A COMBINED MODELING AND EXPERIMENTAL STUDY ASSESSING THE IMPACT OF FLUID PULSATION AND OPERATING SCHEMES ON CHARGE AND ENERGY EFFICIENCY IN CAPACITIVE DEIONIZATION

BY

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THESIS

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ABSTRACT

Cell-cycling performance in capacitive deionization (CDI) can suffer from various charge-efficiency loss mechanisms. In conventional CDI, we show that salt residue within electrodes introduces a temporal lag between charge and desalination stages of a CDI cycle. Without accounting for this effect in the collection of effluent, significant performance degradation occurs as current density increases. To overcome this we use pulse-flow operation to control fresh- and brine-water concentrations. The charge and energy efficiency performance between the two flow-modes is compared using a porous electrode model that is calibrated and validated with experimental data. To quantify specific contributions to charge efficiency losses, the model captures local salt variations resulting from a combination of electrosorption, leakage current, and immobile surface charge. Compared to traditional continuous-flow operation, simulation results show that charge efficiency increases up to 23% in the pulse-flow operation at a current density up to 20 A/m², which leads to a 73% decrease of specific energy consumption (SEC). In addition, the SEC predicted by the pulse-flow operation model closely aligns with the predictions of the continuous-flow model after accounting for temporal lag in effluent salinity. Both simulations and experimental results suggest that pulse-flow operation closely approximates the performance in continuous-flow operation.

We further apply the pulse-flow model to simulate two different CDI architectures (membrane capacitive deionization and flow-through CDI) and focus on the identification
energy losses specific to each system component. The model was used to quantify the effects of ohmic resistance, parasitic faradaic reactions, co-ion repulsion, and incomplete utilization of electrode capacitance on salt specific energy consumption (kJ g-NaCl⁻¹) across a range of current densities and charging voltage limits. We show that significant irreversible energy loss is observed at low and high current density, which is mainly contributed by the parasitic reactions and resistive charge transport dissipation, respectively. However, the greatest source of energy loss can be linked to reverse diffusional flux at the beginning of a charging stage, caused by retention of salt from the brine discharge stage. From this analysis, we show how target effluent concentration and cell architecture can be controlled to reduce energy consumption by greater than one order of magnitude.

**Keywords:** capacitive deionization, flow mode, numerical simulation, porous electrode model, charge efficiency, salt specific energy consumption
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# ABBREVIATIONS

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<tbody>
<tr>
<td>amph-D</td>
<td>amphoteric-Donnan</td>
</tr>
<tr>
<td>BGW</td>
<td>brackish groundwater</td>
</tr>
<tr>
<td>BWRO</td>
<td>brackish water reverse osmosis</td>
</tr>
<tr>
<td>CDI</td>
<td>capacitive deionization</td>
</tr>
<tr>
<td>EDL</td>
<td>electrical double layer</td>
</tr>
<tr>
<td>ele-res</td>
<td>electrode residue</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>FC</td>
<td>flow channel</td>
</tr>
<tr>
<td>FC-res</td>
<td>flow channel residue</td>
</tr>
<tr>
<td>GCS</td>
<td>Guoy-Chapman-Stern</td>
</tr>
<tr>
<td>IEM</td>
<td>ion exchange membrane</td>
</tr>
<tr>
<td>MCDI</td>
<td>membrane capacitive deionization</td>
</tr>
<tr>
<td>mD</td>
<td>modified Donnan</td>
</tr>
<tr>
<td>OCC</td>
<td>open circuit condition</td>
</tr>
<tr>
<td>PZC</td>
<td>potential of zero charge</td>
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<td>RO</td>
<td>reverse osmosis</td>
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SEC  specific energy consumption
USGS  U.S. Geological Survey
### LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>(a^*)</td>
<td>effective surface area for faradaic reactions on porous electrode, m(^2)/cm(^3)-electrode</td>
</tr>
<tr>
<td>(c)</td>
<td>electrolyte concentration, mM</td>
</tr>
<tr>
<td>(c_{\text{ions,mi}})</td>
<td>ionic concentration in micropores, C/cm(^3)</td>
</tr>
<tr>
<td>(C_S)</td>
<td>Stern-layer capacitance, F/g</td>
</tr>
<tr>
<td>(d_c)</td>
<td>radius of a single activated particle, (\mu m)</td>
</tr>
<tr>
<td>(D_0)</td>
<td>bulk diffusion coefficient, cm(^2)/s</td>
</tr>
<tr>
<td>(F)</td>
<td>Faraday constant, C/mol</td>
</tr>
<tr>
<td>(H_{O_2})</td>
<td>Henry's constant of oxygen, -</td>
</tr>
<tr>
<td>(i_{0,O_2})</td>
<td>exchange current density for oxygen reduction, A/cm(^2)-electrode</td>
</tr>
<tr>
<td>(i_{0,C})</td>
<td>exchange current density for carbon corrosion, A/cm(^2)-electrode</td>
</tr>
<tr>
<td>(i_L)</td>
<td>leakage current density, A/cm(^3)-electrode</td>
</tr>
<tr>
<td>(i_C)</td>
<td>capacitive current density, A/cm(^3)-electrode</td>
</tr>
<tr>
<td>(l)</td>
<td>total current applied to the system, A</td>
</tr>
<tr>
<td>(j)</td>
<td>total current density, A/m(^2)</td>
</tr>
<tr>
<td>(k_B)</td>
<td>Boltzmann constant, CV/K</td>
</tr>
</tbody>
</table>
\( N \)  
number of pulses, -

\( Q_{\text{pulse}} \)  
flow rate during the event of pulsing, mL/s

\( \langle r_{ml} \rangle \)  
averaged radius of micropores, nm

\( t_- \)  
transference number of negative ions, -

\( t_+ \)  
transference number of positive ions, -

\( T \)  
temperature, K

\( U_0^\theta \)  
standard potential of oxygen reduction, V vs. SHE

\( U_C^\theta \)  
standard potential of carbon corrosion, V vs. SHE

\( U_\theta \)  
Langmuir adsorption potential, V vs. SHE

\( V_{FC} \)  
open volume in the flow channel, mL

\( V_{cell} \)  
cell voltage, V

\( V_{\text{pulse}} \)  
dispense volume during the event of pulsing, mL

**Greek**

\( \alpha_{O_2} \)  
symmetry factor for faradic reaction of oxygen, -

\( \alpha_C \)  
symmetry factor for faradic reaction of carbon, -

\( \varepsilon_{FC} \)  
flow channel porosity, -
\( \varepsilon_{\text{macro}} \)  
- electrode porosity of macropores and voids between particles, -

\( \varepsilon_{\text{micro}} \)  
- electrode microporosity, -

\( \varepsilon \)  
- total electrode porosity, -

\( \varepsilon \)  
- computational error, -

\( \eta \)  
- overpotential for faradic reactions, V

\( \kappa_0 \)  
- bulk solution conductivity, S/m

\( \kappa_{\text{eff}} \)  
- effective conductivity in electrolyte, S/m

\( \Lambda_{\text{FC}} \)  
- charge efficiency loss due to desalination residue in flow channel, -

\( \Lambda_{\text{co−ion}} \)  
- charge efficiency loss due to co-ion repulsion, -

\( \Lambda_{\text{ele}} \)  
- charge efficiency loss due to desalination residue in electrodes, -

\( \Lambda_{\text{leakage}} \)  
- charge efficiency loss due to leakage current, -

\( \Lambda_{\text{salt}} \)  
- charge efficiency due to salt removal in the effluent, or commonly referred to as charge efficiency, -

\( \phi_e \)  
- solution-phase potential, V

\( \phi_s \)  
- solid-phase potential, V

\( \Delta \phi_D \)  
- Donnan layer potential or voltage drop across the boundary between micropore and macropore, V
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\Delta \phi_S$</td>
<td>voltage drop across the Stern layer, V</td>
</tr>
<tr>
<td>$\rho_{\text{chem},i}$</td>
<td>fixed chemical charge density in micropores, C/cm$^3$</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>electric charge density, C/cm$^3$</td>
</tr>
<tr>
<td>$\rho_{\text{electrode}}$</td>
<td>electrode density, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_{\text{ml},i}$</td>
<td>ionic charge density in micropores, C/cm$^3$</td>
</tr>
<tr>
<td>$\sigma_{s,\text{eff}}$</td>
<td>effective conductivity in solid phase, S/m</td>
</tr>
</tbody>
</table>
1.1 Brackish groundwater desalination

Brackish groundwater (BGW) is increasingly considered a viable resource for freshwater production in water stressed regions.\textsuperscript{1,2} In 2010, about 3,290 Mgal/d of saline groundwater was used in the U.S., which is around 4% of the total ground water usage. The groundwater classification used by the U.S. BGW typically refers to groundwater with a dissolved solids concentration in the range of 1-10 g/L (as shown in Figure 1), according to the 2017 profession paper published by the Department of the Interior and the U.S. Geological Survey (USGS).\textsuperscript{3} Desalination approaches are required to reduce the dissolved solids concentration of saline water for purposes of municipal, agricultural, and industrial applications. The nonmandatory secondary maximum contaminant level for dissolved solids in drinking water set by the U.S. Environmental Protection Agency (EPA) is 0.5 g/L. And water with dissolved solids concentration up to 1.5 g/L can be considered for irrigation purpose. The energy input during desalination stage scales with influent salt concentration.\textsuperscript{4}
Figure 1. Groundwater classification scheme.

In 2012, around 74% of the global desalination capacity is produced by membrane based technology. More than 80% of the membrane based desalination facilities in the U.S. are designed to treated groundwater in the brackish salinity range using reverse osmosis (RO). The reported existing brackish water reverse osmosis (BWRO) plants consume 0.9 – 5.5 kWh m⁻³ of produced water, which is still about 10 times the thermodynamic limit, assuming the effluent salt concentration is 0.5 g/L (Figure 2). Capacitive deionization (CDI) is a promising alternative to BWRO desalination because: 1) it potentially requires less energy to electrochemically remove ions from water for low salinity feed water; 2) a portion of the energy invested during desalination can be recovered during a regeneration step when the system is discharged to generate a concentrated brine; 3) it does not require a high pressure system that could lead to high costs due to installation, operation, and maintenance; and 4) the system performance such as degree of desalination, water production, and brine generation in CDI can be manipulated through changes in operating conditions. In this study, we demonstrate how salt removal and energy
consumption performance for desalination by CDI can be improved through optimizing cell design and operation strategies.

Figure 2. Volumetric energy consumption during brackish water desalination for reverse osmosis and capacitive deionization at 25 °C, a water recovery of 75% and effluent salt concentration of 0.5 g/L. Data in this figure are obtained from Refs. 5,8.

1.2 Background in capacitive deionization

CDI is increasingly considered as an energy efficient technology for desalination of low salinity systems compared to RO and thermal flash desalination.\textsuperscript{1,4,7,9} The electrosorption process in traditional CDI systems relies on conductive porous electrodes that undergo electrical double layer (EDL) charging when an external electric power source is applied.\textsuperscript{4,9-11} A typical CDI cell consists of two conductive electrodes (Figure 3a), two current collectors, and a spacer water channel sandwiched together in a symmetrical
Cation and anion selective membranes can also be placed between the spacer channel and the corresponding deionization electrodes (hereby referred to as MCDI) to improve the salt removal performance (Figure 3b). In the cell charging stage, electric power is applied to drive electrosorption processes within electrodes and to produce desalinated solution in the flow channel. In the discharging stage, the direction of current is reversed to release the charge stored within the EDLs.

Figure 3. Schematic of a (a) CDI cell and an (b) MCDI cell.

The technology of CDI dates back to 1960s, when carbon electrode was the first time used by Murphy and his colleagues in demineralization applications. Johnson and Newman developed the first numerical model in 1971 for a porous carbon electrode desalting system based on porous electrode theory. In 1990s, Farmer and his colleagues tested carbon aerogels as electrodes for removal of different types of ionic species in solution. In 2006, Lee et. al. applied an MCDI cell in treating a thermal power plant wastewater and observed improvements in both cycling stability and salt removal compared to traditional CDI. In the same year, Voltea, a company that commercialized MCDI technology, was funded in the Netherlands to provide economic desalinated brackish water to municipal and industrial uses.
Since 2011, research in the field of CDI has been popular (Figure 4). The number of publications that contain “capacitive deionization” in the title continuously increases at a pace of around 30 papers per year. These CDI papers cover innovations on different areas such as different cell architectures (e.g., flow through CDI, flow electrode CDI, hybrid CDI, and multichannel MCDI), new electrosorption materials (e.g., metal oxides, carbide derived carbon, and surface modified carbon) and electrosorption theories (e.g., modified Donnan theory, ampoteric Donnan theory).

![Figure 4. Number of publications per year containing the phrase “capacitive deionization” in the title. Data are collected based on research articles that are published before 11/27/2017.](image)

1.3 Loss to charge efficiency in capacitive deionization

In CDI, charge efficiency is an important metric, defined as the moles of salt removed per mole of electronic charge transferred to a given electrode. Though theoretical CDI charge efficiencies can approach 100%, a number of factors reduce values observed in
practice. Specifically, previous studies have shown that salt removal performance during CDI cell cycling can suffer from electrode degradation, parasitic side reactions, repulsion of co-ions during the electrosorption process, and low ion uptake capacity. In addition, CDI electrodes must operate at high current density to enable sufficient salt removal rates. In practice, there is a tradeoff between charge capacity and current.

On the other hand, salt adsorption capacity is affected by the charge storage capacity of CDI electrodes. Recent research has been conducted to improve electrosorption capacity by using high surface-area carbons (e.g., activated carbon, carbon aerogel, carbon nanotubes, graphene, and carbide derived carbon), metal oxides, surface-modified carbon, and sodium-ion intercalation materials. Activated carbon is the most common and widely studied material in CDI due to its low cost, abundance, and high surface area to promote electrosorption. However, the stability of activated carbon electrodes is limited by corrosion in aqueous solution in an oxidizing environment. Corrosion could lead to changes in surface chemistry and shifts of potential of zero charge (PZC). Such electrode properties have significant impact on desalination performance as they dictate the direction of the electrosorption process: charge accumulation can be driven either by adsorption of ions with sign opposite to the applied charge (counter-ions) or by repulsion of ions of the same sign (co-ions). On the other hand, immobile surface charge can be also engineered to improve stability and salt removal performance through surface group modification, such as acidification and amination, that leads to positive and negative shift of the electrode PZC, respectively.
Leakage current associated with parasitic side reactions, which is commonly observed during cycling tests of CDI cells, affects cell cycling in different ways.\textsuperscript{26,28,59-61} For example, the irreversible energy loss due to parasitic side reactions increases when CDI cells are cycled at low current density and with a large voltage window\textsuperscript{62} (i.e., the difference between the terminal cell voltage in the charge and discharge stages). Shift in the PZC of electrodes often occurs after long-term cycling due to parasitic faradaic reactions.\textsuperscript{63} In addition, byproducts of side reactions (e.g., water splitting, oxygen reduction, and carbon corrosion) could introduce variations in local pH\textsuperscript{41,64} that can affect acid-base equilibria and influence electrosorption.\textsuperscript{65} Shielding electrodes with a protective skin, such as ion exchange membranes, is a common method to prevent leakage current and improve system stability.\textsuperscript{21,63,66}

Figure 5. (a) Schematic of the simulated flow-by CDI cell. A uniform superficial velocity field advects solution through the flow channel with thickness $w_{fe}$ and length $L$, while
charge is transferred between electrodes of thickness $w_e$. Each electrode consists of activated carbon, polymeric binder, and void space. Activated carbon particles can be further divided into three regions: a solid carbon backbone that conducts electricity, a macropore region filled with electroneutral solution, and a micropore region where electrosorption takes place. The black dashed line represents the interface between macropores and micropores, and the yellow dashed lines represents Stern-layer interfaces. The immobile surface charges are treated as fixed charged groups that reside inside the micropores.33,67 (b) Schematic of the different pathways of charge utilization in the charge stage of a typical flow-by CDI cell. A fraction of externally applied charge is utilized for co-ion repulsion, leakage current, desalination residue in flow-channel, and desalination residue within electrode pores. The fraction of salt removal is based on the salinity difference between the influent and effluent, which is typically referred to as the charge efficiency.

