderate OCV deviation may be amplified into a larger SOC inversion error. Therefore, the maximum SOC error does not necessarily coincide

with either the maximum OCV difference or the highest-current point of the DST profile. This demonstrates that the combined effect of cycling-induced and operating-profile-dependent OCV deviations can lead to substantial SOC estimation error.

More importantly, even when the cycled-CC curve is used as the reference curve, the SOC estimation error under DST operation remains significant. For the cycled-DST curve estimated using the cycled-CC curve, the MAE, RMSE, and MAX are 6.27%, 6.62%, and 8.79%, respectively. Since the two curves correspond to the same cycling history and flow-rate condition, this result provides evidence that the operating profile can noticeably influence OCV-based SOC inversion. Therefore, an SOC-OCV curve calibrated under CC conditions may not be directly applicable to dynamic operating conditions.

The above comparison can also be regarded as a simplified condition-update case. When the initial post-preconditioning CC curve was used to invert the cycled-DST data, the maximum SOC error was 11.36%. Updating the calibration curve to the cycled-CC curve, thereby incorporating the cycling-state information while retaining the operating-profile mismatch, reduced the maximum error to 8.79%. This corresponds to an absolute reduction of 2.57 percentage points and a relative reduction of approximately 22.6%. Therefore, even a single-condition update of the SOC-OCV calibration can reduce the mismatch-induced SOC error. However, the remaining error indicates that matching the cycling state alone is insufficient when the calibration and application operating profiles differ.

Overall, these results show that, under the tested conditions, using a fixed SOC-OCV curve may introduce considerable SOC estimation errors when the actual battery state or operating profile differs from the calibration condition. The SOC error is not determined only by the magnitude of the OCV deviation, but is also related to the local slope of the SOC-OCV curve. In relatively flat regions of the SOC-OCV curve, a small OCV mismatch may be amplified into a large SOC error.

It should be emphasized that the reported maximum error of 11.36% is a case-specific result obtained for the laboratory-scale cell investigated in this study after 50 charge–discharge cycles, at an electrolyte flow rate of 96 mL min^{-1} , and under the adopted DST profile. It should not be interpreted as a universal upper bound for VRFB SOC estimation. The magnitude and location of the maximum error may vary with cycling stage, capacity retention, electrolyte composition, membrane and electrode condition, flow rate, temperature, hydraulic configuration, and dynamic load profile. Therefore, the present result demonstrates the potential severity of SOC-OCV calibration mismatch but does not establish a general error law applicable to all VRFB systems. Practical SOC estimation methods should avoid applying a single SOC-OCV curve outside its calibration domain, particularly under long-term or dynamic operating conditions. The maximum error of 11.36% should therefore be interpreted as the total discrepancy obtained in the present curve-to-curve inversion rather than as a strictly isolated pure SOC-OCV model-mismatch term. Potential contributions include uncertainties in current integration and capacity normalization, voltage acquisition and interpolation, the hydraulic response of the bypass measurement path, and residual temperature variation. The bypass-versus-rest comparison at 96 mL min^{-1} yielded a maximum OCV difference of 1.3 mV, providing an empirical indication of the baseline measurement consistency under the validation condition; however, it does not quantify the additional transport-related uncertainty under DST operation. Nevertheless, all three inversion cases were generated using the same sensors, sampling system, capacity-normalization procedure, common SOC grid, and inverse-interpolation method, and the actual capacity of each test was used. These common procedures reduce nominal-capacity error and common processing bias, so the differences among the three cases primarily reflect the incremental effects associated with calibration-curve mismatch. A strict quantitative decomposition would require an independent SOC reference to-

gether with dedicated uncertainty-propagation, hydraulic-response, and temperature-controlled experiments. Accordingly, the present study does not claim that the entire 11.36% error arises exclusively from SOC–OCV mismatch. Based on the experimental characteristics identified in this study, two feasible routes for correcting this condition-dependent mapping error are discussed in Section 4.2.

4.2. Implications for Model-Based SOC Estimation

The experimental results in Section 3 show that the measured SOC–OCV relationship of the tested VRFB varies with cycling history, electrolyte flow rate, electrolyte/component state, and operating profile. The fixed-curve inversion results in Section 4.1 further demonstrate that these variations can be converted into considerable SOC errors when the calibration curve does not represent the actual battery and operating condition. For model-based estimators, the influence is not limited to direct SOC inversion, because the SOC–OCV relationship is embedded in the voltage model and may therefore affect terminal-voltage prediction, online parameter identification, filtering-based SOC correction, and capacity estimation.

