



A storage-state-based reduced-order electrochemical model for cyclic adsorption–desorption dynamics in membrane capacitive deionization

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HIGHLIGHTS

- A storage-state model captures cyclic MCDI adsorption–desorption dynamics.
- Modified-Donnan-informed storage links electrochemical states to outlet EC.
- Cyclic responses are reproduced without separate adsorption/desorption models.
- Residual storage memory enables continuous non-reset simulation over 20 cycles.
- Stable reproduction is shown across feed ECs of 223–4,000 $\mu\text{S cm}^{-1}$.

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ABSTRACT

Membrane capacitive deionization (MCDI) inherently operates through repeated short-term adsorption–desorption switching cycles, making cyclic state evolution, residual storage memory, and carry-over behavior essential characteristics of the process. However, existing MCDI models often struggle to simultaneously preserve cyclic state continuity, electrochemical interpretability, and computational tractability during long-horizon operation. In this study, a storage-state-based reduced-order electrochemical model was developed to describe cyclic adsorption–desorption dynamics through continuous evolution of internal electrochemical storage states. The model combines a modified-Donnan-informed storage-state formulation with four-zone hydraulic transport, current-limited state transfer, residual storage memory, and excess storage relaxation without separate adsorption/desorption fitting. Continuous non-reset simulations were performed over 12,000 s under five initial feed EC conditions ranging from approximately 223 to 4000 $\mu\text{S cm}^{-1}$. The proposed model reproduced cyclic carry-over behavior, adsorption–desorption continuity, and post-switch desorption peak evolution across the tested initial EC range. Quantitatively, the model achieved a mean all-window weighted absolute percentage error (WAPE) of 13.10%, mean desorption WAPE of 12.04%, mean Nash–Sutcliffe efficiency (NSE) of 0.942 for normalized C/C_0 dynamics, and mean Kling–Gupta efficiency (KGE) of 0.889. These results indicate that key cyclic MCDI dynamics can be captured using an interpretable and computationally tractable electrochemical backbone model, supporting continuous-state simulation and long-horizon analysis of cyclic MCDI operation.

1. Introduction

1.1. Background and technological positioning

Membrane capacitive deionization (MCDI) has gained increasing attention as an electrochemical water treatment technology because of

its low-pressure operation, modular architecture, and potential for energy-efficient ion removal [1–4]. In contrast to pressure-driven membrane processes, MCDI removes ions through electrically driven adsorption–desorption cycles, enabling cyclic operation with controllable electrochemical regeneration [3–8]. Owing to these characteristics, MCDI has been investigated not only for desalination but also for

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selective ion removal, cyclic concentration, and resource recovery under variable feed conditions [5–8].

Because ion removal in MCDI fundamentally relies on repeated polarity switching, cyclic operation is an intrinsic electrochemical characteristic of the process rather than simply an operational option [9–14]. During repeated adsorption–desorption cycles, residual electrochemical storage, incomplete regeneration, and transient relaxation continuously influence subsequent cycle evolution, resulting in carry-over behavior and condition-dependent outlet conductivity responses [12–20].

Practical deployment of MCDI increasingly requires dynamic modeling frameworks capable of describing long-horizon cyclic system behavior beyond single-cycle performance indicators [18–28]. Physically interpretable models that continuously represent internal electrochemical state evolution are therefore essential for operation-oriented simulation, performance assessment, and future model-based control of cyclic MCDI systems [21–32].

1.2. Limitations of existing dynamic MCDI models

Existing MCDI modeling approaches generally fall into three categories. Empirical and semi-empirical models often treat adsorption and desorption separately, limiting mechanistic interpretability and continuity across repeated switching cycles. Data-driven or machine-learning-based models can improve predictive performance but often sacrifice electrochemical interpretability and extrapolation capability under changing operating conditions [28–33].

Physics-based electrochemical models, particularly dynamic modified Donnan (mD) formulations, provide physically meaningful descriptions of ion adsorption and transport [21–27,34–36]. However, these models generally require multiple coupled state variables, extensive parameterization, and relatively high computational cost, making long-horizon cyclic simulation and parameter identification more challenging.

Despite these advances, existing modeling approaches do not simultaneously provide (i) continuous electrochemical state propagation across repeated adsorption–desorption cycles, (ii) reduced computational complexity suitable for long-horizon simulation, and (iii) physically interpretable cyclic storage evolution using a unified parameter set. This gap motivates the development of a storage-state-based reduced-order framework that continuously propagates electrochemical storage states while preserving computational efficiency and electrochemical interpretability. The main conceptual differences between representative cyclic MCDI modeling approaches and the proposed storage-state framework are summarized in Table 1.

1.3. Objectives and scope of this study

The objective of this study was to develop and evaluate a storage-state-based reduced-order electrochemical framework for cyclic MCDI operation. The central hypothesis was that adsorption, desorption, residual storage, carry-over behavior, and transient post-switch responses can be represented through continuous propagation of internal electrochemical storage states without separate adsorption/desorption

fitting.

To test this hypothesis, a modified-Donnan-informed target storage relation was coupled with four-zone hydraulic transport, current-limited state transfer, residual storage memory, and excess storage relaxation. The model was designed to preserve electrochemical interpretability and cyclic state continuity while remaining computationally tractable for long continuous simulations. Continuous non-reset simulations were performed over 12,000 s, corresponding to 20 consecutive adsorption–desorption cycles, across five initial feed EC conditions ranging from approximately 223 to 4000 $\mu\text{S cm}^{-1}$.

The specific aims of this study were to: (i) formulate a compact electrochemical storage-state representation that links modified Donnan equilibrium behavior to dynamic cyclic MCDI response; (ii) evaluate whether continuous state propagation can reproduce carry-over behavior and adsorption–desorption continuity during repeated switching operation; (iii) examine whether transient desorption dynamics can be reproduced within the proposed continuous-state framework without introducing desorption-specific empirical equations; and (iv) assess condition-wise and mode-wise model performance of the proposed storage-state backbone model using long-horizon cyclic experimental data.

Through this storage-state-based reduced-order framework, the present study provides an interpretable and computationally practical approach for cyclic MCDI analysis, long-horizon simulation, and operation-oriented model development. The framework was developed and evaluated under fixed voltage, flow rate, and cycle-duration conditions to isolate conductivity-dependent storage-state evolution. The controlled configuration was intentionally adapted to establish the proposed reduced-order storage-state backbone under well-defined operating conditions. Extension to broader operating-condition spaces, including time-varying feed conditions and more complex feed compositions, remains an important direction for future development.

2. Materials and methods

2.1. Experimental system configuration

The experimental platform was based on a previously reported laboratory-scale MCDI module configuration [32]. The present study used the previously acquired cyclic MCDI dataset for development and evaluation of the proposed storage-state framework. The laboratory-scale membrane capacitive deionization (MCDI) module (O2 & B Co., Seoul, Republic of Korea) was housed in a cylindrical acrylic chamber (outer diameter: 250 mm; height: 320 mm), as illustrated in Fig. 1. The stack consisted of 233 pairs of bipolar activated-carbon electrodes alternately assembled with cation-exchange membranes, anion-exchange membranes, and non-woven spacers.

Each circular electrode had a diameter of 200 mm with a 25 mm center hole for internal flow distribution, yielding an effective active area of approximately 140 cm^2 . The spacer thickness was 0.7 mm. The MCDI module adopts a manifold-type flow configuration in which the influent enters through the bottom inlet, is distributed across the spacer-defined flow channels over the electrode area and is subsequently

Table 1

Comparison of representative cyclic MCDI modeling approaches and the proposed storage-state framework.