In addition to the aforementioned limitations, the impact of flow conditions on the desalination performance of CDI systems has only been explored to a limited extent. For a conventional flow-by CDI system that consists of a pair of porous electrodes and a spacer (Figure 5a), charge accumulation occurs at capacitive interfaces within nanoscopic micropores upon application of external current, according to the widely used Donnan based theory.31,35,68 As ions are removed from, or supplied to, micropores within a given electrode, salt concentration is modulated within larger scale pores, while transport of salt outside of the electrode region is driven by diffusion and migration.10,23,69 At high current density, as we will demonstrate with two-dimensional porous-electrode modeling, the spatial separation of electrode and flow-channel regions results in a lag of effluent salt concentration that reduces salt removal performance. Consequently, losses in charge efficiency during desalination can be attributed to a variety of effects (Figure 5b), including the following: (1) co-ion repulsion during electrosorption process, (2) leakage current due to parasitic side reactions, (3) desalination residue in the pore space.
of electrodes, (4) desalination residue in the flow channel, and (5) salt removal in the effluent.

1.4 Pulse-flow operation in capacitive deionization

Novel CDI flow architectures have been introduced using flow-through\textsuperscript{22,23} and fluidized-bed\textsuperscript{70,71} electrodes, but few studies have focused on understanding the role of flow conditions within flow-by CDI. In the context of electrochemical energy storage intermittent pulse-flow has been used to increase energy and coulombic efficiency in suspension-based flow batteries\textsuperscript{72-75} and flow capacitors,\textsuperscript{76} but the impact of similar flow modes has not been explored in CDI. Continuous flow is most commonly used in CDI studies, in which the influent solution is continuously pumped through the cell at a constant flow rate during cell cycling (as shown in Figure 6a).

Here, we compare the cycling of a flow-by CDI cell in pulse flow and continuous flow operation using a combination of porous electrode modeling and experimental demonstration. Computational models for the two operational schemes are developed, calibrated, and demonstrated with a self-designed CDI cell. We study cycling behavior under constant current operation, which recent work\textsuperscript{77} has demonstrated to be more energy efficient than constant voltage operation when energy recovery is included during the brine generation stage. Figure 6b shows a representative sequence of current and flow pulses applied during pulse-flow operation: (1) solution within electrodes remains stagnant until the average concentration in the flow channel reaches the fresh/brine concentration target, (2) a flow pulse is triggered to replace the solution in flow channel with a new batch of feed solution, and (3) this process is repeated until cell voltage
reaches a pre-specified cutoff voltage. By controlling flow rate based on effluent concentration, the charge stage aligns with the desalination stage during pulse flow operation. In comparison, when continuous flow rate is used with the same average flow rate, a lag is observed between charge and desalination stages. We show here that specific energy consumption levels in continuous flow similar to pulse flow can be achieved by synchronizing effluent sampling based on real-time measurements of salinity.

Figure 6. Schematic of (a) continuous-flow and (b) pulse-flow operation for a flow-by CDI cell. In the continuous-flow operation mode, the desalination stage lags behind the charge stage. In the pulse-flow mode the desalination stage and charge stage coincide.

1.5 Organization of the thesis
In this thesis, a combined modeling and experimental study is presented that explores the impact of fluid pulsation and operating conditions on charge and energy efficiency in a traditional CDI and MCDI systems. The structure of the thesis is organized as follows: 

In Chapter 2, the approach to construct a numerical model for a conventional CDI cell is described; Chapter 3 includes the experimental setup and methods that are used for model calibration and validation; Chapter 4 describes the results for model calibration and validation; In Chapter 5, we discuss how different charge efficiency loss mechanisms contribute to the salt removal performance in a flow-by CDI cell. In addition, we demonstrate how pulse-flow operation improves charge and energy efficiency compared to continuous-flow operation; In chapter 6, we apply the 1-D pulse-flow model on different flow architectures to further reduce energy consumption for salt removal. Chapter 7 contains the conclusion and limitation about this study. In Chapter 8, a new system design, double-sided MCDI stack, is proposed to achieve low energy consumption desalination with continuous production of fresh- and brine-water.
CHAPTER 2 Theory and Modelling

2.1 Electrosorption at the Solid-Liquid Interface

The electrosorption theory applied in CDI modeling dates back to '70s\textsuperscript{10} and has evolved rapidly since 2010.\textsuperscript{23,33,35,69,77-80} The first CDI model was developed by Johnson and Newman\textsuperscript{10} in 1971 based on the classic Helmholtz theory, which assumes that the charged electrode surface behaves like an ideal capacitor where all electric charges on the solid phase are compensated by a single layer of ions with the opposite charge (counter-ions) in the liquid phase. This theory was later adopted by Suss \textit{et al.}\textsuperscript{23} in 2012 in the study of flow-through CDI (i.e., the solution flows along the same direction of the applied current). Both studies assumed a constant capacitance value in the modeling and neglected the effect of co-ion repulsion, which plays an important role in applications of CDI. The concept of charge efficiency, defined as the ratio of equilibrium salt adsorption to accumulated electrical charges,\textsuperscript{37} was later introduced in CDI and MCDI modeling and first simulated with a simplified Guoy-Chapman-Stern (GCS),\textsuperscript{78,81} as shown in Figure 7a. However, obtaining an analytically solution for the classic GCS theory in CDI models is computationally intensive due to the non-linear electrosorption equations\textsuperscript{78}. In addition, the assumption of free extended EDLs in the classic GCS theory disagrees with the fact that the EDLs in micropores are strongly overlapped in nanoporous electrodes.\textsuperscript{4,35} These limitations were addressed in the modified Donnan (mD) theory\textsuperscript{30,82} (Figure 7b), which was later evolved to the improved-modified Donnan (i-mD) theory.\textsuperscript{35} In both theories, the pore-volume inside a carbon particle is treated as two distinct regions: a macropore region where the solution remains electroneutral and a micropore region where charge
separation occurs to drive the electrosorption process. Because the diffusive part of EDLs are strongly overlapped, the solution potential across the micropores is assumed constant, which also simplifies computational processing integrated macroscopic model. In addition, the mD and i-mD theories are also capable of simulating the salt adsorption of un-charged carbon through introducing a chemical attraction energy term ($\mu_{\text{att}}$) in the Boltzmann distribution equation. However, the mD and the i-mD models contain extra fitting parameters (e.g., microporosity, macroporosity, and $\mu_{\text{att}}$) that need to be determined empirically in order to achieve good model fitting. In 2015, the effect electrode surface charges were also modeled through a different Donnan based theory, which latter evolved to the amphoteric-Donnan (amph-D) model. The amph-D model is able to predict the impact of immobile charges in the micropores of electrodes on electrode PZC and the electrosorption process.
Figure 7. Schematic of change in potential governed by the classic GCS model (a) and modified-Donnan (mD) model (b) for electrosorption at the solid-liquid interface. $\phi_s$ represents the potential at the solid phase, $\phi_e$ represent the potential at the liquid phase outside the EDL, $\phi_{St}$ represents the potential at the Stern layer. In (b), the two parallel vertical dashed lines represent the location of Stern layers. Since the EDL are strongly overlapped inside the microspores, an uniform modified Donnan potential exists inside the micropores. The mD based electrosorption theories are commonly used in CDI modeling as it provides an easy physical and numerical description to the EDL overlapping effect of microporous carbon electrodes. The ideal charge efficiency predicted by the GCS model and mD model at different electrode polarization and bulk concentration are shown in (c) and (d), respectively.
2.2 Electrode Surface Charges

Electrode surface chemistry has a profound impact on CDI salt removal performance. As mentioned before, significant deterioration in salt removal capacity has been observed in CDI charging/discharging cycling tests. Specifically, for a conventional CDI cell with symmetric electrode, an “inversion peak” in the effluent concentration as a sign of salt desorption was commonly observed at the beginning of charging (desalinating) over multiple cycles. This unexpected repulsion of salts in the charging stage is mainly due to shift of the anode PZC because parasitic faradaic reactions on the anode (e.g., carbon corrosion) introduce negative immobile charges to the electrode surface. The correlation between electrode charge density and salt removal performance is further described in Figure 8, which shows the electrode salt adsorption, represented as averaged ionic concentration in the micropores $C_{mi}$, as a function of electrode potential with respect to its short-circuit potential. For a CDI cell made of symmetric pristine electrodes (Figure 8a), in the low cell voltage region, the charge storage process is mostly driven by ion-swaping, whereby counter-ions are adsorbed into the micropores while co-ions are simultaneously pushed out. The charge efficiency increases when the system is operated within the desalination cell voltage region. During operation, parasitic faradaic reactions on the anode associated with carbon or surface functional groups (e.g., carbonyl, phenol, lactone, quinone, etc) results in formation of negatively charged immobile groups that shifts the electrode PZC to the positive region. Therefore, desorption of salt is expected if the operating voltage window across the desorption region marked in Figure 8b. In addition, the electrode PZC and surface immobile charges can be engineered through amination (negative shift of PZC) or acidification (positive shift of
PZC, promoting CDI systems with asymmetric electrodes (i.e., inverted-CDI, enhanced CDI, and extended-voltage-CDI) that greatly enhance electrode stability and charge efficiency. Figure 8c shows an example of the impact of electrode surface modification on salt removal performance where the desorption and ion swap regions can be prevented by using aminated electrode as the anode and oxidized electrode as the cathode.

Figure 8. Schematic of electrode salt adsorption represented by the average ionic concentration in the electrode micropore as a function of electrode potential with respect to the short-circuit potential under three conditions: a) pristine carbon electrodes are used as both anode and cathode, b) the anode is oxidized due to carbon corrosion and results
in negatively charged immobile groups, and c) the anode is aminated and the cathode is oxidized. The PZC is defined as the potential at which the electrode has a minimum differential capacitance (where the slope of the micropore concentration curves in this figure is zero). The electrode PZC can be shifted by introducing surface immobile charges through parasitic reactions or surface modification.

2.3 Porous Electrode Modeling

The porous electrodes used in the present CDI study are composed of three distinct regions: a solid region made of carbon, an electroneutral solution residing in so-called macropores, and a charge-accumulating region at solution/solid interfaces (i.e., micropores). The mass and charge transport processes in CDI occur over different length scales: the length of the cell \( L \), the thickness of the electrode \( w_e \), the radius of a single activated particle \( d_c \), and the average radius of micropores \( \langle r_{mi} \rangle \). For a CDI electrode made of activated carbon powder, the four characteristic length scales range from centimeters to atomic, with the following condition typically satisfied: \( L \gg w_e \gg d_c \gg \langle r_{mi} \rangle \).

In the present porous electrode model, we incorporate microscopic electrosorption processes through an EDL model that includes the effects of salt concentration on the selective uptake of cations and anions. To define this model we first consider an activated carbon within the porous medium that is fully wetted with solution at rest. Solution in the macropores consists of positive and negative charged species that participate in the electrosorption process at the boundary of macropores and micropores. In the micropores, the electrosorption process (i.e., charge balancing through repulsion of co-ions or adsorption of counter-ions) takes place as a result of local electrical polarization \( \phi_s - \phi_e \),
where $\phi_s$ and $\phi_e$ are the solid potential and electrolyte potential, respectively. Here, we model the coupling between electrical polarization and stored charge with a Donnan-based theory where EDLs are highly overlapped.\textsuperscript{35}

We use Newman’s macro-homogeneous porous electrode theory\textsuperscript{10,78} to model electron and ion transport through the extent of the electrodes and the flow channel. Here, the contributions of ionic migration and diffusion to the flux of individual species are accounted for explicitly using the Nernst-Planck equations. Presently, we assume solution to be an electroneutral binary electrolyte, in which case the mass conservation equations for the two ionic species of interest ($\text{Na}^+$ and $\text{Cl}^-$) can be combined in such a way to produce an alternative but equivalent pair of governing equations: a potential-independent “salt conservation” equation and a current conservation equation.\textsuperscript{92} Similar equations have been used in modeling transport in other desalination cells.\textsuperscript{23,49,78,79} The salt conservation equation in the electrode of a typical CDI cell in the absence of advection is:\textsuperscript{10}

$$\frac{\partial \varepsilon_{ma} c}{\partial t} + \nabla \cdot (-D_{eff} \nabla c) = \dot{S},$$

where $\varepsilon_{ma}$ is the macroporosity that accounts for both macropore volume and voids among particles, $c$ is local salt concentration, $D_{eff}$ is the effective salt diffusivity that is calculated based on electrode porosity and bulk salt diffusivity $D_0$ as $D_{eff} = D_0 \varepsilon^{1.5}$,\textsuperscript{93} and $\dot{S}$ is a source/sink term that represents the rate of concentration changes due to the electroosorption process and mass transfer.

The amphoteric Donnan (amph-D) model\textsuperscript{33,36,86} is used to determine the volume averaged
source term, \( \hat{S}(\phi_s - \phi_e, c) = -\frac{\varepsilon_{mi}}{F} \frac{\partial c_{ions,mi}}{\partial t} \), accounting for the rate of salt adsorption, where \( \varepsilon_{mi} \) is the microporosity, \( F \) is the Faraday constant, and \( c_{ions,mi} \) is the ionic concentration in micropores. The charge balance equation in micropores with surface immobile charge density, \( \rho_{chem} \), is:

\[
\rho_e + \rho_{mi} + \rho_{chem} = 0,
\]

(2)

where \( \rho_e \) and \( \rho_{mi} \) represent the electronic and ionic charge densities, respectively. The electrode polarization in the amph-D model consists of a potential drop in the Stern layer \( \Delta \phi_S \) and a Donnan potential \( \Delta \phi_D \): \( \phi_s - \phi_e = \Delta \phi_S + \Delta \phi_D \). Assuming the Stern layer capacitance is constant, \( \Delta \phi_S \) and \( \Delta \phi_D \) can be represented as: \( \Delta \phi_S = \frac{F \rho_e}{\rho_{electrode} \varepsilon_S} \), and \( \Delta \phi_D = -\text{arcsinh} \left( \frac{\rho_{mi}}{2c} \right) \). The total ionic concentration in the micropores is given by:

\[
c_{ions,mi}^2 = \rho_{mi}^2 + (2c)^2,
\]

(3)

2.4 Current Conservation

Under the assumption of a symmetric electrolyte (ions with equal valence and equal diffusivity), current conservation can be expressed in terms of the electrostatic potential in solution \( \phi_e \) as:

\[
\nabla \cdot (-\kappa_{eff} \nabla \phi_e) = \varepsilon_{mi} \hat{Q} + i_L,
\]

(4)

where \( \hat{Q} = -\varepsilon_{mi} \frac{\partial \rho_{mi}}{\partial t} \), and \( \kappa_{eff} \) is the local effective ionic-conductivity that depends on porosity \( \varepsilon \) and the corresponding bulk value \( \kappa_0 \) as \( \kappa_{eff} = \kappa_0 e^{1.5} \). The Nernst-Einstein relation is applied here to determine the value of local bulk ionic-conductivity \( \kappa_0 = \frac{2D_0 c_F e}{kT} \).
Eq. 4 also includes leakage current per unit electrode volume $i_L$ due to parasitic faradaic reactions on the electrodes. Note that the above governing equations are valid in either of the two contexts: (1) when parasitic reactions produce negligible amounts of charged species or (2) reaction rates are slow enough that the local solution composition (e.g., pH) is not perturbed by reactions. Otherwise, an asymmetric multi-species transport model based on Nernst-Planck equations is required to obtain accurate prediction of species-concentration distributions.\textsuperscript{41}

Electronic conduction within solid materials (i.e., carbon network, current collector, and the external circuit) is assumed to follow Ohm’s law $\nabla \cdot \left(-\sigma_{s,eff} \nabla \phi_e\right) = -\varepsilon_{ml} \dot{Q} - i_L$. Note that in conventional CDI simulation, the potential drop due to the solid phase resistance in the electrode is often ignored because the electronic conductivity of the carbon network, $\sigma_{s,eff}$, is typically much greater than $\sigma_{e,eff}$.\textsuperscript{62,69}

2.5 Flow Channel

The salt conservation equation in the flow channel is governed by:

$$\varepsilon_{FC} \frac{\partial c}{\partial t} + \nabla \cdot (\overline{v_s} c) + \nabla \cdot (-D_{eff,FC} \nabla c) = 0, \quad (5)$$

where $\varepsilon_{FC}$ is the porosity of the flow channel spacer, $\overline{v_s}$ is the superficial velocity (assumed uniform), and $D_{eff,FC}$ is the effective salt diffusion coefficient in the flow channel. Since the direction of current is perpendicular to the direction of flow, a two-dimensional model is formulated for the continuous-flow operation scheme. In the model of pulse-flow operation, the effect of advection in Eqn. 5 can be neglected if we assume the event of pulsing happens instantaneously. This assumption simplifies the numerical
implementation for pulse-flow operation model and yields a one-dimensional problem because variation along the direction of flow does not occur.