The present study does not challenge the Nernst relationship under ideal balanced conditions. Rather, it examines the practical consequences when the activities, concentrations, and spatial distributions of the redox species no longer satisfy the assumptions underlying a single nominal SOC–OCV mapping. Under such conditions, the Nernst framework remains valid, but the effective relationship between normalized SOC and measured OCV may differ from that obtained under the original calibration condition.

This perspective distinguishes the present work from many estimator-centered studies that primarily improve filtering, observer design, covariance tuning, or parameter identification while retaining a predefined equilibrium-voltage relationship. The results show that even when the estimator itself is appropriately designed and tuned, a systematic error may remain if the embedded voltage map no longer represents the current battery state and operating condition. Therefore, SOC–OCV mismatch should be treated as a source of model-structure uncertainty rather than solely as measurement noise, parameter uncertainty, or filter-tuning error.

For a typical Thevenin equivalent circuit model, as shown in Figure 9, the terminal voltage can be expressed as:

$$U_t(k) = U_{oc}(SOC(k)) - U_p(k) - I(k)R_0 \quad (17)$$

where $U_t(k)$ is the terminal voltage, $U_{oc}(SOC(k))$ is the OCV, $U_p(k)$ is the polarization voltage, $I(k)$ is the current, and R_0 is the ohmic resistance. The OCV term is usually obtained from a predefined SOC–OCV curve calibrated under a specific experimental condition. However, if the actual SOC–OCV relationship deviates from the predefined curve, the voltage model becomes biased. Unlike zero-mean measurement noise, this OCV mismatch may exhibit a persistent SOC-dependent structure. It therefore cannot necessarily be eliminated by increasing filter gain, retuning covariance matrices, or improving the estimation of equivalent-circuit parameters. Instead, the embedded OCV map itself must be corrected, recalibrated, or conditioned on the relevant battery and operating states. Assuming that the fixed reference curve is $OCV_{ref}(SOC)$ and the actual curve is $OCV_{real}(SOC)$, the OCV mismatch can be written as:

$$\Delta OCV(SOC) = OCV_{real}(SOC) - OCV_{ref}(SOC) \quad (18)$$

This mismatch directly enters the terminal-voltage prediction error. Therefore, the voltage residual used by a model-based estimator contains not only the effects of SOC

error, polarization dynamics, parameter uncertainty, and measurement noise, but also the additional contribution caused by SOC-OCV curve mismatch.

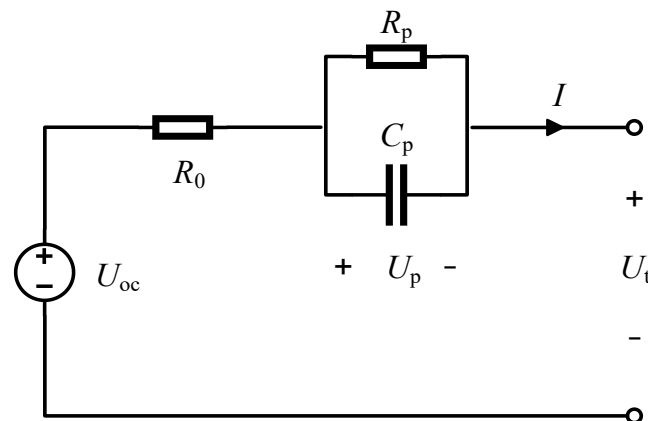


Figure 9. Schematic diagram of the Thevenin model.

For recursive least-squares or other online parameter-identification methods, this effect may lead to biased parameter estimates. The model parameters, such as R_0 , polarization resistance, and polarization capacitance, are commonly identified by minimizing the terminal-voltage residual. If the residual contains an unmodeled OCV mismatch, part of this mismatch may be incorrectly compensated by the equivalent circuit parameters. Consequently, the identified parameters may no longer represent only the true ohmic and polarization characteristics, but may also absorb the error caused by the fixed SOC-OCV curve.

For EKF-, UKF-, and observer-based SOC estimation methods, the influence of SOC-OCV mismatch appears mainly in the measurement update. These algorithms correct the predicted SOC according to the voltage residual between the measured terminal voltage and the model-predicted voltage. When the SOC-OCV curve is mismatched, the residual may not be caused by SOC prediction error alone. If the estimator interprets this residual as SOC error, the SOC state may be corrected in a biased direction. This effect is particularly important in relatively flat regions of the SOC-OCV curve, where a small OCV mismatch can be converted into a relatively large SOC correction error.

The SOC-OCV mismatch may also propagate to capacity estimation. In joint SOC and capacity estimation, the available capacity is commonly inferred from the relationship between current integration and SOC variation. If the SOC trajectory is biased by inaccurate OCV-based correction, the capacity estimator may interpret the distorted SOC variation as a capacity change. As a result, the estimated capacity may deviate from the actual available capacity, especially under long-term cycling or dynamic operating profiles.