Model	State representation	Computational complexity	Calibration	Cyclic continuity
Empirical/semi-empirical	Separate adsorption/desorption models	Low	Condition-specific fitting	Separate adsorption/desorption fitting
Equivalent circuit	Electrical circuit states	Low-Moderate	Multiple electrical-parameter calibration	Continuous electrical-state evolution
Dynamic modified-Donnan	Coupled electrochemical states	High	Extensive electrochemical parameterization	Continuous electrochemical-state evolution
Proposed storage-state framework	Unified electrochemical storage states	Moderate	Unified multi-condition calibration	Continuous storage-state propagation

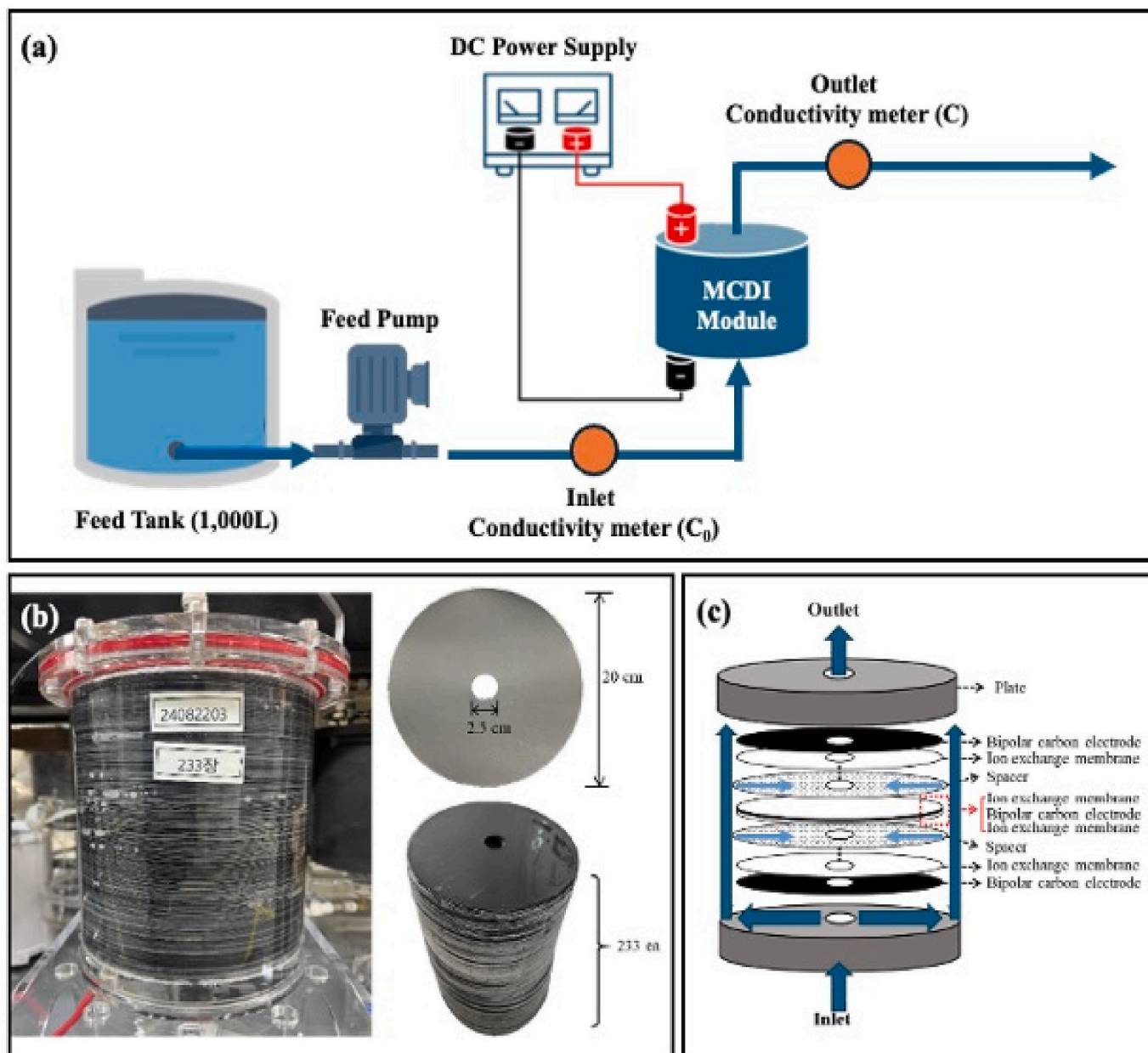


Fig. 1. Laboratory-scale cyclic MCDI system and stack configuration. (a) Experimental flow and electrical configuration with inlet and outlet conductivity monitoring. (b) Photographs of the laboratory-scale MCDI module, circular bipolar electrode, and assembled electrode stack. (c) Schematic illustration of the internal stack architecture showing the electrode-membrane arrangement and flow direction.

collected toward the central outlet located at the top of the stack (Fig. 1c). This flow configuration is designed to promote relatively uniform flow distribution while minimizing preferential flow paths and stagnant regions. Accordingly, the measured outlet conductivity is considered to represent the spatially averaged electrochemical response of the entire electrode stack. The stack assembly was compressed between acrylic endplates and electrically connected to a programmable DC power supply (ITECH IT6726H).

Electrical conductivity (EC) was continuously monitored at 1 Hz at the inlet and outlet using a multi-channel conductivity meter (WTW MultiLine Multi 3630 IDS, Xylem Analytics). All process signals were time-synchronized and exported for subsequent post-processing and cyclic state analysis.

The experimental system and operating conditions were kept consistent with the previously reported configuration to ensure that the present analysis focused on storage-state model development and

evaluation [32].

2.2. Operating conditions and cyclic dataset

A programmable DC power supply (ITECH IT6726H) was operated in constant-voltage mode at ± 279.6 V across the stack, corresponding to 1.2 V per electrode pair. The flow rate was maintained at 3.0 L min^{-1} throughout all experiments.

All experiments were conducted under cyclic adsorption-desorption switching operation with a fixed half-cycle duration of 300 s for adsorption followed by 300 s for desorption, corresponding to a 600 s full cycle. Each experimental run covered 12,000 s of continuous operation, corresponding to 20 consecutive adsorption-desorption cycles.

Five initial feed EC conditions (approximately 223, 1000, 2000, 3000, and $4000 \mu\text{S cm}^{-1}$) were used to construct the cyclic dataset, covering low-to-high conductivity regimes. The experimental dataset

was adopted from our previous study [32]. The lowest-conductivity condition (approximately $223 \mu\text{S cm}^{-1}$) corresponded to tap water, whereas the higher-conductivity conditions were prepared by adding NaCl to deionized water to achieve the target influent conductivity levels. Before each experimental run, the system was operated under a common baseline feed condition until repeatable cyclic behavior was achieved, thereby minimizing inter-run carry-over effects. The operating conditions used for construction of the cyclic dataset are summarized in Table 2.

2.3. Model structure and governing concepts

2.3.1. Reduced-order framework formulation

Prior to establishing the final model structure, multiple reduced-order cyclic formulations were evaluated to identify the dominant mechanisms governing repeated adsorption-desorption behavior in MCDI. Candidate structures included monotonic storage-release formulations, hydraulic-delay-based transport representations, constrained state-transfer formulations, and transient excess-relaxation structures. Each formulation was assessed based on its ability to reproduce cyclic continuity, carry-over evolution, transient desorption overshoot behavior, and long-horizon stability during repeated switching operation.

This development process indicated that transport delay alone was insufficient to represent long-horizon cyclic behavior, while monotonic storage-release assumptions could not adequately reproduce transient desorption peaks immediately following polarity reversal. The final backbone framework therefore combined continuous state propagation, modified-Donnan-informed target storage, current-limited state transfer, residual storage memory, and excess storage relaxation within a single reduced-order cyclic formulation. The resulting framework architecture is summarized schematically in Fig. 2. The framework was designed to preserve electrochemical interpretability while maintaining computational tractability for long-horizon cyclic simulation.

2.3.2. Unified cyclic electrochemical state concept

The central assumption of the proposed framework is that cyclic MCDI behavior can be represented as continuous evolution of latent electrochemical storage states. Adsorption, desorption, residual storage, and switching-induced relaxation are therefore treated within a unified storage-state framework rather than as disconnected operational modes.

In this interpretation, the observable outlet conductivity response is governed by the coupled evolution of hydraulic concentration states and latent electrochemical storage states. The internal storage state is not reset at cycle boundaries; instead, it is propagated continuously across repeated polarity switching events. This enables residual storage and carry-over effects from preceding half-cycles to influence subsequent adsorption and desorption responses. The conceptual evolution of storage states during repeated adsorption-desorption switching is illustrated in Fig. 3.

Table 2

Experimental operating conditions used for cyclic MCDI dataset generation.