2.6 **Boundary and initial conditions**

Boundary and initial conditions applied in the present model are described as follows. Ionic flux (excluding advective contributions) is set to zero at all surfaces except at the flow-channel inlet. When influent solution flows into the flow-channel we impose a constant concentration boundary condition at the flow-channel inlet. In the absence of flow (for the one-dimensional model of the pulse-flow operation) a null-flux condition is imposed at the flow-channel inlet. The total electronic current at the current collector surface of the positive/negative electrode is constrained to the total externally applied current, while the total ionic current is set to zero on these surfaces. In all simulations we initialize salt concentration across the entire cell to the chosen influent concentration, and charge density within the porous electrodes is initially set to zero. From these initial conditions initial cell voltage and ionic concentration inside micropores were calculated.

2.7 **Leakage current**

The voltage applied in CDI cycling is typically not high enough to induce reaction of water splitting. The faradic side reactions we account for in the present model are carbon corrosion and oxygen reduction on the positive and negative electrodes, respectively. The dynamics of carbon corrosion in aqueous environment have been previously described with numerical models. We use Butler-Volmer kinetics to model these faradaic side reactions. On the positive electrode carbon corrosion
occurs:53,95

\[ i_{L,+} = a^* i_{0,C} \theta e^{\left(\frac{\alpha_{i,c} F}{RT}(\phi_s - \phi_e - \theta_U^C)\right)} \]  \hspace{1cm} (6)

\[ \theta = \frac{e^{\left(\frac{F}{RT}(\phi_1 - \phi_2 - \theta_U)\right)}}{1 + e^{\left(\frac{F}{RT}(\phi_1 - \phi_2 - \theta_U)\right)}} \]  \hspace{1cm} (7)

On the negative electrode, oxygen reduction occurs:53,54,94,95

\[ i_{L,-} = -a^* i_{0,O_2} \left\{ \frac{\alpha_{O_2,a} F}{RT}(\phi_s - \phi_e - \theta_U^{O_2}) - \left(\frac{p_{O_2}}{p_{O_2}^*}\right)^{\beta_{O_2}} e^{-\frac{\alpha_{O_2,a} F}{RT}(\phi_s - \phi_e - \theta_U^{O_2})} \right\} \] ,  \hspace{1cm} (8)

where \( \phi_s - \phi_e \) is the local electrode polarization, \( i_{0,i} \) is the exchange current density in A/m\(^2\) active surface area, \( a^* \) is the active surface area per unit volume of electrode, \( \alpha_{i,a} \) and \( \alpha_{i,c} \) are the transfer coefficients for the anodic and cathodic reactions, \( U_i^\theta \) is the standard potential of carbon corrosion (positive electrode) and oxygen reduction (negative electrode), \( p_{O_2} \) is the partial pressure of \( O_2 \), \( p_{O_2}^* \) is the reference partial pressure of \( O_2 \), and \( \beta_{O_2} \) is the concentration factor of \( O_2 \). Here the empirical term53,95, \( \theta \), is adopted to improve model fitting at low voltage polarization region (as discussed in Secs. 4.1 and Figure 10). Leakage current sub-models were calibrated with experimental data. The reaction of carbon corrosion is considered irreversible and thus only the anodic reaction is used in the expression.53,95

2.8 Ion exchange membrane

To model an ideal MCDI cell, we treat the IEMs as ideally permselective boundaries with zero thickness. Therefore, the following boundary conditions are formulated to address
the salt transport and electrolyte potential at the inner (superscript in) and outer (superscript out) surfaces of the membrane:

$$\nabla \cdot (-D_{eff} \nabla c) = \frac{1}{2F} j , \quad (9)$$

$$\phi_{in} - \phi_{out} = \frac{RT}{2F} \ln \frac{c_{in}}{c_{out}} , \quad (10)$$

where $j$ is the total current density.

2.9 Model implementation

The modeling equations listed above lead to a coupled non-linear system that cannot be solved analytically. Numerical solutions were obtained by discretizing over the space and time domain using the finite-volume method. The Crank-Nicolson method with a second-order central difference scheme was applied to diffusion flux and current terms, while an implicit method was used to integrate source terms. Electrode charge density variation with time was modelled using trapezoidal integration of local capacitive current. An algorithm was developed to solve the non-linear behavior wherein the self-consistent solution in the forward time step can be obtained with nested iteration loops. The concentration field was resolved in the inner loop, and the charge density and current distribution were solved in the outer loop. The numerical model was implemented in Matlab (The MathWorks, Inc.). The tolerance for a converged solution at a given time step was set at $10^{-7}$ mM and $10^{-6}$ C/cm$^3$ for the iteration loops of concentration and charge density, respectively.

The Matlab code for a demonstration of the two-dimensional CDI model is in Appendix A. An free CDI modeling tool using this code can be also accessed on NanoHub (as shown
In this chapter, the theory and assumptions for continuous- and pulse-flow CDI modeling are described. The values of modeling parameters are determined in the next two chapters.
CHAPTER 3 Experimental Setup and Methods

3.1 Flow Cell Design and Setup

The model described in Chapter 2 was implemented and validated based on a self-designed and built CDI cell that consists of two identical electrodes separated by a flow channel spacer with thickness of 250 µm. The electrode chamber on the graphite plate, as current collector (depth of 450 µm) was formed by surface etching with a 3D scanning and milling machine (Roland Modela MDX-20). A well-mixed carbon slurry, containing 90 dry-wt% activated carbon (AC) powder (Sigma-Aldrich) and 10 dry-wt% polyvinylidene fluoride (Sigma-Aldrich) in N-methyl-2-pyrrolidone (Alfa Aesar), was directly injected into the electrode chamber and stationed under vacuum at room temperature for 20 minutes to homogeneously fill the chamber and remove air bubbles. Then the graphite plate was placed on a hot plate at 70 °C for 30 mins within a chemical fume hood to evaporate the excess solvent, followed by immersion in deionized water for 24 hours to solidify the binder. The flow channel was cut out from a silicone gasket (SS-0.016-67909, AAA-Acme Rubber CO.), which was compressed by ca. 40% (estimated with a caliper) after assembling. A laser engraver (Epilog Legend Mini 24 Laser) was used to cut the gaskets and acrylic plates that sealed and held the cell together. A multi-channel potentiostat galvanostat (VMP3, Biologic) was used to provide and record electric signals in all flow cell testing.

3.2 Cell Cycling Procedure

In all experiments electrodes were freshly prepared at the beginning of each experiment
with an electrode mass of 21 ± 1 mg/cm² (sample-to-sample mass varied largely due to the repeatability of the electrode casting procedure used). The same electrodes were used for the set of validation tests at four different current densities, while the results in Figs. 14 and 15 were obtained with a different set of electrodes. In order to characterize cycling response for a limiting charge/discharge cycle, the cell was cycled under constant current for more than 30 cycles before limit-cycle data was collected. To further characterize electrode degradation capacitance was measured before and after experiments, where it was found that capacitance decreased by less than 10%.

All flow cell cycling experiments were performed at constant current with an influent NaCl solution at 30 mM. Initially, the flow cell with uncharged electrodes was set to an open circuit condition (OCC), while being simultaneously rinsed with influent solution overnight to reach equilibrium. By applying a constant current density, the charge stage commenced until cell voltage reached its terminal value (1.2 V), after which the direction of current was reversed to induce discharge of the cell. The next charge cycle with the same settings of current density and voltage limit began after V_{cell} decreased to 0 V. In all cases charge/discharge cycles were performed until a limit cycle was reached in which an asymptotic response was observed, such that the difference between the voltage profiles of two consecutive charging cycles was negligible.

In continuous-flow operation, the flow rate, determined based on the average flow rate in the pulse-flow operation under the same testing condition, was maintained constant throughout the cycling experiment. A syringe pump (PHD 2000, Harvard Apparatus) was used in order to reduce fluctuations in flow rate. The conductivity in the effluent was continuously measured and recorded using a flow-through conductivity sensor that has
an internal volume of 93 µL (ET908, EDAQ).

During pulse-flow cycling operation, a programmable peristaltic pump (Masterflex) was used to advance solution through the flow channel. Here, a fixed volume of influent solution was pumped at a high flow rate ($Q_{pulse}$) of 0.7375 mL/s for 1.2 s. To implement the pulse-flow strategy and the cycling tests in a synchronized way, one channel of the potentiostat was used to provide analog signals for pump control. In order to minimize the effect of dispersion and mixing in the dead volume of the system (e.g., volume of adaptors and tube fittings), the volume dispensed in a pulse ($V_{pulse}$) was about twice the volume of the open space in the flow channel ($V_{FC}$). When the system reached a limit cycle, a small vial was used to collect effluent of every one or two pulses for further analysis, depending on whether it was the last pulse in the charge/discharge stage. The conductivity of the effluent samples was measured immediately after the cycling test with a dip-in micro-conductivity probe (InLab 751, Mettler Toledo). The total salt removal/generation was determined based on the total volume of dispensed solution and the difference in salinity between the influent and effluent water samples.
Leakage Current Test

The leakage current due to parasitic reactions was characterized using a setup similar to that of desalination cycling tests (Figure 9). In these experiments, testing solution was continuously pumped through the CDI flow cell and the cell voltage was incrementally increased by 0.1 V from 0 – 1.2 V for a duration of 2 hours every step to ensure completion of the electrosorption process. The current toward the end of every voltage step was recorded as the leakage current, as shown in Figure 10. Meanwhile, the potential of both electrodes was measured with Ag/AgCl reference electrodes placed next to the corresponding graphite plate via a salt bridge filled with the same testing solution. The
solution in the feed tank was sparged with filtered air or nitrogen gas to evaluate the impact of dissolved oxygen on parasitic faradaic reactions of activated carbon electrodes in aqueous environment. In addition, another comparison experiment was performed after covering the positive and negative electrode with an anion exchange membrane (FUJIFILM) and a cation exchange membrane (FUJIFILM), respectively. Such a cell arrangement, commonly referred to as MCDI, was used to confirm that transport of dissolved oxygen from the flow channel to the electrode, which was blocked under the presence of ion exchange membranes, played an important role in the faradic reaction process (Figure 11).

Figure 10. Experimental results of leakage current sampled at 2 hours after voltage is applied and fitted model for the positive electrode. The solid lines represent the model fitting by the classic Butler–Volmer equation, and the dashed lines show that better fitting can be obtained with additional empirical term $\theta$.\textsuperscript{53,95} (See Eqn. 6)
Figure 11. Leakage current as a function of cell voltage for (a) flow by CDI cell and (b) flow by MCDI cell. The feed solution is sparged with oxygen and nitrogen gas continuously during the tests. Influent solution is 30 mM NaCl. The result confirms that aqueous oxygen plays an important role in side reactions in CDI. Covering the electrodes with ion-exchange membranes prevents the direct contact between the electrodes and the solution in the flow channel. As a result, the leakage current in the flow-by MCDI cell, in both N₂ and O₂ sparging conditions, drops to the similar level as the flow-by CDI cell under N₂ sparging.

In this chapter, we show the experimental approaches to obtain the data for model calibration and validation. These data are analyzed to obtain fitting parameters for the model in the next chapter.
CHAPTER 4 CDI Model Calibration and Validation

We calibrated and validated the present porous electrode model using independent experiments (as shown in Chapter 3). The present model contains many parameters (see Table 1), the majority of which were determined from independent experiments or were assumed based on prior literature. Four of these parameters were calibrated to obtain fits between simulated and experimental cycling data (Figure 12): Stern-layer capacitance ($C_s$), immobile surface charge density on the positive electrode ($\rho_{chem}$), exchange current density for oxygen reduction ($i_{0,0_2}$), and effective surface area for faradic reactions ($a^*$). With these fitted parameters independent experiments at other operating conditions were used to validate the model in pulse-flow operation and continuous-flow operation (Figure 13, 14).

4.1 Calibration of Stern-Layer, Immobile Charge, and Kinetic Parameters

Calibration was performed by sequentially adjusting individual model parameters. First, $a^*$ was determined by fitting Eq. 6 to the experimental results from the leakage current test for the positive electrode using the linear least squares method (as shown in Figure 12a). Note that if the adsorption term $\theta$ in Eq. 6 is omitted a classical Butler-Volmer equation results, and the fitted model would deviate from the experimental observation slightly as it over estimated the leakage current at low voltage region (Figure 10). By assuming that the value of $a^*$ in the positive and negative electrodes is the same (since both electrodes were fabricated with the recipe), we can obtain the value of $i_{0,0_2}$ by fitting Eq. 8 to the leakage current testing result for the negative electrode (Figure 12b).
Figure 12. Model calibration. Experimental results in the leakage current tests and model fitting of leakage current density as a function of electrode voltage for the (a) positive and (b) negative electrodes. Experimental results from a limit cycle in the pulse-flow CDI operation at 6 A/cm$^2$ and model fitting for (c) cumulative salt removal and (d) cumulative energy in the charge stage.

After incorporating $\alpha^*$ and $i_{0,o_2}$ into the model, cell cycling experiments and simulations were performed at 6 A/cm$^2$ in the pulse-flow operation with a fixed batch time of 40 s (38.8 s of pump off and 1.2 s of pump on). As the effluent salinity was not continuous in time during pulse-flow operation, we define two desalination metrics for pulse-flow operation based on the number of pulses in a limit cycle. The cumulative salt removal is defined as the sum of salt removed/generated through pulsing since the first pulse in the charge
stage as:

\[ \Sigma(I) = \Sigma_i^N I_i \]  \hspace{1cm} (11)

where \( I_i \) represents the moles of salt removed in pulse number \( i \), which is calculated based on the difference between influent concentration \( (c_0) \) and concentration of the effluent collected from that pulse \( (c_{out,i}) \): \( I_i = (c_0 - c_{out,i})V_{pulse} \). \( N \) is the number of flow pulses used.

The cumulative energy input is calculated based on the cell voltage in the charge stage of a limit cycle:

\[ \Sigma(E) = \int_{t_0}^{t_i} V_{cell}(t) \, I \, dt \]  \hspace{1cm} (12)

where \( t_0 \) and \( t_i \) represents the time at the start of charge stage and the time at the end of pulse number \( i \), respectively.