Therefore, the use of a single fixed SOC-OCV curve may affect multiple levels of model-based SOC estimation, including voltage prediction, parameter identification, SOC correction, and capacity estimation. Based on the experimentally observed SOC-dependent curve intersections, nonuniform cycling-induced deviations, flow-rate dependence, and systematic difference between the CC- and DST-based responses, two complementary routes may be considered to address this condition-dependent model mismatch. The first route is low-dimensional online correction of a calibrated baseline SOC-OCV curve. A nominal relationship $U_{OCV,0}(z)$, where z denotes SOC, may be augmented using slowly varying offset and shape-correction terms:

$$U_{OCV}(z, k) = U_{OCV,0}(z) + b_0(k) + b_1(k)(z - z_c) + b_2(k)\phi(z) \quad (19)$$

where $b_0(k)$ represents an overall voltage-offset correction, $b_1(k)$ represents a slope correction, and $b_2(k)\phi(z)$ represents an optional low-order shape correction. These parameters may be updated using bypass-OCV measurements, sufficiently long rest periods, or reliable low-current operating intervals through recursive least squares, Kalman filtering, Bayesian estimation, or constrained optimization. Because the experimentally measured curves exhibited both SOC-dependent intersections and nonuniform deviations, an offset-only correction may be insufficient; a combined offset and slope/shape correction is more consistent with the observed behavior. To maintain physical plausibility, the correction parameters should be bounded, and the corrected relationship should remain continuous and monotonic over its valid SOC range. The second route is a condition-indexed SOC-OCV mapping. In this approach, OCV is represented as a function of both SOC and measurable or estimable operating-condition variables:

$$U_{OCV} = f(z, F, T, H_{Ah}, Q_{ret}, \eta_c, \chi_{load}) \quad (20)$$

where F is electrolyte flow rate, T is cell/stack or electrolyte temperature, H_{Ah} is cumulative ampere-hour throughput used as a more informative cycling-history indicator than cycle count alone, Q_{ret} is a capacity-retention indicator, η_c is a coulombic-efficiency or self-discharge indicator, and χ_{load} represents recent operating-profile features. The load-profile descriptor is not intended to imply that instantaneous current directly changes the ideal thermodynamic OCV; instead, it may represent dynamic concentration redistribution, transport delay, and incomplete equilibration. Such a condition-dependent model may be implemented using a multidimensional lookup table, a recursively updated parametric surface, or a physics-informed data-driven model.

In practical implementation, the two routes need not be mutually exclusive. A condition-indexed SOC-OCV map may first provide a baseline relationship selected or interpolated according to measurable variables such as electrolyte flow rate, temperature, cumulative ampere-hour throughput, and capacity retention. The remaining mismatch may then be compensated online through slowly varying offset and slope/shape parameters using bypass-OCV measurements or reliable relaxed-voltage information. This hybrid structure would combine the broader operating-domain coverage of condition indexing with the local tracking capability of online correction.

The first route has lower online computational complexity and is suitable when reliable OCV-reference information is intermittently available. The second route can represent a broader range of conditions but requires a sufficiently comprehensive calibration dataset. The present study provides experimental motivation for both approaches, whereas their online implementation and validation remain subjects for future work. The principal contribution of the present work is therefore to experimentally identify a source of structural model mismatch that is commonly hidden within the predefined SOC-OCV term of VRFB estimators.

4.3. Limitations and Future Work

Several limitations should be considered when interpreting the present results. First, although the ambient temperature was maintained approximately within 25 ± 1 °C and no abnormal surface-temperature rise was observed during the periodic infrared checks, neither the cell nor the circulating electrolytes were actively temperature-controlled, and the internal electrolyte temperature was not continuously or precisely recorded. Temperature was therefore not treated as an independent experimental variable in the present study. A residual thermal contribution to the measured OCV variation cannot be com-

pletely excluded, and the observed differences among the comparative tests should not be attributed exclusively to cycling, flow rate, renewal condition, or operating profile. Future studies should incorporate synchronized electrolyte-temperature measurements and active thermal control to quantitatively separate the independent and coupled effects of temperature, cycling, and electrolyte flow rate.

Second, the bypass OCV cell measures the voltage associated with the electrolyte transported through the external circulation path rather than the instantaneous local electrolyte state inside the porous electrodes of the main cell. Consequently, the measured response may include the effects of hydraulic residence time, reservoir mixing, transport delay, and spatial concentration redistribution. The observed flow-rate dependence should therefore be interpreted as the combined result of intrinsic mass-transfer behavior and the representativeness of the bypass measurement path. Spatially resolved concentration measurements and hydraulic or computational-fluid-dynamics modeling would help distinguish these effects.