Category	Parameter	Value	Unit
Electrical operation	Applied voltage	± 279.6	V
	Voltage per electrode pair	1.2	V
Hydraulic operation	Flow rate	3.0	L min ⁻¹
Cyclic operation	Adsorption duration	300	s
	Desorption duration	300	s
	Full cycle duration	600	s
	Total operation time	12,000	s
	Number of cycles	20	–
Feed conditions	Initial feed EC	223, 1000, 2000, 3000, 4000	$\mu\text{S cm}^{-1}$
	EC sampling frequency	1	Hz

2.3.3. Modified-Donnan-informed target storage state

The electrochemical storage target was derived from a reduced-order modified Donnan interpretation of ion distribution in porous carbon electrodes. In the modified Donnan framework, the equilibrium concentration of ion species i inside the micropore domain can be expressed as [34–36]:

$$c_i = c_{i,\text{bulk}} \exp(-z_i \Delta \phi_D)$$

where $c_{i,\text{bulk}}$ is the effective bulk concentration of ion species i , z_i is the ionic valence, and $\Delta \phi_D$ is the dimensionless Donnan potential. The corresponding equilibrium concentration change is:

$$\Delta c_i = c_{i,\text{bulk}} [\exp(-z_i \Delta \phi_D) - 1]$$

Because the purpose of the present model is not to resolve spatially detailed micropore ion distributions, these ion-level equilibrium changes were integrated into a normalized electrochemical storage target:

$$n_{\text{eq},j} = v_{\text{scale},j} \sum_i |z_i| |\Delta c_{i,j}|$$

where $n_{\text{eq},j}$ is the equilibrium target storage state in active zone j , and $v_{\text{scale},j}$ is an effective lumped scaling parameter representing accessible storage domain, pore accessibility, and normalization effects. Importantly, $n_{\text{eq},j}$ is a dimensionless normalized latent state variable representing the relative electrochemical storage tendency of the active storage domain under the local concentration and voltage conditions. It is not interpreted as a direct measure of stored ion amount, salt adsorption capacity, state of charge, or charge density. Instead, it serves as a reduced-order internal state governing the dynamic evolution of electrochemical storage within the proposed framework. Unlike salt adsorption capacity or stored charge, which represent measurable physical quantities, the storage state is introduced to continuously describe the evolution of the internal electrochemical state. Consequently, variations in the storage state correspond to the relative evolution of electrochemical storage tendency rather than to an absolute measurable storage quantity. Accordingly, the storage state is dimensionless and is intended to describe relative electrochemical state evolution within the proposed framework rather than to enable direct quantitative comparison with experimentally measurable storage quantities.

The effective Donnan potential was represented as:

$$\Delta \phi_{D,j} = \beta_D \max \left[\frac{V_{\text{pair}}}{2V_T} - \phi_{\text{loss}}(C_{\text{eff},j}), 0 \right]$$

where $\Delta \phi_{D,j}$ is the effective dimensionless Donnan potential in active zone j , β_D is an effective voltage-utilization factor, V_{pair} is the applied voltage per electrode pair, V_T is the thermal voltage, and ϕ_{loss} is an effective concentration-dependent loss term. The loss term lumps membrane resistance, concentration polarization, ionic shielding, ohmic loss, and other unresolved voltage losses into a compact reduced-order expression. It is not intended to explicitly represent individual Faradaic reactions or charge-transfer kinetics. Instead, any reduction in the electrochemical driving force arising from unresolved non-ideal processes, including possible parasitic Faradaic charge losses during prolonged operation, is implicitly represented through the effective loss term. Accordingly, these aggregate voltage-loss effects influence the calculation of the target electrochemical storage state through the resulting effective Donnan potential.

The present formulation is inspired by the modified Donnan equilibrium but does not attempt to resolve detailed ion distributions within the micropore domain [34–36]. In the present framework, the modified-Donnan formulation is used only to define the conductivity-dependent target storage state, whereas the subsequent evolution of the storage state is governed by the reduced-order storage-state dynamics, including

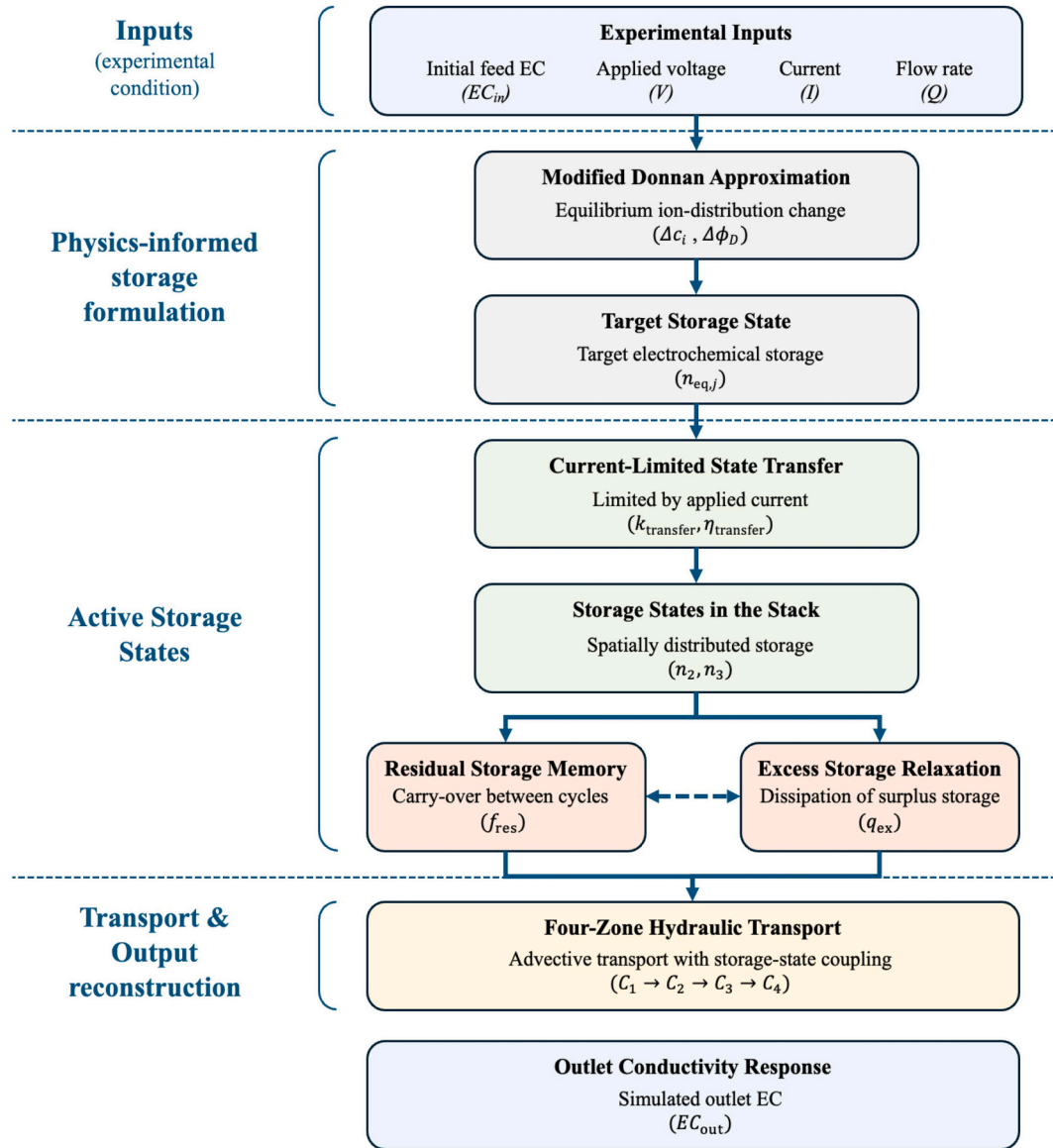


Fig. 2. Overview of the proposed storage-state framework for cyclic MCDI modeling. A modified-Donnan-informed formulation defines the conductivity-dependent target storage state, while storage-state dynamics govern the evolution of two active storage domains (q_2 and q_3) through current-limited transfer, residual memory, and excess-storage relaxation. The resulting storage states are coupled with a four-zone hydraulic transport model to reconstruct the outlet conductivity response.

state transfer, residual memory, and excess-storage relaxation. This formulation provides a physically interpretable target storage representation suitable for reduced-order cyclic simulation.

2.3.4. Residual storage memory

Although adsorption and desorption share the same state-evolution structure, the target storage state differs according to operating mode. During adsorption, the storage state moves toward the modified-Donnan-informed equilibrium target. During desorption, the target is defined by a residual storage fraction from the storage state at the adsorption-to-desorption transition:

$$n_{\text{target},j} = \begin{cases} n_{\text{eq},j}, & \text{adsorption} \\ f_{\text{res}} n_{0,\text{des},j}, & \text{desorption} \end{cases}$$

where f_{res} is the residual storage fraction and $n_{0,\text{des},j}$ is the storage state at the start of desorption. This formulation reflects incomplete regeneration and preserves cycle-to-cycle memory without forcing the storage state to return to zero after each desorption period.