Even though the electrodes were freshly prepared prior to experiments, the stability of electrodes changed during cell cycling, which has been commonly observed in conventional flow-by CDI system.\textsuperscript{32,38,43,58,99} This electrode degradation effect, resulting in gradual decrease in salt adsorption capacity, is mainly due to shift of the PZC of positive electrode as parasitic reactions (such as carbon corrosion) introduce changes in the immobile charges \( (\rho_{chem}) \) to the electrode surface. Previous work reported an increase of the equilibrium potential of the positive electrode by ca. 500 mV, while the PZC of the negative electrode remained almost the same after 50 charge/discharge cycles in a flow-by CDI cell.\textsuperscript{63} Therefore, in the present model, we assume that changes in \( \rho_{chem} \) only
occur on the positive electrode due to parasitic reaction of carbon corrosion. Furthermore, we set the value of $\rho_{chem}$ for both the acidic and alkaline groups of the pristine electrode to zero in order to reduce the total number of fitting parameters. Note that this assumption yields the same equations of a Donnan based theory used in Ref. 86, which is also an extreme case in the amph-D theory\textsuperscript{33,36} in which the chemical charge density of the positive and negative regions of un-treated electrodes are 0 C/cm$^3$.

Figures 12c,d show the experimental results obtained in the charge stage of a limit cycle for pulse-flow operation in order to extract the values of $C_S$ and $\rho_{chem}$. Since the effect of these two parameters is coupled within the model, we first set $\rho_{chem}$ to 0 C/cm$^3$ and tuned the value of $C_S$ in model predictions until a good fit was obtained (Figure 12c), wherein the sum of squared differences in $\Sigma(E)$ between model prediction and experimental measurement was minimized. Next, we fixed the value of $C_S$ and tested the sensitivity of $\rho_{chem}$ from 0 C/cm$^3$ to 10 C/cm$^3$ to determine the optimum value of $\rho_{chem}$ based on the profile of $\Sigma(I')$ (Figure 12d and Figure 13a). These two steps were iterated upon to produce adequate model fitting, as adjustments of $\rho_{chem}$ affect $\Sigma(E)$ on a relatively small scale (see Figure 13b). In summary, the values of all the fitting parameters were determined as follows: $C_S = 49$ F/g, $\rho_{chem} = 4$ C/cm$^3$-electrode, $i_{0,0.2} = 5.5 \times 10^{-6}$ A/m$^2$, and $a^* = 1.1$ m$^2$/cm$^3$-electrode. All simulation results presented in following sections are based on these four values. We note that the fitted value of $i_{0,0.2}$ may be biased by the value for $i_{0,c}$ assumed from the literature.
Figure 13. Simulation results of changes of surface charge density (in C/cm$^3$) of the positive electrode on (a) cumulative salt removal and (b) cumulative energy input during the charge stage in pulse-flow operation. Experimental observations are also shown as open circles to determine the value of fitting parameter $\rho_{chem}$.

4.2 Validation of Pulse-Flow Operation

Salt removal and energy consumption for the present CDI device were found to vary with applied current density. Here tests in pulse-flow operation were conducted with current densities of 3 A/m$^2$, 6 A/m$^2$, 12 A/m$^2$, and 20 A/m$^2$ and constant batch times of 80s, 40s, 20s, and 12s, respectively. As shown in Figure 14, both $\Sigma(\Gamma)$ and $\Sigma(E)$ decreased significantly at high current densities. The model predictions aligned well with the evolution of $\Sigma(\Gamma)$ and $\Sigma(E)$ measured in experiment for the charge stage of a limit cycle.
Figure 14. Model validation for pulse-flow operation. Cumulative salt removal (top row) and energy input (bottom row) for a number of pulses during the charge stage of pulse-flow operation at current densities from 3 A/m² to 20 A/m². The testing case at 6 A/m² was used as model calibration.

4.3 Validation of Continuous-Flow Operation

The continuous-flow operation model was validated under the same current densities as that in pulse-flow operation, in which the total number of pulses occurred in the charge stage was used to determine the equivalent flow rate applied in the continuous-flow operation test at the same current density. Model prediction and experimental data for effluent concentration and cell voltage are shown in Figure 15. Compared to the cumulative metrics applied in pulse-flow operation, effluent concentration and cell voltage are used here because: (1) they preserve the most representative information of the system as they were obtained directly in the experiment without further processing, and (2) small discrepancy between the model and experimental results are easily
The continuous-flow operation model accurately predicted the cell voltage (bottom row in Figure 15) and captured the trend of effluent concentration (top row in Figure 15). However, a discrepancy between model prediction (plotted in solid red lines) and experimental data (plotted in solid black lines) is evident in the profiles of effluent concentration. We attribute this discrepancy mainly to the effect of mixing within the dead-volume (0.46 mL) between the end of desalination flow channel (0.34 mL) and the conductivity sensor in the experimental setup (see Figure 16). To corroborate this idea, we also modeled the dead-volume as a simple well-mixed reactor taking the effluent from the flow channel as influent to the tank, the details of which are described in Figure 16. The results after considering this effect of mixing are plotted in dashed red lines in Figure 15. Agreement between model and experiment improved when accounting for this effect, but the effect of mixing is hereafter omitted from subsequent results because: (1) the dead-volume should be minimized in a better designed cell, and (2) neglecting mixing enables direct comparison between the continuous- and pulse-flow operation modeling results.
Figure 15. Model validation for continuous-flow operation at different current densities. Top row: effluent concentration as a function of time in a limit cycle. The red dashed lines are the simulated effluent concentration after accounting for the effect of mixing in the dead volume (e.g., adaptor and tube fitting) between the conductivity sensor. Bottom row: experimental and simulated results of cell voltage as a function of time in a limit cycle.
Figure 16. (a) Schematic of the modeling component of a flow-by CDI cell. The dead-volume before and after the desalination flow channel are modelled as well-mixed tanks. The volume in the mixing tanks is estimated in the following approach. After assembling the CDI flow cell system, we rinsed the cell with 30 mM NaCl solution for two hours to fully saturate the pores in the electrodes. Then we disconnected the flow cell and emptied the flow channel and dead-volume at the inlet/outlet port with air using a syringe (2.5 mL). After that, we injected solution slowly to fill the cell again. This process was repeated for three times. And the total volume (\(V_{\text{total}} = V_{\text{dead}} + V_{\text{FC}} + V_{\text{dead}}\)) was determined based on the average volume used to fill the cell during solution injection. Since the flow cell was symmetrically designed, the volume in the inlet/outlet mixing tank can be obtained by subtracting the flow channel volume from the total volume. (b) Schematic of the modeling of the dead-volume at the outlet port. Assuming the dead-volume is a well-mixed tank, the change in concentration in the tank is \(\frac{dc_{\text{out}}}{dt} = \frac{Q(c_{\text{in}} - c_{\text{out}})}{V_{\text{dead}}}\), where \(c_{\text{in}}\) is the effluent concentration from the CDI model, \(c_{\text{out}}\) is the new effluent concentration accounting for the effect of mixing, \(Q\) is the flow rate.
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<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell design and testing parameter</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>298.16</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Electrode density</td>
<td>$\rho_{\text{electrode}}$</td>
<td>0.4664</td>
<td>g/cm³</td>
<td></td>
</tr>
<tr>
<td>Transference number of cations</td>
<td>$t_+$</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity of spacer</td>
<td>$\varepsilon_{\text{FC}}$</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Projected surface area</td>
<td>$W_{\text{ele}}$</td>
<td>18</td>
<td>cm²</td>
<td></td>
</tr>
<tr>
<td>Thickness of the positive electrode</td>
<td>$W_{\text{pos}}$</td>
<td>450</td>
<td>µm</td>
<td></td>
</tr>
<tr>
<td>Thickness of the negative electrode</td>
<td>$W_{\text{neg}}$</td>
<td>450</td>
<td>µm</td>
<td></td>
</tr>
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<td>Thickness of flow channel</td>
<td>$W_{\text{fc}}$</td>
<td>250</td>
<td>µm</td>
<td></td>
</tr>
<tr>
<td>Resistance of current collector, contact resistance, wires, and power supply</td>
<td></td>
<td>0.5</td>
<td>Ω</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient of NaCl in dilute environment</td>
<td>$D_0$</td>
<td>1.61x10⁻⁵</td>
<td>cm²/s</td>
<td></td>
</tr>
<tr>
<td>Carbon matrix resistance</td>
<td>$\sigma_{\text{eff}}$</td>
<td>7.57</td>
<td>S/m</td>
<td></td>
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<tr>
<td><strong>Electrosorption model parameters</strong></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Stern layer capacitance</td>
<td>$C_S$</td>
<td>49</td>
<td>F/g</td>
<td>*</td>
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<tr>
<td>Macro-porosity of electrode</td>
<td>$\varepsilon_{\text{macro}}$</td>
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<td></td>
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<tr>
<td>Micro-porosity of electrode</td>
<td>$\varepsilon_{\text{micro}}$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Charge density on positive electrode</td>
<td>$\rho_{\text{chem}}$</td>
<td>4</td>
<td>C/cm³</td>
<td></td>
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<tr>
<td><strong>Faradaic reaction parameters</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen reduction exchange current</td>
<td>$i_{0,O_2}$</td>
<td>5.5x10⁻⁶</td>
<td>A/m²</td>
<td>*</td>
</tr>
<tr>
<td>Henry's constant of oxygen</td>
<td>$H_{O_2}$</td>
<td>0.032</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen reduction potential at pH 7</td>
<td>$U_{O_2}^\theta$</td>
<td>0.81</td>
<td>V vs. SHE</td>
<td></td>
</tr>
<tr>
<td>Symmetry factor for oxygen reaction</td>
<td>$\alpha_{O_2}$</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon oxidation exchange current</td>
<td>$i_{0,C}$</td>
<td>2.5x10⁻¹⁰</td>
<td>A/cm²</td>
<td>32,68</td>
</tr>
<tr>
<td>Carbon oxidation standard potential</td>
<td>$U_{C}^\theta$</td>
<td>0.207</td>
<td>V vs. SHE</td>
<td>32,68</td>
</tr>
<tr>
<td>Symmetry factor for carbon reaction</td>
<td>$\alpha_{C}$</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Active surface area for faradaic reaction</td>
<td>$\alpha^*$</td>
<td>1.1</td>
<td>m²/cm³</td>
<td>*</td>
</tr>
<tr>
<td>Langmuir adsorption potential</td>
<td>$U_B$</td>
<td>1</td>
<td>V vs. SHE</td>
<td>32,68</td>
</tr>
</tbody>
</table>

* Fitting parameters
CHAPTER 5 Comparison Between Pulse- and Continuous-Flow Operation

In the previous chapter, we have determined the parameters for the model. We now analyze the desalination performance of pulse- and continuous-flow modes using the calibrated and validated porous electrode model, after which we compare performance for these modes from experimental data. The overall system performance was evaluated by calculating the salt specific energy consumption for three conditions: (1) pulse-flow operation, (2) continuous-flow operation, and (3) continuous-flow operation accounting for the temporal displacement between the desalination stage and charge stage. Subsequently, we quantify the contributions of different sources of loss to charge efficiency. The spatiotemporal variation of concentration, charge density, and voltage are presented to identify charge-efficiency loss mechanisms. Finally, we report experimental data for a self-designed CDI cell and demonstrate that pulse-flow operation is a promising alternative to continuous-flow operation in CDI cycling.

5.1 Specific Energy Consumption of Salt Removal

The specific energy consumption \( SEC \) of salt removal was chosen to evaluate the overall desalination performance for a limit cycle of a CDI cell. \( SEC \) for the three testing conditions was calculated as:

\[
SEC_{pf} = \frac{\Sigma(E)}{M_{NaCl} \Sigma(r)} \quad \text{for pulse-flow operation,} \quad (13)
\]
\[ SEC_c = \frac{\int_{t_{SD}}^{t_{SC}} V_{cell} dt}{M_{NaCl} I_{t_{SD}} (C_0 - C_{eff}) Q dt} \] for continuous-flow operation, and \[ SEC_{c,displace} = \frac{\int_{t_{SC}}^{t_{t_{SD}}} V_{cell} dt}{M_{NaCl} I_{t_{0}} (C_0 - C_{eff}) Q dt} \] for continuous-flow operation with displacement. (14)

Here \( \Sigma(E) \) and \( \Sigma(I) \) represent the cumulative energy and salt removal in the pulse-flow operation, respectively. \( M_{NaCl} \) is the molecular weight of sodium chloride. \( V_{cell} \) is the cell voltage. \( Q \) is the flow rate in the continuous-flow operation. \( t_{SC}/t_{SD} \) represents the starting time for the charge/discharge stage. \( t_0/t_1 \) represents the time at the start/end of desalination stage (see Figure 6a).

The \( SEC \) of the two operating schemes was measured with a range of current densities from 2.2 A/m\(^2\) to 20 A/m\(^2\), as shown in Figure 17. Assuming 100% charge efficiency these current densities correspond to salt removal rates between 0.023 mmol/m\(^2\)-s and 0.21 mmol/m\(^2\)-s. The pulse-flow and continuous operation behave similarly at low current density region (i.e., less than 6 A/m\(^2\)) but the two curves deviate significantly with increasing current density. For example, by increasing the current density from 6 A/m\(^2\) to 18 A/m\(^2\), a six-fold increase in \( SEC \) was observed in the continuous-flow operation while the \( SEC \) of the pulse-flow operation only increased by 50%. Note that the production rate (i.e., total volume of solution treated in the charge stage) of the two operation modes was almost the same in the simulation (see Section 3.2).

The effect of displacement between the desalination stage and the charge stage in continuous-flow operation plays an important role in calculating the total salt removal within a limit cycle for constant current operation. After considering this effect, the \( SEC \) of
continuous-flow operation dropped substantially, especially at high current densities (i.e., greater than 10 A/m²). We also observed that the SEC of the pulse-flow operation is located very close to the SEC of continuous-flow operation after accounting for the effect of displacement. This effect indicates that the pulse-flow 1-D model can be used to predict the system performance during continuous-flow operation.

Figure 17. Simulation results of specific energy consumption of salt removal for pulse-flow operation and continuous-flow operation at current densities of 2.2 - 20 A/m² and with C₀ = 30 mM and C_eff = 20 mM.

In addition to SEC we calculated the average effluent salinity and salt removal rate for current densities towards the low and high ends of the tested range (Table 2). At 6 A/m², pulse- and continuous flow perform similarly in terms of effluent salinity, salt removal capacity, water production rate, and salt removal rate. At 16 A/m² average effluent salinity in continuous-flow increases to 26.3 mM, resulting in low salt removal (3.94 mmoles/cm²), high SEC (9.61 kJ/g-NaCl), and low salt removal rate (0.019 mmol/m²-s) in comparison with pulse-flow and continuous-flow with displacement.

5.2 Charge Efficiency Loss Mechanisms
Here we analyze the sources of loss in charge efficiency for the two operation schemes of interest. The total electrical charge (including both positive and negative charges), $Q_T$, applied to a given electrode during the charge stage is:

$$Q_T = 2I(t_{SD} - t_{SC}).$$  \hspace{1cm} (16)

Utilization of applied charge for salt removal in a CDI system can be characterized into five distinct pathways denoted as follows: co-ion repulsion during electrosorption process (co-ion), leakage current due to parasitic faradaic reactions (leakage), observed salt removal in the effluent (salt), desalination residue in the flow channel (FC-res), and desalination residue in the macropores of electrodes (ele-res). Note that, for a CDI system operated under constant voltage, the contributions from the latter two mechanisms can be negligible if the cell reaches a uniform equilibrium concentration of $C_0$ towards the end of charge/discharge stage. The charge efficiency of each process ($\Lambda_i$) can be calculated as the ratio of total changes in electronic or ionic charge associated with that process to $Q_T$:

$$\Lambda_{salt} = \frac{2F \int_{t_{SC}}^{t_{SD}} (C_0 - C_{eff}) dt}{Q_T}$$

for salt removal, \hspace{1cm} (17)

$$\Lambda_{co-ion} = \frac{(\sum |Q_{mi,t_{SD}}| - \sum W_{mi,t_{SD}}) - (\sum |Q_{mi,t_{SC}}| - \sum W_{mi,t_{SC}})}{Q_T}$$

for co-ion repulsion, \hspace{1cm} (18)

$$\Lambda_{leakage} = \frac{\int_{t_{SC}}^{t_{SD}} (\oint i_L dV_{electrode}) dt}{Q_T}$$

for leakage current, \hspace{1cm} (19)

$$\Lambda_{FC-res} = \frac{(\oint c_{SC} dV_{FC} - \oint c_{SD} dV_{FC}) 2F}{Q_T}$$

for flow-channel residue, and \hspace{1cm} (20)
\[ \Lambda_{\text{ele-res}} = \frac{\left( \int c_{\text{SC}} dV_{\text{electrode}} - \int c_{\text{SP}} dV_{\text{electrode}} \right)^2 F \varepsilon_{\text{macro}}}{Q_T} \] for flow-channel residue, (21)

where \( \sum Q_{mi,t_i} \) and \( \sum W_{mi,t_i} \) represent the total number of charges and ions in the micropores of electrode at time instant \( t_i \) as \( \sum Q_{mi,t_i} = \varepsilon_{\text{micro}} \times \int \rho_{mi,t_i} dV_{\text{electrode}} \), and \( \sum W_{mi,t_i} = \varepsilon_{\text{micro}} \times \int c_{\text{ions,mi,t_i}} dV_{\text{electrode}} \). Note that, from the standpoint of charge conservation at the cell level, the component-wise calculation of charge efficiency also serves as a metric to quantify the computational error (\( \varepsilon \)) in the simulation, represented as \( \varepsilon = 1 - \sum \Lambda_i \). Here, we find \( \varepsilon \) to be less than 0.1% in all cases.