The generalizability of the present results should also be interpreted with caution. The experiments were conducted using a laboratory-scale single cell with a $2\text{ cm} \times 2\text{ cm}$ active area, a Nafion 212 membrane, 1.7 M vanadium electrolyte in 4.2 M sulfuric acid, and a specific circulation configuration. The qualitative conclusion that the measured SOC–OCV relationship can depend on operating and battery conditions is expected to remain relevant to other VRFB systems because crossover, electrolyte imbalance, flow-dependent transport, and component-state evolution are common processes. However, the quantitative curve deviations, intersection locations, and flow-rate trends observed here should not be directly extrapolated to other cells or stacks. Differences in membrane selectivity, cell or stack scale, hydraulic configuration, and electrolyte composition may either amplify or attenuate these effects. Therefore, system-specific calibration and validation are required before the present numerical trends are transferred to other VRFB configurations.

Finally, the mechanistic interpretation of the cycling and refreshing experiments remains semi-quantitative. The comparison was limited to the initial post-preconditioning state and the state after 50 cycles, and separate membrane-only and electrode-only replacement tests were not conducted. Residual cycled electrolyte may also have remained within the circulation tubing, membrane, and porous electrodes after electrolyte-only renewal, potentially leading to an underestimation of the recovery achievable through complete electrolyte replacement. Therefore, the observed recovery supports a combined electrolyte–component interpretation but does not independently quantify the contributions of the electrolyte, membrane, and electrodes. Direct electrolyte analysis together with membrane and electrode characterization is required for further verification. Although the simplified condition-update case demonstrates the benefit of calibration-state matching, full implementation of the adaptive correction and condition-indexed SOC–OCV strategies requires broader datasets covering multiple temperatures, flow rates, cycling stages, and dynamic operating profiles.

5. Conclusions

This study experimentally investigated the condition-dependent SOC–OCV behavior of a vanadium redox flow battery and evaluated its implications for SOC estimation using a laboratory-scale system equipped with a bypass OCV cell.

First, the bypass OCV method showed good agreement with the intermittent discharge–rest method over the full SOC range, with OCV deviations below 5 mV. This confirms that the bypass cell can provide a reliable external voltage reference for continuous SOC–OCV characterization under the tested conditions.

Second, the measured SOC-OCV relationship varied with both cycling history and electrolyte flow rate. After 50 charge–discharge cycles, the curve exhibited an SOC-dependent redistribution rather than a uniform voltage shift. As the flow rate increased from 36 to 120 mL min^{−1}, the curve intersection shifted toward lower SOC and the accumulated absolute OCV deviation increased, indicating that cycling-induced changes are coupled with flow-dependent electrolyte transport and mixing.

Third, electrolyte replacement alone produced only limited recovery of the initial SOC-OCV relationship, whereas simultaneous replacement of the electrolyte, membrane, and electrodes substantially reduced the remaining deviation. These results support a combined electrolyte–component interpretation and suggest that membrane- and electrode-related changes also contribute to the measured SOC-OCV evolution.

Fourth, the operating profile affected the measured SOC-OCV relationship even under the same cycling history and flow-rate condition. The DST-based curve differed systematically from the CC-based curve, demonstrating that dynamic operation can modify the apparent OCV response through concentration redistribution, transport delay, and incomplete equilibration.

Finally, fixed-curve SOC inversion showed that calibration mismatch can introduce considerable SOC errors. When the initial post-preconditioning CC curve was applied to the cell after 50 cycles under the tested DST condition, the maximum error reached 11.36%. Although this value is specific to the present 50-cycle, 96 mL min^{−1} case, updating the calibration curve to the corresponding cycling state reduced the maximum error to 8.79%, confirming the benefit of condition-matched SOC-OCV calibration.

Overall, the SOC-OCV relationship of a VRFB should be treated as a condition-dependent mapping rather than an invariant calibration characteristic. Applying a single fixed curve outside its calibration domain may affect SOC correction, terminal-voltage prediction, parameter identification, and capacity estimation. Two practical directions are therefore suggested for future estimators: online offset and slope/shape correction of a calibrated baseline curve, and condition-indexed SOC-OCV mapping using variables such as flow rate, temperature, cumulative ampere-hour throughput, capacity retention, and recent operating-profile information. Their implementation and validation under broader operating conditions remain subjects for future work.

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Abbreviations

The following abbreviations are used in this manuscript:

OCV	Open-circuit voltage
SOC	State of charge
VRFB	Vanadium redox flow batteries
CC-CV	Constant-current-constant-voltage
DST	Dynamic stress test
MAE	Mean absolute error
RMSE	Root mean square error
EM	Electrochemical model
ECM	Equivalent circuit model

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