Rather than introducing an empirical carry-over correction, the

residual storage term represents the physically expected persistence of electrochemical storage resulting from incomplete regeneration during finite desorption periods.

2.3.5. Four-zone hydraulic transport and storage coupling

Hydraulic transport was represented using four sequential concentration states. This compartmental representation follows residence-time-distribution and tanks-in-series concepts commonly used to approximate non-ideal flow, mixing, and transport delay in continuous-flow systems [37]. The inlet and outlet zones describe mixing and smoothing behavior, while the two intermediate active zones are coupled to electrochemical storage/release:

$$V_1 \frac{dC_1}{dt} = Q(C_{\text{in}} - C_1)$$

$$V_2 \frac{dC_2}{dt} = Q(C_1 - C_2) - S_q \frac{dn_2}{dt}$$

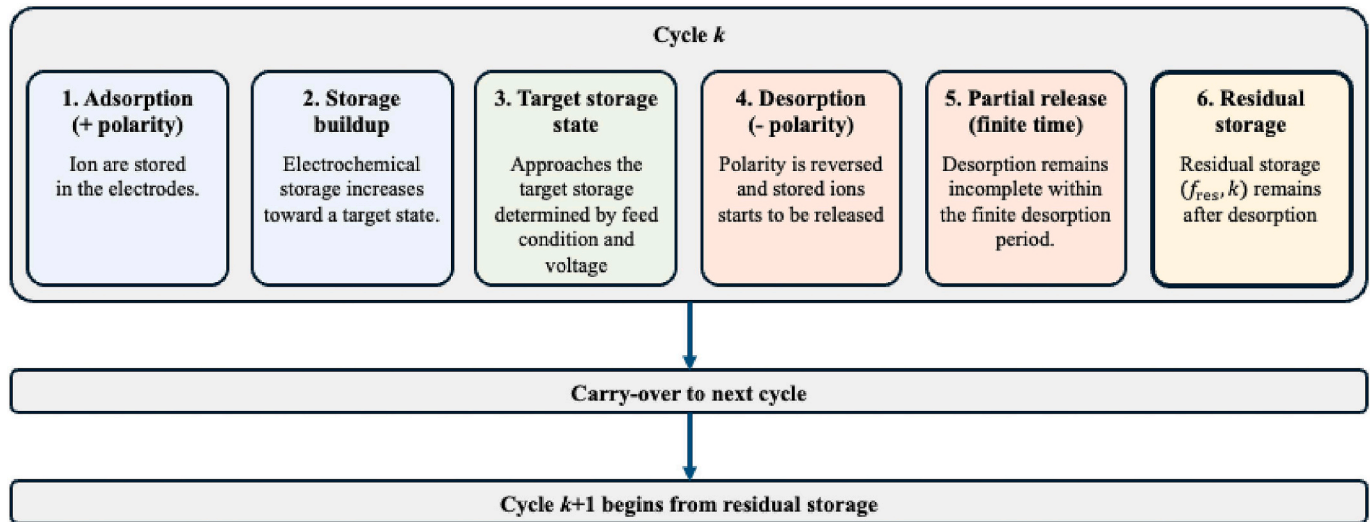


Fig. 3. Schematic representation of continuous electrochemical storage-state propagation during cyclic MCDI operation. Storage accumulated during adsorption is only partially released during finite desorption periods, leaving residual storage that is propagated into subsequent cycles through carry-over behavior.

$$V_3 \frac{dC_3}{dt} = Q(C_2 - C_3) - S_q \frac{dn_3}{dt}$$

$$V_4 \frac{dC_4}{dt} = Q(C_3 - C_4)$$

where $C_1 \sim C_4$ are hydraulic concentration states, Q is the flow rate, $V_1 \sim V_4$ are effective zone volumes, and S_q is the coupling factor converting storage-state evolution into a concentration-equivalent source/sink term. The final outlet conductivity is reconstructed from the fourth concentration state:

$$EC_{out,model} = \frac{C_4}{\gamma_{EC}}$$

2.3.6. Current-limited state transfer and excess storage relaxation

The slow storage-state evolution was represented as target-state tracking constrained by the available current, hereafter referred to as current-limited state transfer. This bounded transfer prevents physically unrealistic instantaneous jumps in internal storage state during polarity switching:

$$\left(\frac{dn_j}{dt} \right)_{slow} = \text{sgn}(n_{target,j} - n_j) \min \left[k_{transfer} |n_{target,j} - n_j|, \eta_{transfer} \frac{N_{pair}|I|}{F} \right]$$

where $k_{transfer}$ is the first-order transfer coefficient, $\eta_{transfer}$ is the effective current utilization efficiency, N_{pair} is the number of electrode pairs, I is current, and F is the Faraday constant. The current constraint is used here as a Faraday-equivalent ion-transfer limit and does not imply that Faradaic reactions dominate the capacitive storage mechanism [11,12,16,17,21,22].

To reproduce transient desorption peaks following switching, an excess storage relaxation term was added. This additional term is introduced to represent transient redistribution and delayed release of ions immediately following polarity reversal, which cannot be captured by the slower current-limited storage evolution alone.

$$\left(\frac{dn_j}{dt} \right)_{excess} = -k_{ex} q_{ex,j} G_j(t)$$

$$G_j(t) = \exp \left[-\frac{t - t_{switch}}{\tau_{ex}} \right]$$

where $q_{ex,j}$ represents the activated excess storage component after switching, k_{ex} is the relaxation coefficient, and τ_{ex} is the relaxation time

constant. This term is interpreted as transient redistribution or release of excess storage rather than as an independently fitted desorption equation.

The final storage-state equation is:

$$\frac{dn_j}{dt} = \left(\frac{dn_j}{dt} \right)_{slow} + \left(\frac{dn_j}{dt} \right)_{excess}, \quad j = 2, 3$$

This unified equation is applied across adsorption and desorption. Mode differences are introduced through the target state and current condition, not through separate empirical equations. Although the present framework was developed and evaluated under constant-voltage operation, the current-limited state-transfer formulation is not inherently restricted to this operating mode because the applied voltage and current are treated as independent model inputs. Under constant-current operation, the prescribed current profile could directly drive the state-transfer dynamics, while the corresponding time-varying voltage would be used to determine the target storage state. Its applicability to constant-current operation remains to be experimentally validated. Physically, the excess-storage relaxation term represents the delayed release and redistribution of ions stored within microporous electrode domains immediately following polarity reversal. Although simplified, the relaxation mechanism provides a physically interpretable representation of transient post-switch conductivity responses.

Immediately following polarity reversal, ions accumulated within the microporous electrode domains are not instantaneously redistributed to the surrounding macropore solution. Instead, redistribution is assumed to proceed progressively as the electrochemical equilibrium shifts under the reversed electric field. The exponential relaxation term therefore provides a reduced-order approximation of this transient redistribution process by representing the gradual decay of the excess storage state toward the new equilibrium, rather than serving solely as an empirical fitting function for the initial desorption peak.

2.4. Continuous-state simulation protocol

The proposed framework was evaluated using continuous-state simulations under the five experimental initial feed EC conditions. A common reduced-order model structure was maintained across all simulations, and internal hydraulic and electrochemical states were propagated continuously throughout the simulation horizon.

Unlike cycle-by-cycle approaches that reset internal states at switching boundaries, the present framework retained both hydraulic concentration states and electrochemical storage states throughout

repeated adsorption–desorption operation. Consequently, residual storage, carry-over behavior, and switching-induced transient responses evolved naturally as a result of preceding state history.

Continuous simulations were performed over the full 12,000 s experimental duration, corresponding to 20 consecutive adsorption–desorption cycles for each initial EC condition. This non-reset simulation protocol enabled direct evaluation of cyclic state continuity, long-horizon stability, and condition-dependent response evolution within a unified storage-state framework.

The present analysis focused exclusively on the physics-based backbone model. Remaining localized mismatch between observations and simulations was therefore interpreted as a limitation of the reduced-order representation itself rather than corrected using post hoc residual models or data-driven compensation approaches.