Figure 18. Simulation results for the contributions to charge efficiency for pulse-flow operation and continuous-flow operation in the charge stage of a limit cycle at current densities between 2.2 – 20 A/m² and with \( C_0 = 30 \) mM. The charge efficiency and theoretical charge efficiency are outlined using solid and dashed lines, respectively.

The simulation results of individual charge efficiency as a function of current density for the continuous- and pulse-flow operation modes are summarized in Figure 18. Similar
monotonic changes in co-ion repulsion and leakage current are observed for both operation schemes: leakage current consumed the largest percentage of total charge (44.8% in continuous-flow operation and 43.4% in pulse-flow operation) at the lower end of tested current density (2.2 A/m²), and the effect of co-ion repulsion dominated the usage of total charge (45.0% in continuous operation and 42.8% in pulse-flow operation) at the higher end of tested current density (20 A/m²). This trend agrees with previous studies on energy breakdown of a CDI cell operated under constant current mode.62

Theoretical charge efficiency indicates the total capacity of salt removal that a given CDI system could achieve without changing the electrode composition, cell architecture, and operation scheme. In the present models, it was calculated as the sum of $\Lambda_{\text{salt}}$, $\Lambda_{\text{FC-res}}$, and $\Lambda_{\text{ele-res}}$. The charge efficiency due to salt removal in the effluent $\Lambda_{\text{salt}}$ is highlighted in the figure using a black solid line. Both operation schemes showed similar theoretical charge efficiency, which gradually increases with current density and exhibits a plateau of 52% in the continuous-flow operation and 55% in the pulse-flow operation. The charge efficiency first increased with current density to a maximum value at around 6 A/m² and then decreased. In pulse-flow operation, the charge efficiency dropped to 25% at 20 A/m², however the charge efficiency of the continuous-flow operation at such current density decreased to a minimum of 7%.

To compare the sources of loss in charge efficiency, the difference of individual charge efficiency loss between the pulse-flow operation and continuous-flow operation are plotted in Figure 19. It appears that, in the high current density region (e.g., greater than 8 A/m²), the desalination residue in the flow channel and electrode are the two leading mechanisms, followed by the effect of co-ion repulsion, that favor the salt removal
performance in pulse-flow operation compared to the continuous-flow operation. For example, contributions from $\Lambda_{FC}$ and $\Lambda_{ele}$ consumed additional 10.2% and 7.3% of the total applied charge in continuous-flow operation compared to the pulse-flow operation at a current density of 18 A/m$^2$. This finding indicates that minimizing the volume of free space (i.e., flow channel and void-space of electrodes) can lead to more efficient desalination of CDI.

![Figure 19](image)

Figure 19. Difference in charge efficiency loss between pulse-flow operation and continuous flow operation for the four loss mechanisms to charge efficiency: desalination residue in flow channel, desalination residue in electrode, leakage current, and co-ion repulsion.

5.3 Spatial Distribution of Salinity and Charge Density

In the previous sections, we have compared the desalination performance between the pulse- and continuous-flow operation modes based on cumulative metrics including $SEC$ and current efficiency. The two-dimensional distribution of salinity and charge density are discussed in this section to show the direct impact of different charge utilization mechanisms on salt removal.
The positive and negative electrodes in the present model are symmetrically arranged. However, they perform asymmetrically due to different settings on immobile surface charge density and faradaic reactions (see Eqn. 6-8 and Section 4.1). Here we selected three points inside the cell, indicated using blue (located at $x = 0.9L, y = 1.5w_e + w_{fc}$), red (located at $x = 0.9L, y = w_e + 0.5w_{fc}$), and green (located at $x = 0.9L, y = 0.5w_e$) circles on the color maps in Figures 20 and 21 to show the evolution of $c$, the ratio of leakage current to capacitive current ($i_L/i_C$), and $\rho_{mi}$ at 3 A/m$^2$ (Figures 20 a-c) and 18 A/m$^2$ (Figures 21 a-c). Note that the blue and green points, located in the positive and negative electrode respectively, are symmetric with respect to the red point, which resides on the center line of the flow channel. The spatial distribution of local concentration at time instants T1 (start of charge stage) and T2 (start of discharge stage) are shown in two-dimensional contour plots.

At low current density, no distinct differences are observed between the evolutions of local concentration among the two cases (Figure 20a(i)), indicating a small degree of concentration polarization. The local concentration during continuous-flow operation reached a minimum in the charge stage at a time when the development of cell voltage also deviated from the original trajectory (Figure 20a(iv)). This effect occurs because leakage current consumes more current than the capacitive current when operating at low current density and as cell voltage increases (Figure 20a(ii)). This effect also leads to sluggish electrosorption as the development of micropore charge density slows down (Figure 20a(iii)). Similar trends of leakage current, charge density, and cell voltage are observed during pulse-flow operation (Figure 20b(ii-iv)). Despite these similarities, local concentration variations are less extreme for pulse-flow (ca. 20 mM - 40 mM, see Figure
20b (i)), as a result of the target concentration of product and brine solution being pre-defined. This finding indicates that better control of effluent salinity can be achieved in pulse-flow operation.

An inversion of salt electrosorption, defined as desorption in the charge stage and adsorption in the discharge stage, is evident on the positive electrode at the beginning of the charge stage and towards the end of the discharge stage (Figure 20(i-ii)). The degree of inversion, quantified by the micropore charge density on the positive electrode, dropped by 31% at T1 when current density increased from 3 A/m$^2$ ($\rho_{mi,pos} = 3.77$ C/cm$^3$ – electrode) to 18 A/m$^2$ ($\rho_{mi,pos} = 2.61$ C/cm$^3$ – electrode). However, the charge efficiency loss due to co-ion repulsion, which increases as a result of electrosorption inversion, is the dominant mechanism at high current density (see, also, Section 5.2 and Figure 18). The effect of inversion on charge efficiency is exacerbated at high current because of the pronounced cell polarization due to Ohmic drop.$^{15,84}$ Polarization at high current decreases the achievable charge utilization within the defined cell voltage window. As a result, the inversion process occurs over a larger fraction of the total cycle time at high current (Figure 21(iii)).

Concentration polarization between the flow channel and electrode is more pronounced (Figure 21a-b(i) and Figure 21c-d) as current density increases, resulting in further decrease in desalination performance due to desalination residue in the electrodes. In addition, the impact of leakage current on charge efficiency is negligible at high current density as the columbic efficiency is close to unity (i.e., the coulombs removed during discharge balances with those supplied during charge).
Pulse-flow operation model results reveal that concentration polarization along the direction of flow (longitudinal) is absent during such a flow scenario (as shown in the salinity maps in Figures 20-21). However, during continuous-flow operation, the limitation of the longitudinal concentration polarization on salt removal performance increases with current density as large local concentration gradient develop. Such sharp concentration gradients could trigger additional side effects. For example, in the continuous-flow operation mode, concentration depletion is observed at the right bottom corner of negative electrode toward time instance T2 (Figure 21c). Ion starvation resulting from diffusion limitations inside porous electrodes was also observed in previous CDI models under constant voltage operation.69 Meanwhile, the cell voltage rapidly approaches the voltage cutoff limit (Figure 21a(iv)), resulting in a decrease in the length of charge stage compared with pulse-flow operation.
Figure 20. Time evolution of (i) salt concentration, (ii) leakage current (normalized by the capacitive current), (iii) ionic charge density within micropores, and (iv) cell voltage in a limit charge/discharge cycle at low current density of 3 A/m² for (a) continuous- and (b) pulse-flow operation modes. Two-dimensional contour plots show the distribution of salt concentration at time instant T1 (start of charge stage) and T2 (start of discharge stage) for (c) continuous- and (d) pulse-flow operation. The color scheme in (i-iii) corresponds to the three colored dots located in the contour plots.
Figure 21. Time evolution of (i) salt concentration, (ii) leakage current (normalized by the capacitive current), (iii) ionic charge density in micropores, and (iv) cell voltage in a limit charge/discharge cycle at high current density of 18 A/m$^2$ for (a) continuous- and (b) pulse-flow operation modes. The two-dimensional contour plots are distribution of local concentration at time instant T1 (start of charge stage) and T2 (start of discharge stage) for (c) continuous- and (d) pulse-flow operation. The color scheme in (i-iii) corresponds to the three colored dots located in the contour plots.

5.4 Experimental Comparison between Pulse-Flow and Continuous Operation

To confirm the previous findings from numerical simulations, here we present experimental data obtained using a self-designed CDI cell to compare the desalination
performance of pulse-flow operation and continuous-flow operation. Implementing the proposed pulse-flow operation in the experiments requires in situ measurement of local concentration and a feed-back control algorithm. In lieu of that approach we performed simplified pulse-flow tests by setting the batch-time constant (see Section 3.2). The flow rate in the continuous operation was determined accordingly. The experimental results in Figure 22 showed a monotonic increase of SEC as current density increased from 3 - 20 A/m². While these results indicate that pulse-flow operation has lower SEC than continuous-flow operation (after accounting for displacement), SEC deviates between the two cases by 37% and 9.3% at low and high current density, respectively. Furthermore, lower SEC in continuous-flow operation is expected if the dead-volume effects can be eliminated.

Figure 22. Experimental results of specific energy consumption for pulse-flow operation vs. continuous-flow operation at current density for 3 - 20 A/m² and C₀ = 30 mM.
Table 2. Comparison of salt removal metrics between pulse- and continuous flow operation. The results are based on simulation at constant current of 6 A/m$^2$ and 16 A/m$^2$ in the charging stage (desalination stage for the continuous-flow with displacement condition) within a limiting cycle.

<table>
<thead>
<tr>
<th>Flow mode</th>
<th>Current density A/m$^2$</th>
<th>Salt removal mmoles/cm$^2$</th>
<th>Produced water in a single cycle L/m$^2$</th>
<th>Avg. effluent salinity mM</th>
<th>Salt removal rate* mmol/m$^2$/s</th>
<th>SEC kJ/g-NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse-flow</td>
<td>6</td>
<td>20.4</td>
<td>2.10</td>
<td>20.3</td>
<td>0.025</td>
<td>2.80</td>
</tr>
<tr>
<td>Continuous</td>
<td>6</td>
<td>19.0</td>
<td>2.11</td>
<td>21.0</td>
<td>0.024</td>
<td>2.94</td>
</tr>
<tr>
<td>Continuous with displacement</td>
<td>6</td>
<td>22.6</td>
<td>1.83</td>
<td>17.7</td>
<td>0.033</td>
<td>2.47</td>
</tr>
<tr>
<td>Pulse-flow</td>
<td>16</td>
<td>11.9</td>
<td>1.23</td>
<td>20.3</td>
<td>0.053</td>
<td>3.72</td>
</tr>
<tr>
<td>Continuous</td>
<td>16</td>
<td>3.94</td>
<td>1.06</td>
<td>26.3</td>
<td>0.019</td>
<td>9.61</td>
</tr>
<tr>
<td>Continuous with displacement</td>
<td>16</td>
<td>10.0</td>
<td>0.90</td>
<td>18.9</td>
<td>0.057</td>
<td>3.76</td>
</tr>
</tbody>
</table>

* The salt removal rates in pulse-flow and continuous-flow operation are based on the length of charging stage. In continuous-flow operation with displacement, the length of the desalination stage is used to calculate the salt removal rate.
A model that provides a component-wise identification of the energy loss mechanisms within a CDI cell can guide the development of highly energy-efficient desalination.

In this chapter, we aim to quantify the electronic and ionic energy losses that amplify CDI SEC by using the previously developed pulse-flow model. We explore a range of different operating strategies, including by varying current density, voltage cutoff, flow mode, and membrane configurations. To identify mechanisms that most significantly influence energy consumption and salt removal during galvanostatic cycling, we benchmark the flow-by CDI system with models for MCDI and flow-through CDI. We also explore a variety of operating strategies (e.g., current density, operating voltage window, and target effluent/brine concentration) to demonstrate the sensitivity of energy efficiency of salt removal for a CDI system.

Here we explore the SEC for a flow-by CDI cell at a limiting cycle with four energy metrics: 1) the total energy input normalized by the total salt removal in the charging stage ($E_T$), 2) the net energy input after energy recovery during the discharge stage ($E_R$), 3) the total energy loss due to leakage current by parasitic faradaic reactions ($E_L$), and 4) the total energy dissipation due to charge transport in both solid and liquid phases ($E_D$). All energy consumption values are normalized by the total salt removal in the charging stage. To highlight the impacts of cell architecture and ion-selectivity, we benchmark our calibrated and validated flow-by CDI model against simulated results for a MCDI cell with ideal
permselective membranes and an ideal flow-through CDI cell.

6.1 **Effect of current density and target effluent concentration on desalination energy consumption**

For the modeled CDI cell, a minimum of the specific energy consumption normalized to salt removal is observed near 6 A/m² where faradiac and dissipative losses are both minimized. The contribution of resistive dissipative energy increases with current density while the magnitude of energy loss from faradaic reactions responds oppositely. Increasing current density reduces the operating time spent at high overpotential regimes for faradaic leakage current. However, further increase in current density leads to rapid charge transport dynamics and resistive dissipation. These simulations corroborate recent experimental findings related to faradaic and dissipative energy loss in CDI cells. An operational benefit of CDI is that adjusting target freshwater and brine concentrations can reduce energy consumption. By raising the target effluent concentration from 10 mM to 20 mM can be reduced by 40 – 60% (Figure 23) and observed charge efficiency can be increased by 0.12 – 0.39 (Figure 27).
Figure 23. Salt specific energy consumption (SEC, in joules per gram of NaCl) for CDI at effluent concentration of 10 and 20 mM (A, B) and for MCDI at effluent concentration of 20 mM (C) (C_{in}=30mM). Simulations show that CDI is limited by faradaic reactions and resistive dissipation at low and high current, respectively. In comparison, ion-selective membranes in MCDI reduce the energy consumption but introduce Donnan potential and membrane resistance.

Constant current operation allows for the recovery of energy stored within the EDLs during the charging stage. Since 75% (Figure 23A and B) of the total energy input during the charging stage is stored in EDLs, maximizing energy recovery will be critical to lowering the SEC of CDI systems. Since energy is also lost during cell discharge, energy recovery also depends on system operation. If the magnitude of current is held constant but reversed in the discharging stage, 30 – 60% (Figure 23A and B) of the stored capacitive energy in the charging stage is lost to faradaic reactions and ohmic dissipation. Maximum efficiency was observed at 6 A/m². In contrast, the ideal MCDI could operate at energy recovery between 60 – 90%, with the maximum efficiency being observed at 2 A/m². To increase energy recovery in CDI, more rigorous understanding of energy dissipation is required.
6.2 Comparing energy dissipation and charge leakage in the cycling behaviour of flow-by CDI and ideal MCDI

Differences in simulated energy loss for the flow-by CDI and MCDI systems highlight the impacts of leakage current and reverse salt flux in the transition between desalination and brine generation. From the standpoint of energy dissipation, the IEMs in the MCDI system also create a barrier to prevent direct contact between the carbon electrode and the aqueous oxygen in the flow stream, and energy loss due leakage current is minimal (Figure 23C and 24F). We confirmed experimentally that the magnitude of leakage current of an MCDI cell is close to that in the CDI cell without aqueous oxygen (see Figure 11). Eliminating leakage current leads to desalination of more batches with a shorter charging cycle length (Figure 24A and B).

Figure 24. Averaged concentration in the flow channel, whole cell voltage, and power as a function of time during the limit cycle of a galvanostatic charge/discharge process with a current density of 6 A/m² for flow-by CDI and MCDI. The influent, target effluent, and target brine concentrations are 30, 20, and 40 mM, respectively. Roman numerals
correspond to time points for which the concentration profile within each cell configuration are presented in Figure 25 (i, ii, iii).

The quantity of salt removed in a flow-by CDI cell operated at constant current is strongly limited by the time and adsorbed charge required to desalinate the 1\textsuperscript{st} batch at the beginning the charging stage (Figure 24). During this first batch, the average concentration in the flow channel of a flow-by CDI cell initially becomes greater than the influent concentration (30 mM), and the first batch takes much longer than the successive ones in order to reach the effluent concentration target. As observed in the distribution of local macroscopic concentration across the cell, the concentration gradient between solution in the electrode and the flow channel causes salt to diffuse into the flow channel (Figure 25A, profile i). Since the salt retained from the previous discharge event must be adsorbed before reaching the target effluent concentration, the first batch consumes 3.75 kJ/g-NaCl, which is 1.7 times greater than the average SEC in successive batches for the same charging event, when the electrode solution concentration is below the influent (Figure 25A, profile ii).
Figure 25. Concentration profile in a cross-section of a (A) CDI and (B) ideal MCDI cell at different time steps during a limit cycle: i, beginning of the 1\textsuperscript{st} batch, ii, beginning of the 5\textsuperscript{th} batch, and iii, end of the 5\textsuperscript{th} batch in the charging stage.

Since our model neglects mixing between influent solution pulsing events, simulations may overestimate the concentration gradient between the electrode and flow-channel. If this were the case, projections for energy dissipation due to reverse ionic flux during the first desalination batch would increase. Also, it is important to note that the reverse ionic flux observed in flow-by CDI simulations is different from the co-ion repulsion peak commonly observed for CDI cells operated under constant voltage which are caused by electrode degradation and shifts in PZC.\textsuperscript{32, 33, 56} If both phenomena were to occur at the start of a charging cycle (which the present validation experiments indicate), the first batch
would actually take longer than expected and the SEC of the first batch would be higher than the simulated values.

In the simulated ideal MCDI cell, all desalination and brine batch times are the same because the IEMs segregate the concentration profiles of the electrodes and flow channel, preventing reverse ionic flux (Figure 25B). As a result, the ideal MCDI cell is able to treat more bed-volumes of solution in a single charging stage compared to the CDI cell under the same condition. For example, at the current density of minimum energy consumption for modeled flow-by CDI cell (6 A/m$^2$), six more batches are desalinated in the charging stage within a shorter time when ideal IEMs are included in the model (Figure 24 A and B). In addition, the energy dissipation due to ionic transport within the porous electrode in an MCDI cell is also smaller since the average local concentration in the electrode macro-pore volume is higher than CDI during the majority of time during the charging stage (Figure 25 A and B).

6.3 Reducing CDI energy consumption with flow-through architecture

To highlight the impact of reverse ionic flux on flow-by CDI SEC, we apply the concept of transverse flow-through electrodes$^{49}$ and simulate an ideal case where all the solution within the cell, in both flow channel and electrode pore volume, can be obtained through the event of pulsing. Recovering desalinated solution from the electrodes could prevent reverse ionic flux, and increase the number of desalination batches, leading to significant improvements in simulated SEC (Figure 26A and B). Note that the flow is perpendicular to the direction of the applied current, while in other reported flow-through CDI systems the flow is in the same direction along the applied current$^{23,99}$. The SEC without recovery
of the ideal flow-through CDI and flow-by MCDI are similar, with differences caused by leakage current, co-ion repulsion (flow-through CDI) and Donnan potential (MCDI). Since leakage current would still occur, energy recovery for flow-through CDI (0.30 – 0.65) would still be significantly lower than MCDI. If the charging voltage is held below 800 mV, specific energy consumption for flow-by and flow-through CDI (Figure 26A and B) could be reduced further, where the impacts of dissipation (primarily reverse ionic flux) and leakage current are both minimized.

Figure 26. Effect of flow architecture and operating voltage limit on energy consumption per salt removal with $J = 6$ A/m$^2$, $C_0 = 30$ mM, $C_{\text{eff}} = 20$ mM, and $C_{\text{brine}} = 40$ mM. The energy consumption for ideal flow-through CDI system is comparable to flow-by MCDI with IEMs.

Improved charge efficiency is the primary driver of improved energy consumption in flow-through CDI. By introducing advection to eliminate reverse ionic flux in the first desalination batch, the simulated charge efficiency increased to 0.85 – 0.90 across the operating potential range (Figure 27), which reflects reported charge efficiency values for MCDI (Table 1). However, as mentioned earlier, this analysis neglects the long term
impact of faradaic reactions on anode PZC, which would limit flow-through CDI long term performance in the presence of dissolved oxygen\textsuperscript{66,99}. To date, the charge efficiency of reported flow-through CDI system is in the range of 0.41-0.69\textsuperscript{23,100,101}, which are much smaller than the predicted values. These simulation results indicate potential for reduction of the total cost of a capacitive desalination system by removing IEMs without sacrificing system performance. However, the ideal flow-through architecture may be difficult to implement in real application considering the microscopic size of pores and their tortuosity.

![Figure 27. Simulated charge efficiency for conventional flow-by CDI and ideal flow through CDI within a limiting cycle at different voltage window.](image)

Figure 27. Simulated charge efficiency for conventional flow-by CDI and ideal flow through CDI within a limiting cycle at different voltage window.
CHAPTER 7 Conclusion

Conventional flow-by CDI suffers from a number of charge-efficiency loss mechanisms, including leakage current, co-ion repulsion, and residue of desalinated solution within electrodes and the flow channels. In this thesis, we have demonstrated that the commonly used continuous flow operation in CDI can lead to significant performance degradation at high current density if the temporal lag between the charge stage and desalination stage is not accounted for in the collection of effluent. To demonstrate this, we have used a porous electrode model, which has been calibrated and validated based on a self-designed and fabricated flow cell. Simulations with this model reveal local regions of salt accumulation that are affected by the specific flow mode used. We showed that, without changing the system architecture, electrode composition, and operation metrics (i.e., operating voltage window, current density, and average flow rate), salt removal performance of a CDI system can be improved by using pulse-flow operation. Compared to traditional continuous-flow operation, simulation results showed that charge efficiency increased up to 23% at current density of 20 A/m² in the pulse-flow operation, which leads to 73% decrease of specific energy consumption (kJ/mol-NaCl). In addition, the specific energy consumption and the degree of desalination predicted by the model of pulse-flow operation closely align with the predictions of the continuous operation model, if the temporal lag between the charge and desalination stages (so-called displacement) is accounted for. Aside from its immediate application toward enhancing the performance of continuous-flow CDI, this finding suggests that one can approximate the performance in continuous-flow operation with predictions based on a one-dimensional pulse-flow
The present models incorporate the following non-ideal mechanisms in a CDI system: additional immobile surface charges on the positive electrode as a result of electrode degradation, leakage current due to different parasitic faradic reactions on the positive and negative electrodes, repulsion of co-ions during electrosorption process, and microscopic diffusive/advective salt transport. We also showed the experimental procedures and approaches necessary to extract the principle fittings parameters associated with different sub-modeling components. However, the model did not consider transport of minor ionic species such as H\(^+\) and OH\(^-\), which could play a role especially when the faradic reactions dominate utilization of current. With the addition of such effects within a porous electrode model, predicted charge efficiency and energy consumption for the various flow modes could be affected at low operating currents. In addition, future improvement to the model can be made by obtaining values for the PZC experimentally by measuring acidic and alkaline charge densities.

We further applied the 1D pulse-flow model to identify energy losses specific to each system components for different cell architectures. This study highlights how salt specific energy consumption due to diffusional limitations of flow-by CDI can largely be addressed by introducing flow through the electrode structure or implementation of ion exchange barriers at the electrode surfaces. However, introducing advection would not have a significant impact on CDI energy recovery since faradaic reactions still occur in the presence of oxygen.
CHAPTER 8 Future Work: Double-side MCDI Stacks

The ion uptake capacity of conventional carbon based CDI electrodes is typically lower than ion intercalating/metal oxide electrode material, as shown in Figure 28. Operation of CDI based systems normally requires frequent switching between charging and discharging stages, resulting in dramatical changes of concentration in the volume of flow channel, electrodes, and downstream tubing. As shown in section 4.3, the effluent salinity can be further affected by diffusion and internal mixing in these volume during switching of charging/discharging stages. One possible solution is to use a slurry based electrode, commonly referred to as flow-electrode CDI, and recirculate the anolyte and catholyte electrodes back to flow-electrode reservoir, generating a stream of desalinated solution continuously. However, the energy recovery process, which can offset up to 83% of total energy input, in these types of flow-electrode CDI is not easy to implement because the positively and negatively charged electrodes are discharged via short-circuit when they are mixed together. Meanwhile, additional approaches are needed to maintain the salt concentration and temperature in the reservoir, otherwise it would keep increasing due to discharging.
Figure 28. Reported values of salt adsorption normalized by electrode weight by different electrode material tested in CDI system. Data in the figure were obtained from Refs. 27,29,31,44-46,51.

In this chapter, the concept of a MCDI based cell architecture is described to separate the fresh- and brine-water streams during CDI operation (as shown in Figure 29). In addition, continuous flow of fresh and brine stream can be produced through a two-layer-stack arrangement, where one layer of electrodes are in charging stage and the other layer of electrodes are under discharging stage. Energy during discharging stage can be harvested and supply the charging process simultaneously.
Figure 29. Schematic of membrane based capacitive deionization systems with separated flow channels for fresh water and brine, which can be produced continuously by switching the changing/discharge stages in the top and bottom array of cells alternatively.

In these double-sided MCDI stacks, ion exchange membranes cover both sides of a single electrode. Assuming the membranes are ideally permselective, ionic flux can flow through both the front and back sides to an electrode, depending on the direction of potential field. Operation of the double-sided MCDI stacks contains two stages, as shown in Figure 29. In state 1, the electrodes on the top row are in the charging stage, generating desalinated solution in the fresh-water stream, indicated by green lines. Once it reaches the maximum voltage limit, the top row electrodes are switched to the discharging stage, represented as stage 2 in Figure 29. Note that ions in the discharging stage flow into the brine stream, indicated by red lines, as external electric wires connect different pairs of electrodes after switching stage. At the same time, the electrodes in the bottom row are in the charging stage, producing desalinated water in the fresh stream. Stage 2 ends when the cell voltage at the bottom row electrodes reaches the maximum voltage limit.
By switching between these two stages, we can obtain a continuous generation of fresh- and brine-water streams with energy recovery.
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APPENDIX A: Matlab Demo Code for CDI Modeling

%% Capacitive deionization 2D simulation DEMO
%%
%% Developed by: Xia Shang
%% Advisors: Prof. Kyle Smith, Prof. Roland Cusick
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%% University of Illinois at Urbana-Champaign
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%%
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%%
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%% PROCUREMENT OF SUBSTITUTE GOODS OR SERVICES; LOSS OF USE, DATA,
%% OR PROFITS; OR BUSINESS INTERRUPTION) HOWEVER CAUSED AND ON ANY THEORY OF
%% LIABILITY, WHETHER IN CONTRACT, STRICT LIABILITY, OR TORT (INCLUDING
%% NEGLIGENCE OR OTHERWISE) ARISING IN ANY WAY OUT OF THE USE OF THIS
%% SOFTWARE, EVEN IF ADVISED OF THE POSSIBILITY OF SUCH DAMAGE.

clc; clear; close all;
tic

%% cell operating parameters
C0=30;       % mM, influent concentration
V_max=1200;  % mV, cell voltage
J= 1;        % mA/cm², projected area
Cycle_limit = 8;   % -, total cycle number
Q_FC = 0.0736;  % mL/min, flow rate suggested range (0.05 - 1 mL/min)

%% Cell design
T_CC1 = 0;    % um, thickness of current collector 1
T_pos = 450;  % um, thickness of Cathod
T_FC = 250;   % um, thickness of Flow channel
T_neg = 450;  % um, thickness of Anode
T_CC2 = 0;    % um, thickness of current collector 2
L_FC = 9; % cm, Length of flow channel
W_FC = 2; % cm, Width of flow channel
V_internal = 0.455; % mL, volume of a well mixed internal tank, dead-volume

% Electrode Porosities
M_e = 0.4214; % g/cm3; electrode density
C_Measured = 49; % F/g; Stern-layer capacitance, this value can be initially estimated based on the whole cell capacitance measured in CV at low scan rate (e.g., < 1mV/s) in 1 M NaCl
Q_fix_pos = -4; % C/cm3, immobile charge density
Q_fix_neg = 0; % C/cm3, immobile charge density
uatt=0; % -, attractive chemical force using in the mD theory
R_Macro = 0.4; % Macropore ratio
R_Micro = 0.2; % Micropore ratio
R_FC = 0.7; % Average porosity of flow channel
R_e= 1-(1-R_Macro)*(1-R_Micro); % Total porosity of electrode

% numerical parameters
dt = 0.008; % s, dt
dx = 25; % um
dy=200*L_FC; % um

% data storage to reduce membrane usage
tmin = 0; % s, starting time
tmax = round(800*Cycle_limit*1.2/J); % s, ending time, this value can be adjusted
dt_record=1; % s, time step to record data
Nt=round((tmax-tmin)/dt); % total number of nodes in time
Nt_r = round((tmax-tmin)/dt_record); % no. of stored nodes in time

% other related parameters
E_Dielectric = 80.4; % dielectric constant of water
E_Permittivity = 8.85*10^-12; % F/m; permittivity of free space
r_Na = 0.16; % nm, radius of Na+ ion
d_H2O = 0.29; % nm, diameter of a H2O molecule
d_Helmholtz = (r_Na + d_H2O)/10^9; % m
c_Helmholtz = E_Dielectric*E_Permittivity/d_Helmholtz; % F/m2
A_effective = C_Measured/c_Helmholtz; % m2/g; effective surface area
Temp = 298.16; % K, temperature
KB = 1.38*10^-23; % C V K-1; Boltzmann constant
e = 1.602*10^-19; % C;
Na = 6.02*10^23; % mol-1;
F = 96485.3365; % C mol-1; Faraday constant
M_NaCl=58.44; % g/mole
z_a =-1; % valence of anion
z_c = 1; % valence of cation
q_a = 1; % charge of anion
q_c = 1; % charge of cation
t_Na = 0.5; % transference number of Na+
t_Cl = 1-t_Na; % transference number of Cl-

% Diffusion coefficient
D_NaCl = 1.61*10^-5; % cm2/s; diffusion coeff. in spacer
\[ D_e = D_{NaCl} \times 10^8 \times R_{Macro}^{0.5}; \text{ \% um2/s, effective diffusion coefficient in electrode} \]
\[ D_{FC} = D_{NaCl} \times 10^8 \times R_{FC}^{0.5}; \text{ \% um2/s, effective diffusion coefficient} \]
\[ D_{mid} = 2 \times D_{FC} \times D_e / (D_{FC} + D_e); \]