2.5. Parameter identification

Model parameters were identified using a combination of physically informed estimation and multi-condition cyclic calibration. Hydraulic-zone parameters were first estimated from the observed transport delay and residence-time characteristics of the experimental system. Electrochemical storage parameters governing the target-state formulation were subsequently refined using all five initial feed EC conditions simultaneously.

Parameter calibration was performed by minimizing the combined simulation error across all five initial feed EC conditions while preserving stable cyclic state evolution. Parameters associated with hydraulic transport, electrochemical storage, current-limited state transfer, residual storage memory, and excess storage relaxation were adjusted to reproduce conductivity dynamics over the full 12,000 s simulation horizon.

The same parameter set was applied across all five initial feed EC conditions without condition-specific recalibration. This strategy was adopted to evaluate whether the proposed storage-state framework could reproduce conductivity-dependent cyclic behavior using a unified reduced-order representation rather than condition-dependent empirical fitting.

Particular emphasis was placed on preserving cyclic continuity, adsorption–desorption transition behavior, transient desorption responses, and long-horizon stability. Parameter selection therefore balanced simulation accuracy and physically interpretable state evolution rather than maximizing goodness-of-fit for individual operating conditions.

The calibration was intended to identify a single physically constrained backbone parameter set capable of reproducing multi-condition cyclic dynamics, rather than to provide condition-wise or mode-wise empirical fits. Accordingly, no parameters were re-estimated for individual cycles, half-cycle windows, adsorption/desorption modes, switching events, or conductivity-specific operating conditions.

Although the residual-storage-memory and excess-storage-relaxation parameters influence post-switch desorption behavior, they were calibrated as part of the same unified parameter set applied across all operating modes and conductivity conditions. The objective of the present evaluation was to assess whether a single physically constrained parameter set could consistently reproduce cyclic MCDI dynamics across multiple experimentally defined operating conditions. Accordingly, the reported performance metrics quantify the reproducibility of the proposed reduced-order framework across the investigated operating range rather than predictive generalization beyond the calibration conditions. Independent validation using additional experimental operating conditions beyond the present calibration dataset remains an important direction for future studies.

To improve parameter identifiability, a unified multi-condition optimization procedure was employed in which all five initial feed EC conditions were simultaneously considered under physically constrained parameter bounds. This strategy reduced parameter

compensation among interacting model components by requiring a single parameter set to consistently reproduce cyclic responses across the investigated operating conditions.

The identified parameters can be categorized into parameter groups associated with each framework component, as summarized in Table 3. The principal calibrated parameters included a residual storage fraction of 0.24, a voltage-utilization factor of 0.126, a current-transfer efficiency of 0.601, and an excess-relaxation time constant of 10 s. The final parameter set was obtained through multi-condition calibration against the complete experimental dataset. To improve transparency and reproducibility, the complete calibrated parameter values are summarized in Supplementary Table S1, together with the parameter-identification workflow, optimization procedure, and source code used throughout this study.

2.6. Model evaluation metrics

2.6.1. Error metrics

Model performance was evaluated using mean absolute error (MAE), root mean square error (RMSE), weighted absolute percentage error (WAPE), Nash–Sutcliffe efficiency (NSE), and Kling–Gupta efficiency (KGE). Absolute EC-based metrics were used to quantify simulation error in conductivity units, while normalized concentration-based NSE and KGE were used to evaluate dynamic agreement across initial EC conditions [38].

2.6.2. Window-wise cyclic evaluation

To reflect cyclic operation characteristics, metrics were computed over repeated 300 s half-cycle windows and separated by adsorption and desorption mode. The first 35 s immediately after each switching event were excluded from metric computation to reduce the influence of switching-edge artifacts and sensor-lag-dominated transients. This exclusion was applied only to performance evaluation; the continuous-state simulation itself propagated model states over the full time horizon.

This exclusion affected only metric computation; post-switch trajectories were still simulated continuously and inspected for qualitative agreement with the observed desorption relaxation pattern.

2.6.3. Condition-wise and mode-wise assessment

Performance was summarized across initial EC conditions and separately for adsorption and desorption windows. This evaluation structure was used to assess whether the proposed storage-state framework preserved cyclic continuity and reproduced condition-dependent response patterns without relying on separate mode-specific fitting. Particular attention was given to desorption behavior because transient

Table 3

Framework components, governing parameters, and roles in the storage-state model.

Framework component	Parameter group	Parameter	Role in the framework
Modified-Donnan-informed target storage	Target storage-state parameters	$\gamma, \beta, \phi_{\text{loss}}, K_{\text{loss}}$	Determines conductivity-dependent target storage state
Residual storage memory	Residual-memory parameters	f_{res}	Preserves carry-over effects between successive cycles
Four-zone hydraulic transport	Hydraulic transport parameters	$V_1 - V_4, V_{\text{eff}}$	Represents residence-time distribution and transport delay
Current-limited state transfer	State-transfer parameters	$k_{\text{transfer}}, \eta_{\text{transfer}}$	Controls finite-rate evolution toward the target storage state
Excess storage relaxation	Excess-relaxation parameters	$k_{\text{ex}}, \tau_{\text{ex}}$	Reproduces transient post-switch desorption relaxation

desorption peaks and residual storage release are sensitive indicators of carry-over and electrochemical memory effects.

3. Results and discussion

3.1. Development of the storage-state framework

To establish a reduced-order framework capable of reproducing long-horizon cyclic MCDI behavior, multiple candidate formulations were evaluated sequentially and compared against the observed conductivity response. The development process focused on identifying the minimum set of mechanisms required to reproduce cyclic continuity, carry-over behavior, and transient desorption dynamics under repeated adsorption–desorption switching.

The simplest formulation consisted of a monotonic storage–release representation in which stored ions accumulated during adsorption and were released during desorption through a single relaxation process. Although this formulation reproduced the overall cyclic trend, it systematically underestimated the transient conductivity increase immediately following polarity reversal. This result indicated that desorption behavior could not be represented as a simple inverse of adsorption or as a purely monotonic release process.

The introduction of hydraulic transport delay improved representation of temporal lag between electrochemical state evolution and outlet conductivity response. Transition timing and conductivity smoothing were better reproduced; however, transport effects alone were insufficient to preserve cyclic carry-over behavior during extended repeated operation. The simulated response gradually lost continuity because persistent electrochemical memory was not adequately represented.

Current-limited state transfer was subsequently introduced to limit unrealistically rapid storage-state transitions during polarity switching. This modification improved numerical stability and produced more realistic adsorption–desorption transitions. Nevertheless, localized desorption peaks immediately after polarity reversal remained under-predicted, suggesting that an additional short-time relaxation mechanism was required.

The final improvement was achieved by incorporating excess storage relaxation within the continuous-state framework. This mechanism enabled temporary release of excess stored ions immediately after switching and better represented the observed transient desorption behavior while preserving long-horizon cyclic continuity.

Based on these observations, the final backbone model integrated modified-Donnan-informed target storage, four-zone hydraulic transport, current-limited state transfer, residual storage memory, and excess storage relaxation within a unified storage-state framework. Importantly, cyclic adsorption and desorption behavior emerged from

continuous state propagation rather than from independently fitted mode-specific equations.

3.2. Reproduction of cyclic adsorption–desorption behavior

The proposed storage-state framework was evaluated under five initial feed EC conditions ranging from approximately 223 to 4000 $\mu\text{S cm}^{-1}$ to assess its ability to reproduce cyclic MCDI behavior during repeated adsorption–desorption operation. Across all investigated conditions, the framework successfully reproduced the overall cyclic conductivity trajectory without introducing separate adsorption and desorption equations. Repeated switching behavior, conductivity oscillation patterns, and long-horizon response evolution emerged naturally through continuous propagation of internal electrochemical storage states.

Condition-wise comparisons between experimental and simulated conductivity responses under the tap-water condition are presented in Fig. 4. The proposed framework successfully reproduced the overall cyclic adsorption–desorption behavior and conductivity evolution throughout the 20-cycle operation period. However, relatively larger deviations were observed during the early desorption period immediately following polarity reversal. In particular, the model tended to overpredict the transient conductivity peak under the 223 $\mu\text{S cm}^{-1}$ condition. This behavior is attributed, at least in part, to the simplified NaCl-based electrochemical representation adopted in the present framework, whereas the tap-water feed contained multiple ionic species that were not explicitly represented in the model. Nevertheless, the overall cyclic topology, switching timing, and long-horizon response evolution remained consistent with the experimental observations.