% resistance
\[ R_{contact} = 29.33; \text{ \% ohm cm2} \]
\[ R_{electrode} = 0.1625; \text{ \% ohm*m} \]

% flow rate and mixing in the dead-volume
\[ v_{FC} = Q_{FC} / T_{FC} \times 10^4 / W_{FC} / 60 \times 10^4; \text{ \% um/s, flow velocity, assume uniform} \]
flow profile in the cross section
\[ k_{mix} = Q_{FC} / 60 / V_{internal}; \text{ \% /s, factor used in the equation} \]
accounting for the effect of mixing in the dead-volume

% Leakage current sub-models
% B-V model parameter
\[ a_{ele} = 11000; \text{ \% cm2/cm3 electrode volume} \]
\[ I_{0_C} = 2.5 \times 10^{-7}; \text{ \% mA/cm2} \]
\[ I_{0_O2} = 5.5 \times 10^{-7}; \text{ \% mA/cm2} \]
\[ E_{0_C} = 0.207; \text{ \% V, vs SHE} \]
\[ E_{0_O2} = 0.81; \text{ \% V, vs SHE} \]
\[ R_T_F = 0.0592; \text{ \% V} \]
\[ a_C = 0.5; \]
\[ a_{O2} = 0.5; \]
\[ E_{0_An} = 0.5419; \text{ \% V, vs SHE, measured at equilibrium condition when two electrodes were short circuited} \]
\[ E_{0_Ca} = 0.5419; \text{ \% V, vs SHE, measured at equilibrium condition when two electrodes were short circuited} \]

% Impirical limiting current model parameter
\[ E_{half} = 0.124; \text{ \% V, vs SHE} \]
\[ I_{L_O2} = 3.558; \text{ \% mA/cm3-electrode} \]

% Indexing
% Current collector
\[ xmin_{CC1} = 0; \text{ \% um, minimum value of x} \]
\[ xmax_{CC1} = (xmin_{CC1} + T_{CC1}) / dx; \text{ \% um, maximum value of x} \]

% Positive electrode
\[ xmin_{pos} = xmax_{CC1}; \text{ \% left boundary node point of the positive electrode} \]
\[ xmax_{pos} = (xmin_{pos} + T_{pos}) / dx; \text{ \% right boundary node point of the positive electrode} \]
\[ L_{pos} = L_{FC}; \text{ \% cm, length of the positive electrode} \]
\[ W_{pos} = W_{FC}; \text{ \% cm, width of the positive electrode} \]
\[ A_{edge} = 0; \text{ \% cm2, area of cathod in the triangular spot} \]
\[ A_{pos} = L_{pos} \times W_{pos} \times A_{edge}; \text{ \% cm2, area of projected area of the positive electrode} \]
\[ V_{pos} = T_{pos} / 10000 \times A_{pos}; \text{ \% cm^3, volume of the positive electrode} \]

% Flow channel
\[ xmin_{FC} = xmax_{pos}; \text{ \% left boundary node point of FC} \]
\[ xmax_{FC} = xmin_{FC} + T_{FC} / dx; \text{ \% right boundary node point of FC} \]
A_edge_FC = 0; % cm², area of flow channel in the triangular spot
A_FC = L_FC*W_FC + A_edge_FC; % cm², projected area of flow channel
Vol_FC = T_FC/10^4*A_FC/1000*R_FC; % L, Volume of flow channel

% Negative electrode
xmin_neg = xmax_FC; % left boundary node point of the negative electrode
xmax_neg = xmin_neg+T_neg/dx; % right boundary node point of the negative electrode

% Current collector 2
xmin_CC2 = xmax_neg; % um, minimum value of x
xmax_CC2 = xmin_CC2+T_CC2/dx; % um, maximum value of x

% indexing of vectors and matrix
nx = xmax_CC2-xmin_CC1; % total number of compartments in the cell
ny=L_FC*10000/dy; % ny
N=T_pos/dx; % total number of compartments in the electrode
N_FC=T_FC/dx; % total number of compartments in the FC
V_i = W_pos*dy/10000*dx/10000; % cm³, volume per compartment

x_ind=[1:xmax_pos, xmin_neg+1:xmax_neg]; % indexing for the electrodes
FC_ind=[xmax_pos+1:xmin_neg]; % indexing for the flow channel

FC_ind_A = zeros(numel(FC_ind)*ny,1); % indexing for the flow channel in 2D
for i=1:ny
    FC_ind_A(1+(i-1)*numel(FC_ind):i*numel(FC_ind)) = FC_ind + (i-1)*nx;
end

%% Initiation
vt=zeros(Nt_r, 4); % mV, 1st column: electrode voltage, 2nd column: IEM resistance voltage, 3rd column: spacer resistance voltage, 4th total voltage
T0=0; % s previous time step
T1=0; % s current time step
T_r=zeros(Nt_r,1); % s, reduced time domain for data storage
Cycle_index=zeros(100,1); % index of cycles
Discharge_index=zeros(100,1); % index of discharge cycles
VV_0 = zeros(nx,ny); % mV, Voltage matrix in the electrode
V_N = zeros (nx, ny); % mV, Voltage matrix of ionic resistance in the electrode
II_0 = zeros(nx,ny); % mA, Current matrix: current passing each capacitor
II_1 = zeros(nx,ny); % mA, Current matrix: current passing each capacitor
Ri_M =zeros(nx,ny); % ohm, individual ionic resistor matrix
Re_M =zeros(nx,ny); % ohm, individual electronic resistor matrix
Cond_M = zeros(nx,ny); % Conductivity matrix
IL = zeros(nx,ny); % mA, Current matrix: current passing each resistor in parallel to the capacitor
I_Ri = zeros (nx,ny); % mA, Current matrix: current passing each ionic resistor
I_Re = zeros (nx,ny); % mA, Current matrix: current passing each electronic resistor
C_0 = zeros (nx,ny); % mM, Concentration matrix corresponding to the capacitor matrix
C_1 = zeros (nx,ny); % mM, Concentration matrix corresponding to the capacitor matrix
C1 = zeros(nx,ny); % mM, concentration matrix
C_re = zeros(nx,ny,Nt_r); % mM, recorded concentration tensor
I_re = zeros(nx,ny,Nt_r); % mA, recorded current tensor
Q_mi_re = zeros(nx,ny,Nt_r); % mV, recorded charge density tensor
I_L_re = zeros(nx,ny,Nt_r); % mA, recorded leakage density tensor
QT_0 = zeros (nx,ny); % C, charge density matrix
QT_1 = zeros (nx,ny); % C, charge density matrix
QT_e=QT_0; % C, charge density matrix
QT_m=QT_0; % C, charge density matrix
V_D=zeros(nx,ny); % mV, Donnan potential matrix
C_mi_0=zeros(nx,ny); % mmol-L micropores, ionic charges matrix inside micropores
C_mi_1=zeros(nx,ny); % mmol-L micropores, ionic charges matrix inside micropores
C_eff = zeros(Nt_r,1); % mM avg effluent concentration per batch
C_eff_mix = C_eff; % mM, true effluent considering the effect of well mixed condition at the end of effluent

% Initial concentration and polarization
C_0(:,:,)=C0; % mM, Initial concentration profile in the electrode phase
C_1(:,:,)=C0; % mM, Initial concentration profile in the electrode phase
VV_0(:,:,)=0; % mV, Initial polarization profile in the electrode phase

% determine the initial current distribution across the cell
I = J*A_FC; % mA, total current applied
indx=(1:nx)';
indx_1=circshift(indx,1);
indx_0=circshift(indx,-1);
indy=(1:ny)';
indy_1=circshift(indy,1);
indy_0=circshift(indy,-1);

% calculate ionic conductivity S/cm
Cond_M(:,:,)=2*D_NaCl*C_0(:,:,)/KB/Temp/1000000*F*e*R_e^1.5;
Cond_M((xmax_pos+1:xmin_neg,:)=2*D_NaCl*C_0(xmax_pos+1:xmin_neg,:)/KB/Temp/1000000*F*e*R_FC^1.5;
Cond_M(1:xmax_pos-1,:)=2.*Cond_M(1:xmax_pos-1,:).*Cond_M(index_0(1:xmax_pos-1,:))/(Cond_M(1:xmax_pos-1,:)+Cond_M(index_0(1:xmax_pos-1,:));
Cond_M(index_0(1:xmax_pos-1,:)=2.*Cond_M(index_0(1:xmax_pos-1,:))/(Cond_M(index_0(1:xmax_pos-1,:);)
Cond_M(index_0(xmin_neg+1:xmax_neg-1,:)=2.*Cond_M(index_0(xmin_neg+1:xmax_neg-1,:))/(Cond_M(index_0(xmin_neg+1:xmax_neg-1,:));
Cond_M(index_0(xmin_neg+1:xmax_neg-1,:)=2.*Cond_M(index_0(xmin_neg+1:xmax_neg-1,:))/(Cond_M(index_0(xmin_neg+1:xmax_neg-1,:));

Ri_M(:,:,)=1./Cond_M(:,:,)*dx/dy/W_FC;
Ri_S=zeros(ny,1);
Ri_S=ones(ny,1);
% calculate the current distribution in the electrode
M_I = zeros(ny,ny); % Coefficient matrix for current distribution in the electrode
M_I(1:(ny+1):(end-ny))=Ri_S(1:(end-1));
M_I((ny+1):(ny+1):end)=-Ri_S(2:end);
M_I(ny,:)=1;
S_I=sparse(M_I);
B_I =zeros(ny,1); % vector for current distribution in the electrode
B_I(1:end-1)=VV_0(xmax_pos,indy_0(1:(end-1)))-VV_0(xmin_neg+1,indy_0(1:(end-1)))-VV_0(xmax_pos,1:(end-1))+VV_0(xmin_neg+1,1:(end-1));
B_I(end)=I;
I_y=S_I\B_I; % solve the current distribution in the electrode in the y-direction

% calculate the leakage current in the positive electrode
Oe = 0; % set the electronic resistance
IL(1:xmax_pos,1)=a_ele*I0_C*V_i*exp(a_C/RT_F.*(VV(1:xmax_pos,1)/1000+E0_An-E0_C));
IL(1:xmax_pos,:)=0;

% update the current distribution in the positive electrode
II_0(2:xmax_pos-1,:)=-IL(2:xmax_pos-1,:)+(VV_0(index_2:xmax_pos-1,:),:)/(Oe+Ri_M(2:xmax_pos-1,:))-(VV_0(index_2:xmax_pos-1,:),:)/((Oe+Ri_M(index_2:xmax_pos-1,:),:));
II_0(1,:)=-IL(1,:)+(VV_0(2,:),:)-VV_0(1,:))/(Oe+Ri_M(1,:));
II_0(xmax_pos,:)=I_y'+IL(xmax_pos,1)-sum(II_0(1:xmax_pos-1));

% calculate the leakage current in the negative electrode
IL(xmin_neg+1:xmax_neg,1)=a_ele*I0_O2*V_i*(exp(a_O2/RT_F.*(VV(xmin_neg+1:xmax_neg,1)/1000+E0_Ca-E0_O2))-
%IL(xmin_neg+1:xmax_neg,1)=
IL_O2*V_i./(1+exp((VV_0(xmin_neg+1:xmax_neg,:)/1000+E0_Ca-E_half)/RT_F));

% update the current distribution in the negative electrode
II_0(xmin_neg+2:end-1,:)=-IL(xmin_neg+2:end-1,:)+(VV_0(index_1(xmin_neg+2:end-1),:)-VV_0(index(xmin_neg+2:end-1),:))/(Oe+Ri_M(index(xmin_neg+2:end-1),:));
II_0(end,:)=-IL(end,:)+(VV_0(end-1,:)-VV_0(end,:))/(Oe+Ri_M(end,:));
II_0(xmin_neg+1,:)=-I_y'-sum(II_0(xmin_neg+2:end,:))-sum(IL(xmin_neg+1:end,:));

% calculate the ionic current in the electrode
A = tril (ones(N));
A1=A';
A2=tril(ones(N_FC))';
I_Ri(1:xmax_pos,1)=A*(IL(1:xmax_pos,1)+II_0(1:xmax_pos,1));
I_Ri(xmax_pos+1:xmin_neg,1)=I_y(1);
I_Ri(xmin_neg+1:xmax_neg,1)=
A1*(IL(xmin_neg+1:xmax_neg,1)+II_0(xmin_neg+1:xmax_neg,1));

% B.C vector
bc=zeros(nx,ny);
bc(1,:) = 0; bc(nx,:) = 0; % Neumann B.Cs
bc(:,1) = 0; bc(:,ny) = 0;
% bc(xmax_pos+1:xmin_neg,1)=C0/dy^2; % Dirichlet B.Cs

% B.Cs at the corners:
bc(1,1) = 0; bc(nx,1) = 0;
bc(1,ny) = 0; bc(nx,ny) = 0;
bc(x_ind,:) = D_e*dt*bc(x_ind,:);
bc(FC_ind,:) = D_e*dt*bc(FC_ind,:);

% Calculating the coefficient matrix for the implicit scheme
Ex = sparse(2:nx,1:nx-1,1,nx,nx);
Ax = Ex + Ex' - 2*speye(nx);
Ay = sparse(2:ny,1:ny-1,1,ny,ny);
A_y = kron(Ay/dy^2,Ex);
D = R_Macro*speye((nx)*(ny));
D(FC_ind_A,:) = D(FC_ind_A,:) / R_Macro*R_FC;
D = Ex + Ex' - 2*speye(nx) - 2*speye(1:ny-1,1:nx,1:nx,1:ny);
D_x = kron(Ax/dx^2,Ex);
D_x(FC_ind_A,:) = D_x(FC_ind_A,:) / D_e*D_FC;

% update the diffusion coefficient in the flow channel
D_x(length(D_x)*(xmax_pos-1)+xmax_pos+1:length(D_x)*nx+nx:end) =
D_x(length(D_x)*(xmin_neg-1)+xmin_neg+1:length(D_x)*nx+nx:end) =
(D_mid+D_e)*dt/dx^2;

% update the diffusion coefficient at the interfaces between electrode and flow channel
D_x(length(D_x)*(xmax_pos-1)+xmax_pos+1:length(D_x)*nx+nx:end) =
D_x(length(D_x)*(xmin_neg-1)+xmin_neg+1:length(D_x)*nx+nx:end) =
(D_mid+D_FC)*dt/dx^2;

D = D - D_x - D_y;
% D = D - D_x;
D = D - D_e*dt*(kron(Ay/dy^2,speye(nx)) + kron(speye(ny),Ax/dx^2));
D = (size(D,1)+1) * (size(D,1)+1); clear D_x D_y;
% Other initial values
C_eff(1)=C0;
Qt_0(:, :)=0; % C/cm^3-electrode; Initial charge density at time step n=1
Count_C = zeros(Nt,1); % Iteration number for the concentration matrix for the last current matrix iteration at each time step
Count_Q = zeros(Nt,1); % Iteration number for the current matrix at each time step
Error_Q = 0; % error of the charge iterative loop
flag_0=1; % flag for the current convergence loop
flag_1=1; % flag for the concentration convergence loop
flag_3=0; % flag for adjusting the concentration convergence loop
flag_4=1; % flag for the technique after charging
flag_5=1; % flag for the technique after discharging
flag_6=1; % flag for ocv study
flag_7=0; % flag for iterative time step
flag_8=0; % flag for iteration loops
Cycle_number=1;
n_r=1;
ind_B=(1:size(D,1))';
ind_B1=circshift(ind_B,1);
ind_B0=circshift(ind_B,-1);
err=zeros(500,1);
Vt_1=zeros(4,1);