Condition-wise comparisons under the NaCl-amended feed conditions are presented in Fig. 5. As the initial feed EC increased from 1000 to 4000 $\mu\text{S cm}^{-1}$, model agreement improved substantially. Both adsorption and desorption trajectories were closely reproduced throughout repeated operation, including transient switching responses and cyclic conductivity oscillations. The framework accurately captured peak conductivity levels during desorption as well as the subsequent conductivity decay behavior over multiple cycles. Agreement between simulations and measurements was particularly strong under the intermediate conductivity conditions (2000–3000 $\mu\text{S cm}^{-1}$), where the observed and simulated conductivity profiles remained closely matched throughout the entire simulation horizon with minimal cycle-to-cycle deviation.

Importantly, model performance remained stable throughout the full 12,000 s operation period without noticeable drift or loss of cyclic continuity. Because no state reinitialization was imposed at switching boundaries, conductivity evolution emerged naturally from the

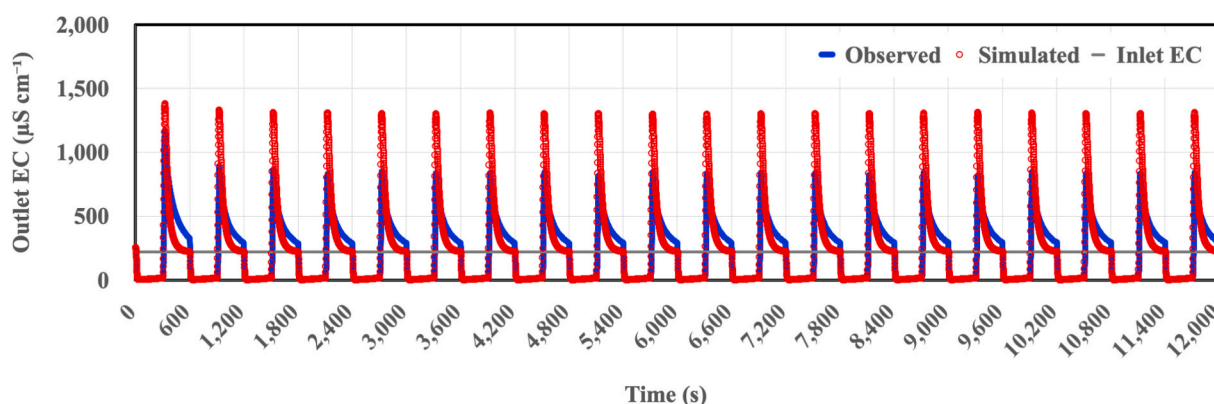


Fig. 4. Comparison of experimental and simulated outlet conductivity profiles under the tap-water feed condition (initial feed EC = 223 $\mu\text{S cm}^{-1}$). The proposed storage-state framework successfully reproduces the overall cyclic adsorption–desorption behavior and long-horizon conductivity evolution over 20 consecutive cycles. Larger deviations are observed during the early desorption period immediately following polarity reversal, which may be attributed to limitations of the simplified NaCl-based electrochemical representation under the multi-ionic tap-water condition.

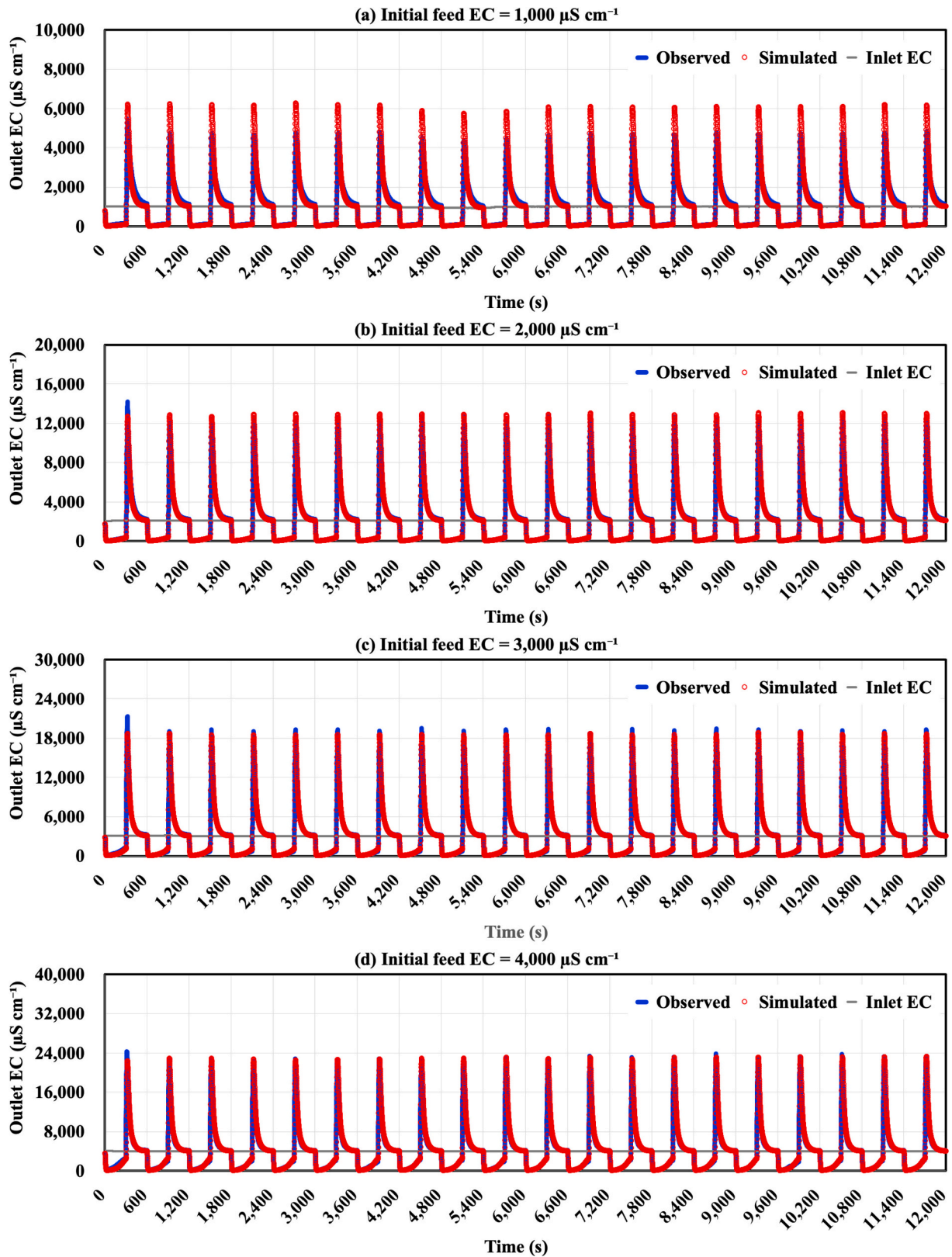


Fig. 5. Comparison of experimental and simulated outlet conductivity profiles under NaCl-amended feed conditions (initial feed EC = 1000–4000 $\mu\text{S cm}^{-1}$). The proposed storage-state framework accurately reproduces repeated adsorption–desorption cycles, transient switching responses, and long-horizon conductivity evolution over 20 consecutive cycles. Agreement between simulations and measurements improves with increasing feed conductivity, with particularly strong agreement observed under the 2000 and 3000 $\mu\text{S cm}^{-1}$ conditions.

accumulated storage history of preceding cycles. These results demonstrate that the proposed storage-state framework can reproduce condition-dependent cyclic MCDI behavior across a broad conductivity range while preserving a compact and physically interpretable model structure. Quantitative model performance is presented in Section 3.5.

3.3. Evolution of internal storage states and carry-over behavior

A key feature of the proposed framework is the continuous propagation of internal electrochemical storage states throughout repeated adsorption–desorption operation. To investigate the mechanism underlying cyclic continuity, the temporal evolution of the active storage states (q_2 and q_3) and the total storage state was examined under all initial EC conditions.

As shown in Fig. 6, the storage states evolved continuously during repeated adsorption–desorption switching. The active storage states increased during adsorption as the electrochemical storage tendency developed within the active storage domain and decreased during desorption as stored ions were released. The resulting total storage state exhibited repeated accumulation–release cycles, with the amplitudes of the normalized storage states increasing systematically as the feed conductivity increased. This behavior was consistently observed across the entire initial feed EC range.