% Calculate the initial charge storage and Donnan layer potential
Qt_mi(1:xmax_pos,:) = -Qt_e(1:xmax_pos,:) - Q_fix_pos;
Qt_mi(xmin_neg+1:end,:) = -Qt_e(xmin_neg+1:end,:) - Q_fix_neg;
V_D(x_ind,:)=-asinh(Qt_mi(x_ind,:)/R_Micro*10^6/F/2./(C0)/exp(uatt)); % non-dimentional Donnan layer potential
VV_0(x_ind,:)=V_D(x_ind,:)*25.7+Qt_e(x_ind,:)/C_Measured/M_e*1000; % mV, electrode polarization
C_mi_1(x_ind,:)=2*(C0)*exp(uatt).*cosh(V_D(x_ind,:)); % mmol-L micropores
C_eff_0 = C0;
C_mix_0 = C0;

% Calculate the initial voltage distribution
V_N(xmin_neg+1:xmax_neg,1)=A1*(Ri_M(xmin_neg+1:xmax_neg,1).*I_Ri(xmin_neg+1:xmax_neg,1))+Oe*I_y(1)-VV_0(xmax_neg,1); % lIquid potential across one electrode when the cathod is grounded
V_N(xmax_pos+1:xmin_neg,1)=A2*Ri_M(xmax_pos+1:xmin_neg,1).*I_y(1)+V_N(xmin_neg+1,1); % liquid across Flow channel
V_N(1:xmax_pos,1)=A1*(Ri_M(1:xmax_pos,1).*I_Ri(1:xmax_pos,1))+V_N(xmax_pos+1,1); % lIquid across one electrode
Vt (1,1)=V_N(1,1)+I_y(1)*Oe+VV_0(1,1); % mV, voltage in the solution
Vt (1,2)=R_contact*J; % mV, voltage due to the resistance of two IEMs and external resistance
Vt (1,3)=0; % mV, membrane Donnan potential
Vt (1,4)=sum(Vt(1,1:3)); % mV, Cell voltage

%% Main time loop
for n=2:1:Nt % time step n
    flag_7=0; % reset flag_7
    C_0=C_1; % update concentration field
    C_mi_0=C_mi_1; % update micro-pores ionic concentration field
    Qt_0=Qt_1; % update charge density field
    T0=T1; % update time
    while flag_7==0; % adaptive time loop
        flag_8=0; % reset flag 8
        C_0=C_1; % update concentration field
        C_mi_0=C_mi_1; % update micro-pores ionic concentration field
        Qt_0=Qt_1; % update charge density field
        T0=T1; % update time
        while flag_7==0; % adaptive time loop
            flag_8=0; % reset flag 8
            flag_0=1; % reset flag_0 for the current while loop
            flag_3=0; % reset flag_3
            T1=T0+dt;

            % guess electric charge density based on the information at the
            % previous time step
            Qt_e(:, :) = Qt_0(:, :) + II_0(:, :) * dt / 10^3 / V_i; % C/cm^3-electrode
            Count_Q(n) = 0;
            while flag_0==1 % charge density iterative loop
                flag_1=1; % reset flag_1 for the concentration while loop
                % guess Ce* based on the calculated charge efficiency at time
                step n-1
                C_i=C_0;
                Count_C(n) = 0;
                while flag_1==1 % concentration iterative loop
                    % Solve for total ionic charge density in the micropores
                    Qt_mi(1:xmax_pos,:) = -Qt_e(1:xmax_pos,:) - Q_fix_pos;
                    Qt_mi(xmin_neg+1:end,:) = -Qt_e(xmin_neg+1:end,:) -
                    Q_fix_neg;
                    V_D(x_ind,:) =
                        asinh(Qt_mi(x_ind,:)/R_Micro*10^6/F/2./(C_0(x_ind,:))/exp(uatt)); % non-dimentional Donnan layer potential
                    VV_0(x_ind,:) = V_D(x_ind,:) * 25.7 + Qt_e(x_ind,:) / C_Measured / M_e * 1000; % mV, electrode polarization
                    C_mi_1(x_ind,:) = 2 * (C_0(x_ind,:)) * exp(uatt) .* cosh(V_D(x_ind,:)); % mmol-L micropores

                    % Solve for new Ce including the effect of diffusion
                    (implicit, forward time, CN in diffusion, upwind explicit in advection)
                    C_i=C_1;
                    C_i(x_ind,:) = R_Macro*C_0(x_ind,:) - (C_mi_1(x_ind,:)-
                        C_mi_0(x_ind,:))/2*R_Micro;
                    C_i(FC_ind,:) = R_FC*C_0(FC_ind,:);
                    C_i(FC_ind,2:end) = C_i(FC_ind,2:end) + v_FC*dt/dy*(C_0(xmax_pos+1:xmin_neg,indy_1(2:end))-C_0(xmax_pos+1:xmin_neg,indy(2:end)));
                    C_i(FC_ind,1) = C_i(FC_ind,1) + v_FC*dt/dy*(C_0-
                        C_0(xmax_pos+1:xmin_neg,1));
                    C_i = reshape(C_i + bc,[],1);
                    C_i = D\C_i;
                    C_i = reshape(C_i,nx,ny);

                    % check for convergence
\[
\text{err}(\text{Count}_C(n)+1,1) = \max(\max(\text{abs}(C_1-C_{1,1})./C_1));
\]

\[
\text{if} \ \text{err}(\text{Count}_C(n)+1,1)<10^{-7};
\]

\[
\begin{align*}
\text{flag}_1 &= 0; \\
\text{flag}_8 &= 1; \\
C_{1,1} &= C_1;
\end{align*}
\]

\[
\text{end}
\]

\[
\text{Count}_C(n) = \text{Count}_C(n)+1;
\]

\[
\text{end}
\]

\[
\%	ext{ update the current and voltage distribution}
\]

\[
\text{Cond}_M(:,:,1) = 2 * D_{NaCl} * C_1(:,:,1)/\text{KB}/\text{Temp}/1000000 * F * e * R_e^{1.5};
\]

\[
\% \text{ S/cm conductivity matrix}
\]

\[
\text{Cond}_M(x_{\text{max},\text{pos}}+1:x_{\text{min},\text{neg}},:) = 2 * D_{NaCl} * C_1(x_{\text{max},\text{pos}}+1:x_{\text{min},\text{neg}},:)/\text{KB}/\text{Temp}/1000000 * F * e * R_{FC}^{1.5};
\]

\[
\% \text{ S/cm conductivity matrix}
\]

\[
\text{Cond}_M(x_{\text{max},\text{pos}}+1:x_{\text{min},\text{neg}},:) = 2 * D_{NaCl} * C_1(x_{\text{max},\text{pos}}+1:x_{\text{min},\text{neg}},:)/\text{KB}/\text{Temp}/1000000 * F * e * R_{FC}^{1.5};
\]

\[
\% \text{ S/cm conductivity matrix}
\]

\[
\text{R}_i_M(:,:,1) = 1./\text{Cond}_M(:,:,1) * dx/dy/W_{FC};
\]

\[
\% \text{ ohm, resistance matrix}
\]

\[
\text{R}_i_S(:,:,1) = \text{sum}(\text{R}_i_M(x_{\text{max},\text{pos}}:x_{\text{min},\text{neg}},:));
\]

\[
\% \text{ calculate the current distribution in the electrode}
\]

\[
\text{M}_i(1:(ny+1):(end-ny)) = \text{R}_i_S(1:(end-1));
\]

\[
\text{M}_i((ny+1):(ny+1):end) = -\text{R}_i_S(2:end);
\]

\[
\text{S}_i = \text{sparse}(\text{M}_i);
\]

\[
\text{B}_i(1:end-1) = \text{VV}_0(x_{\text{max},\text{pos}},indy_0(1:(end-1)))-\text{VV}_0(x_{\text{min},\text{neg}},indy_0(1:(end-1)))-\text{VV}_0(x_{\text{max},\text{pos}},1:(end-1))+\text{VV}_0(x_{\text{min},\text{neg}},1:(end-1));
\]

\[
\text{B}_i(1:end-1) = \text{I};
\]

\[
\text{B}_i(end) = \text{I};
\]

\[
\text{I}_y = \text{S}_i \text{B}_i;
\]

\[
\% \text{ solve the current distribution in the y-direction}
\]

\[
\%	ext{ calculate the leakage current}
\]

\[
\text{IL}(1:x_{\text{max},\text{pos}},:) = a_{\text{ele}*}\text{I}^0_{\text{C}*V_i}*\exp(a_{\text{C}/\text{RT}_F}*(\text{VV}_0(1:x_{\text{max},\text{pos}},:)/1000+E_{\text{An},C});
\]

\[
\% \text{ VB model}
\]

\[
\%	ext{IL}(1:x_{\text{max},\text{pos}},:) = 0; \% \text{ no leakage current}
\]

\[
\%	ext{ Update the current distribution in the anode}
\]

\[
\text{II}_1(1:2:x_{\text{max},\text{pos}},:) = -(\text{IL}(1:x_{\text{max},\text{pos}}-1,:),:)+\text{VV}_0(index_0(2:x_{\text{max},\text{pos}}-1,:),);/\text{Oe}+\text{R}_i_M(index_2(2:x_{\text{max},\text{pos}}-1,:),:)-\text{VV}_0(index_0(2:x_{\text{max},\text{pos}},:),:);/\text{Oe}+\text{R}_i_M(index_2(2:x_{\text{max},\text{pos}}-1,:),:));
\]

\[
\%	ext{II}_1(1,:) = \text{IL}(1,:)+\text{VV}_0(0,;)-\text{VV}_0(1,:)]/\text{Oe}+\text{R}_i_M(1,:));
\]

\[
\text{II}_1(\text{xmax},:,:) = \text{I}_y'-\text{sum}(\text{II}_1(1:x_{\text{max},\text{pos}}-1,:));
\]

\[
\%	ext{ calculate the current distribution in the Cathode}
\]

\[
\%	ext{IL}(x_{\text{min},\text{neg}}+1:x_{\text{max},\text{neg}},:) = 0; \% \text{ no leakage current}
\]

\[
\text{IL}(x_{\text{min},\text{neg}}+1:x_{\text{max},\text{neg}},:) = -\text{IL}_0_{2V_i}/(1-\exp((\text{VV}_0(x_{\text{min},\text{neg}}+1:x_{\text{max},\text{neg}},:)/1000+E_{\text{Ca},E_{\text{half}}}/\text{RT}_F));
\]

\[
\%	ext{ Limiting current model}
\]
\[
\% IL(x_{min\_neg+1: xmax\_neg, :}) = a_{ele}\times I_0_{O2}\times V_i\times (\exp(a_{O2}/RT_F\times(VV_0(x_{min\_neg+1: xmax\_neg, :})/1000+E_{0\_Ca}-E_{0\_O2})) - \exp(-a_{O2}/RT_F\times(VV_0(x_{min\_neg+1: xmax\_neg, :})/1000+E_{0\_Ca}-E_{0\_O2}))); \\
\% BV model
\]

\[
% update the current distribution in the cathode \\
I_1(x_{min\_neg+2:end\_neg-1,:}) = -IL(x_{min\_neg+2:end\_neg-1,:}) + (VV_0(indx_1(x_{min\_neg+2:end\_neg-1,:})))/(Oe + Ri_M(indx_1(x_{min\_neg+2:end\_neg-1,:}))) - (VV_0(indx(x_{min\_neg+2:end\_neg-1,:})))/(Oe + Ri_M(indx(x_{min\_neg+2:end\_neg-1,:}))); \\
II_1(end,:) = -IL(end,:) + (VV_0(end,:))/(Oe + Ri_M(end,:)); \\
II_1(x_{min\_neg+1,:}) = -I_y' - sum(II_1(x_{min\_neg+2:end,:})) - sum(IL(x_{min\_neg+1:end,:})); \\
% Calculate the charge density \\
Qt_1(:,:, :) = Qt_0(:,:, :) + (II_0(:,:, :) + II_1(:,:, :))/2/1000/V_i*dt; \\
% Check for convergence \\
Error_Q = max(max(abs(Qt_1 - Qt_e))); \\
if (Error_Q<10^{-7} || Count_Q(n)>200) && flag_8==1; \\
flag_0=0; \\
flag_7=1; \\
II_0=II_1; \\
else \\
Qt_e=Qt_1; \\
end \\
Count_Q(n) = Count_Q(n)+1; \\
end \\
\]

\[
C_{eff\_1} = mean(C_1(x_{max\_pos+1:x min\_neg, ny})); \\
C_{mid} = (C_{eff\_1} + C_{eff\_0})/2; \\
C_{mix\_1} = C_{mid} - (C_{mid} - C_{mix\_0})\times\exp(-k_{mix}dt); \\
C_{eff\_0} = C_{eff\_1}; \\
C_{mix\_0} = C_{mix\_1}; \\
% Calculate the voltage distribution \\
Vt_1(1) = VV_0(x_{min\_neg+1:end}) + I_y(end)\times Ri_S(end) + VV_0(x_{max\_pos, end}); \quad \% mV, \\
voltage in the solution \\
Vt_1(2) = R_{contact}/A_{FC}\times I; \quad \% mV, voltage due to the resistance of two IEMs and external resistance \\
Vt_1(3) = 0; \quad \% mV, Donnan potential \\
Vt_1(4) = sum(Vt_1(1:3)); \\
\]

\[
% check if cell voltage reaches the maximum voltage limit \\
if Vt_1(4)>V_{max} && flag_4==1; \\
I=-1; \\
Discharge_index(Cycle_number)=n_r; \\
flag_4=0; \\
flag_5=1; \\
end \\
\]

\[
% check if cell voltage reaches the minimum voltage limit \\
if Vt_1(4)<0 && flag_5==1 && n_r>100 \\
I=-1; \\
\]

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Cycle_number=Cycle_number+1
Cycle_index(Cycle_number)=n_r;
flag_5=0;
flag_4=1;
end

% check for data storage
if T1-T_r(n_r)>=dt_record
    n_r=n_r+1;
    T_r(n_r)=T1;
    C_eff(n_r)=C_eff_1;
    C_eff_mix(n_r)=C_mix_1;
    Vr(n_r,:)=Vr_1(:,);
    C_re(:,:,n_r)=C_1(:,);
    II_re(:,:,n_r)=II_1(:,);
    Q_mi_re(:,:,n_r)=Qt_mi;
    IL_re(:,:,n_r) = IL;
end

% check if the maximum cycle limits is reached
if Cycle_number==Cycle_limit;
    %I=0;
    flag_6=0;
    break
end

%%%post-treatment, save data in file
filename = sprintf('CDI_2D_target_effluent_%icm_%imV_%imM_amph_D_%iA_%iFg_%iC_%s.mat',L_FC, V_max,C0,int32(J*10),C_Measured,Q_fix_pos,date);
save(filename,'Vol_FC','V_max','n_r','T_r','II_re','C_re','C_eff','C_eff_mix','Vr','Q_mi_re','Cycle_index','Discharge_index','L_FC','Q_FC','J','A_FC','dx','dy','Batch_index','B_number','IL_re','C_Measured','Q_fix_pos','Q_fix_neg','k_mix')
toc
APPENDIX B: Simulation Tool on NanoHub

The above code is embedded in a simulation tool published on the NanoHub (nanohub.org). This tool was developed using the Rappture API to provide an intuitive way of using the program without coding background. People who do not have Matlab installed can access to this tool on the NanoHub under the name of “CDI_simulation_tool”.

Figure 30. Snapshot of the control panel of the CDI simulation tool on NanoHub.

The program interface of the current version of the simulation tool is shown in Figure 30. On the left side, users can adjust the modeling parameters for a conventional flow-by CDI cell operated under constant current and continuously-flow with fixed influent concentration. Users have the freedom to change modeling parameters regarding cell operation, cell design, leakage current, electrode surface immobile charges, and numerical computations. The simulation normally takes a few hours to complete depending on the simulation test conditions. During simulation, the right side of the panel outputs the simulated cell cycling time, cell voltage, and effluent concentration in real time. Once the simulation is done, the evolution of cell voltage and effluent concentration are
plotted on the right panel. Users can download these figures and the raw data as a csv file.