Importantly, the storage states were not independently reinitialized at each cycle. Instead, state evolution was governed by continuous propagation of the preceding electrochemical condition. Consequently, the conductivity response at a given cycle depended not only on the instantaneous operating mode but also on the accumulated storage-state history from previous cycles.

These results indicate that cyclic MCDI dynamics are governed by the persistent evolution of the internal electrochemical storage state rather than by isolated adsorption and desorption events, supporting the interpretation that long-horizon cyclic operation can be represented without cycle-specific fitting or artificial state resetting.

3.4. Desorption dynamics and transient relaxation behavior

One of the distinguishing features of cyclic MCDI operation is the transient conductivity response immediately following polarity reversal. As observed in Figs. 4–5, desorption periods were characterized by rapid conductivity increases followed by gradual relaxation toward quasi-steady desorption behavior. The magnitude and temporal evolution of these transient peaks varied with initial feed EC condition and accumulated storage history.

The storage-state analysis presented in Fig. 6 provides a mechanistic interpretation of this behavior in terms of storage accumulation during adsorption and subsequent release following polarity reversal. During adsorption, ions were continuously accumulated within the electrochemical storage domain, resulting in progressive growth of the active and total storage states. Following polarity reversal, part of this stored ionic inventory was released rapidly, producing the transient conductivity peak observed during the early desorption period.

This behavior indicates that desorption cannot be interpreted simply as the reverse of adsorption or as an independent equilibrium–relaxation process. Instead, desorption dynamics are strongly influenced by the storage state inherited from the preceding adsorption period. Consequently, the conductivity response immediately after switching reflects both the instantaneous operating mode and the residual electrochemical memory accumulated during previous operation.

Within the proposed framework, this behavior is represented through the combined effects of residual storage memory, finite state-transfer dynamics, and excess storage relaxation. Because these mechanisms are embedded within a unified continuous-state formulation, transient desorption responses emerge naturally from storage-state evolution without requiring separate empirical equations for adsorption and desorption.

These observations suggest that transient desorption peaks can be interpreted as a manifestation of cyclic electrochemical memory and storage-state redistribution. The successful reproduction of this behavior further supports the interpretation that long-horizon MCDI dynamics can be described through continuous propagation of internal electrochemical storage states rather than through independently fitted operational modes.

In the desorption windows, the model achieved a mean WAPE of 12.04% across the five initial EC conditions, indicating that the proposed storage-state formulation captured the major desorption-phase conductivity dynamics despite localized deviations during early post-switch periods.

3.5. Condition-wise model performance metrics

Quantitative model performance was evaluated using MAE, WAPE, NSE, and KGE across the five initial feed EC conditions. The corresponding condition-wise performance metrics are summarized in Table 4.

Overall, the proposed storage-state framework demonstrated stable cyclic-response reproduction across a broad initial feed EC range. The mean MAE was $157.4 \mu\text{S cm}^{-1}$, while the mean all-window WAPE, NSE, and KGE were 13.10%, 0.942, and 0.889, respectively. These results indicate that the model successfully reproduced both absolute conductivity responses and normalized cyclic dynamics during long-horizon operation. The reported mean all-window WAPE was calculated as the arithmetic mean of the condition-wise all-window WAPE values, with equal weighting assigned to each initial feed EC condition.

Condition-wise evaluation revealed improved agreement with increasing initial feed EC. The all-window WAPE values were 27.0%, 15.6%, 6.6%, 6.0%, and 10.3% for the 223, 1000, 2000, 3000, and 4000 $\mu\text{S cm}^{-1}$ conditions, respectively. The lowest error was observed under the 3000 $\mu\text{S cm}^{-1}$ condition, whereas the largest percentage error occurred under the 223 $\mu\text{S cm}^{-1}$ condition.

As shown in Table 4, the corresponding MAE values provide a complementary measure of the absolute conductivity error in the original conductivity units ($\mu\text{S cm}^{-1}$), whereas the percentage-based WAPE increased markedly under the lowest feed conductivity condition.

The elevated WAPE observed under the lowest initial feed EC condition should be interpreted with caution because percentage-based metrics become increasingly sensitive as conductivity magnitude decreases. Under low-EC conditions, relatively small absolute deviations can produce disproportionately large percentage errors. The low-EC regime is also expected to be more sensitive to unresolved voltage losses, membrane resistance effects, and sensor-level baseline fluctuations, which become proportionally more influential when the conductivity magnitude is small. Consistent with these considerations, the corresponding NSE and KGE values remained acceptable, indicating that the overall cyclic response pattern was still reproduced successfully.

The mean desorption WAPE was 12.04%, demonstrating that the framework maintained comparable reproduction capability during the desorption phase despite the presence of rapid post-switch transients. This result is particularly significant because desorption behavior is strongly influenced by residual storage release and cyclic memory effects, making it inherently more challenging to reproduce than adsorption behavior.

Although reproduction accuracy varied across initial feed EC conditions, the framework consistently preserved cyclic continuity, response timing, and overall conductivity evolution throughout the full 20-cycle simulation period. These results demonstrate that the proposed storage-state framework provides reliable reproduction of long-horizon cyclic MCDI behavior using a unified reduced-order representation.

3.6. Interpretation and implications of the unified framework

The present results demonstrate that cyclic adsorption–desorption

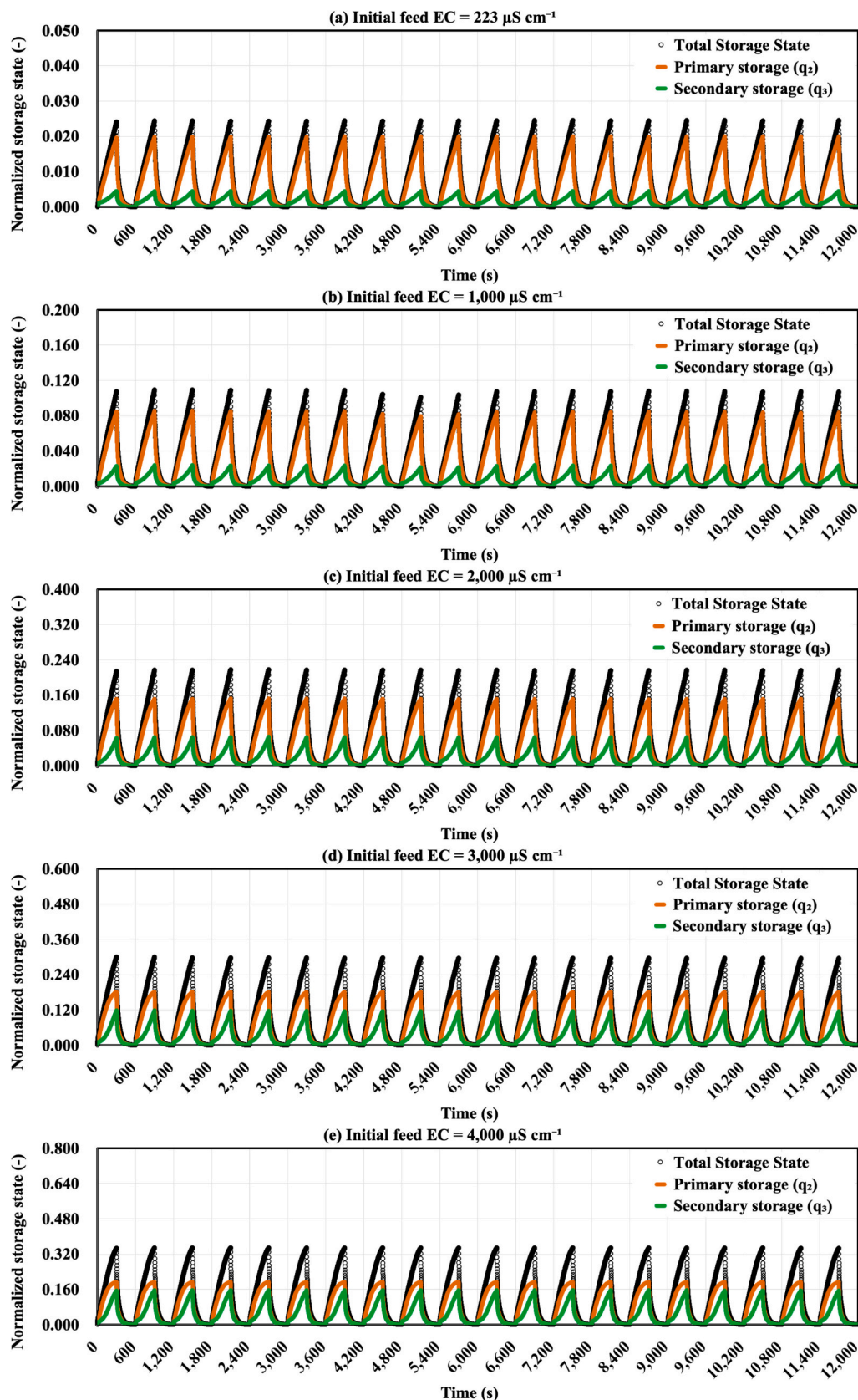


Fig. 6. Evolution of the normalized internal storage states (q_2 , q_3 , and total storage state) during repeated adsorption–desorption operation under different initial feed conductivity conditions. The primary storage state (q_2) and secondary storage state (q_3) evolve continuously throughout repeated switching cycles, while the total storage state represents their combined normalized electrochemical storage state. The amplitudes of the normalized storage states increase with increasing feed conductivity, indicating a greater electrochemical storage tendency under higher ionic loading. The continuous propagation of these internal states provides the basis for cyclic carry-over behavior and non-reset simulation.

Table 4

Condition-wise model reproduction metrics for the proposed storage-state framework under five initial feed EC conditions.

Initial feed EC ($\mu\text{S cm}^{-1}$)	MAE ($\mu\text{S cm}^{-1}$)	WAPE (%)	NSE	KGE
223	58.25	27.0	0.841	0.859
1000	141.62	15.6	0.944	0.889
2000	116.72	6.6	0.987	0.953
3000	146.11	6.0	0.991	0.938
4000	324.44	10.3	0.946	0.808
Mean $\pm$ SD	157.4 $\pm$ 99.7	13.1 $\pm$ 8.8	0.942 $\pm$ 0.062	0.889 $\pm$ 0.054

behavior in MCDI systems can be interpreted through continuous evolution of internal electrochemical storage states. Rather than treating adsorption and desorption as independent operational modes, the proposed framework represents cyclic behavior as a continuous state-propagation process in which residual storage memory and finite state-transfer dynamics govern subsequent system responses. The successful reproduction of cyclic continuity, carry-over behavior, and transient desorption responses supports this interpretation.

From a modeling perspective, the framework occupies an intermediate position between empirical cycle-wise fitting approaches and high-dimensional electrochemical simulations. Unlike purely empirical formulations, the proposed model preserves electrochemical interpretability through a modified-Donnan-informed storage-state representation. At the same time, the reduced-order structure remains computationally tractable for long-horizon cyclic simulation and operation-oriented analysis.

The results further suggest that major cyclic MCDI dynamics can be reproduced without introducing separate adsorption and desorption equations. Instead, repeated conductivity responses emerge naturally from continuous propagation of storage states coupled with hydraulic transport, current-limited state transfer, residual storage memory, and excess storage relaxation mechanisms. Hydraulic transport accounts for finite residence-time effects, current-limited state transfer represents finite electrochemical response kinetics, residual storage memory preserves carry-over between successive adsorption-desorption cycles, and excess storage relaxation captures transient desorption behavior immediately following polarity switching. Together, these coupled mechanisms enable accurate reproduction of the dominant cyclic MCDI dynamics while maintaining a reduced-order formulation suitable for long-horizon simulation. This finding supports the use of unified state-based formulations for analysis of long-duration cyclic operation and reinforces the interpretation that cyclic MCDI behavior is fundamentally governed by evolving electrochemical storage states.

Several limitations should nevertheless be acknowledged. The present framework was developed and evaluated using conductivity-based cyclic experiments and does not explicitly resolve pore-scale ion transport, membrane-specific resistance distributions, concentration polarization, ion selectivity, or detailed activity-coefficient effects. The framework was evaluated using conductivity-based cyclic datasets consisting of one tap-water condition ($223 \mu\text{S cm}^{-1}$) and four NaCl-amended feed conditions. Although the present formulation was parameterized using single-salt (NaCl) feed solutions, the storage-target formulation is structurally expressed as a summation over ion species and can therefore be extended to multi-ion systems by incorporating species-specific equilibrium relationships accounting for ion valency, hydrated radius, and competitive electrosorption. Such an extension would require additional parameterization and validation using systematically controlled multi-ion datasets and more complex water matrices. Consequently, the model should be interpreted as a reduced-order representation of dominant cyclic behavior rather than a

complete electrochemical description of all transport processes.

Although the present framework was calibrated using a laboratory-scale MCDI module, the proposed storage-state formulation is not inherently restricted to a particular system scale. The underlying storage-state evolution and reduced-order electrochemical framework are expected to remain applicable provided that the dominant hydraulic transport and electrochemical mechanisms are preserved. However, several lumped parameters associated with the framework components summarized in Table 3 are expected to depend on module geometry, hydraulic residence-time distribution, and operating conditions. Accordingly, these scale-dependent parameters would require re-identification for different module configurations, and additional validation using pilot- and full-scale MCDI systems remains an important direction for establishing the scalability of the proposed framework.

Despite these limitations, the proposed framework provides a practical basis for long-horizon simulation, cyclic operation analysis, and future model-based control of MCDI systems. Because the internal states evolve continuously throughout repeated operation, the framework is particularly well suited for applications requiring continuous simulation and eventual prediction of future system behavior under changing operating conditions. Such a framework may therefore facilitate optimization of adsorption-desorption switching schedules, prediction of carry-over accumulation, mitigation of transient desorption peaks, and future adaptive operation through model-based control under dynamically changing operating conditions. Accordingly, the main contribution of the proposed framework is not replacement of detailed electrochemical simulations, but provision of an interpretable continuous-state backbone capable of bridging electrochemical insight and operation-oriented long-horizon cyclic analysis. The proposed storage-state framework therefore provides a practical and physically interpretable foundation for future development of adaptive operation, model-based control, and condition-aware MCDI operation strategies.

4. Conclusions

This study developed and evaluated a storage-state-based reduced-order electrochemical framework for describing cyclic adsorption-desorption dynamics in membrane capacitive deionization (MCDI) under repeated switching operation. The proposed framework successfully reproduced major cyclic MCDI behaviors, including adsorption-desorption continuity, cycle-to-cycle carry-over, and transient desorption responses. Across the five initial feed EC conditions, the model achieved a mean all-window WAPE of 13.10%, a mean desorption WAPE of 12.04%, a mean NSE of 0.942, and a mean KGE of 0.889. These results indicate that dominant cyclic MCDI dynamics can be reproduced using a single unified parameter set without separate adsorption-desorption fitting or mode-specific empirical equations. Analysis of the internal storage-state evolution further showed that cyclic MCDI behavior can be interpreted as a continuous electrochemical state-propagation process rather than as a sequence of independent adsorption and desorption events. Within the operating conditions investigated in this study, the proposed framework provides a practical foundation for long-horizon simulation, cyclic performance assessment, and future development of model-based operation and control strategies for MCDI systems. The present framework was developed and evaluated under constant-voltage operation using conductivity-based datasets consisting of one tap-water condition and four NaCl-amended feed conditions. Accordingly, its applicability to dynamically varying feed conditions, multi-ion systems, and more complex water matrices remains to be established through future studies. Future studies should extend validation to dynamically varying feed conditions, multi-ion systems, ion-selective MCDI operation, and more complex water matrices, while exploring integration of the proposed storage-state framework with adaptive control, condition-aware operational optimization, and future model-based control of cyclic MCDI systems.

CRediT authorship contribution statement

Jusuk An: Conceptualization, Methodology, Software, Formal analysis, Investigation, Data curation, Visualization, Writing – original draft, Writing – review & editing. **Seungjae Yeon:** Investigation, Writing – review & editing. **Changseog Oh:** Data curation, Writing – review & editing. **Bokjin Lee:** Investigation, Writing – review & editing. **Woosik Jung:** Data curation, Writing – review & editing. **Jeongmin Yun:** Data curation, Writing – review & editing. **Seungwoo Baik:** Data curation, Writing – review & editing. **Joonhong Park:** Conceptualization, Supervision, Project administration, Funding acquisition, Writing – review & editing.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.desal.2026.120603>.

Data availability

Data will be made available on request.

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