Energy breakdown in capacitive deionization

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ABSTRACT

We explored the energy loss mechanisms in capacitive deionization (CDI). We hypothesize that resistive and parasitic losses are two main sources of energy losses. We measured contribution from each loss mechanism in water desalination with constant current (CC) charge/discharge cycling. Resistive energy loss is expected to dominate in high current charging cases, as it increases approximately linearly with current for fixed charge transfer (resistive power loss scales as square of current and charging time scales as inverse of current). On the other hand, parasitic loss is dominant in low current cases, as the electrodes spend more time at higher voltages. We built a CDI cell with five electrode pairs and standard flow between architecture. We performed a series of experiments with various cycling currents and cut-off voltages (voltage at which current is reversed) and studied these energy losses. To this end, we measured series resistance of the cell (contact resistances, resistance of wires, and resistance of solution spacers) during charging and discharging from voltage response of a small amplitude AC current signal added to the underlying cycling current. We performed a separate set of experiments to quantify parasitic (or leakage) current of the cell versus cell voltage. We then used these data to estimate parasitic losses under the assumption that leakage current is primarily voltage (and not current) dependent. Our results confirmed that resistive and parasitic losses respectively dominate in the limit of high and low currents. We also measured salt adsorption and report energy-normalized adsorbed salt (ENAS, energy loss per ion removed) and average salt adsorption rate (ASAR). We show a clear tradeoff between ASAR and ENAS and show that balancing these losses leads to optimal energy efficiency.

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1. Introduction

Energy has traditionally been the dominant cost component for many desalination systems such as those applying distillation, which is highly energy intensive (Anderson et al., 2010). Reverse osmosis (RO) has dramatically reduced the energy requirements for desalination, with modern systems achieving roughly 50% energy efficiency for treating seawater based on the thermodynamic ideal free energy of mixing (Elimelech and Phillip, 2011). However, RO fares significantly worse for water with lower concentrations of dissolved solids, such as brackish water, where it only reaches 10% or less efficiency (Shrivastava et al., 2014). RO forces all treated water through the active membrane, with energy losses (and plant size) roughly corresponding to the total throughput of the plant.

Capacitive deionization (CDI) is a method of desalination that directly acts on the ions in solution and sequesters them into electric double layers leaving purified water, which is flushed from the cell. CDI has been investigated in various forms for over 50 years (Blair and Murphy, 1960; Johnson and Newman, 1971), but has recently seen a rapid increase in activity. Because the ions themselves are directly targeted, the energy consumption of this technique largely scales with the amount of salt removed (i.e. throughput times input concentration). This scaling promises higher energy efficiency for CDI compared to competing technologies when treating waters with lower dissolved solid concentrations than seawater (e.g. brackish water) (Zhao et al., 2013). There are a variety of operational parameters that can be tuned for CDI, including time dependence of charging voltage or current, level of cell charging (i.e. final cell voltage), and flow rate. The choice of these can dramatically influence the energy efficiency achieved in operation, and a consistent framework for determining optimal conditions for operation of CDI cells is still lacking.

We note that electric double layer capacitors, or supercapacitors, rely on very similar physics to CDI and have been optimized to maximize charge/discharge cycle efficiency and energy storage.
density. A number of studies have looked at the loss mechanisms present in supercapacitors (Conway, 2013), including series resistance (Conway and Pell, 2002; Yang and Zhang, 2013), charge redistribution loss, and parasitic reaction loss (Ike et al., 2016). However, the design and operational regimes of supercapacitors are very different than CDI. Importantly, there is generally no electrolyte flow, and organic solvent based, high concentration electrolytes are commonly used to achieve high operating voltage windows and minimize resistance. The goal of supercapacitor operation is solely the storage and recovery of energy. Further, supercapacitors are often applied in high current applications, and this requires a focus on series resistive losses. This focus has led to substantial supercapacitor optimization and sub-milliOhm equivalent series resistances are commonly achieved (Yu et al., 2013).

The promise of CDI for energy efficient processing of lower concentration inlet feeds has led to a number of studies concerning energy loss (Alvarez-Gonzalez et al., 2016; Choi, 2015; Demirer et al., 2013; Dykstra et al., 2016; García-Quismondo et al., 2015; García-Quismondo et al., 2013; Kang et al., 2014; Zhao et al., 2012a). These have generally focused on the total energy loss of the process, which is useful for comparison with different technologies or among different CDI designs, but provides little insight for optimizing CDI operation or refining current CDI designs. One element that has been studied in some detail is the choice of operation of CDI cells with constant current charging versus constant voltage charging (Choi, 2015; Kang et al., 2014; Zhao et al., 2012a). Constant current operation generally leads to superior energy performance with energy usage reduced by up to 30% (Kang et al., 2014), and some studies have dealt with the specific mechanisms of loss operative in CDI. Alvarez-Gonzalez et al. (2016) developed a simple model accounting for resistive and parasitic losses consisting of series and parallel resistances and parameterized this model using experimental data. They then optimized cell geometry and charging current in terms of cell energy loss using this model and showed good agreement with experiments. Detailed studies have also been conducted on the series resistance of CDI cells, e.g. (Qu et al., 2015). Improved understanding of the constituent energy loss mechanisms in CDI offers the opportunity for more efficient operation of existing cells and improved future designs, and hence, motivates this work.

Here, we experimentally quantify the specific energy loss mechanisms operative during CDI with constant current charging. These mechanisms separate roughly into those dominant at high or low charging currents. The mechanisms dominant at high currents motivate slow charging of the cell. We attribute these losses mostly to resistive dissipation during charge and discharge and, to a lesser degree, redistribution of accumulated charge within electrodes. We perform in situ, real-time measurements of cell series resistance as a function of charging current and time within the charging phase. The dominant losses at low charging currents, corresponding to parasitic currents in the cell, prompt acceleration of the charge phase and a reduction of charge time. We perform an independent set of constant voltage experiments to measure parasitic currents vs. cell voltage. We characterize both loss categories over a broad operational parameter space and show that balancing these losses leads to optimal energy efficiency. Total salt removed per cycle is another key parameter for CDI operation. We define two figures of merit (FOMs) relevant for practical CDI operation and plant design, salt removed per unit time and salt removed per unit energy. These provide quantitative metrics for evaluating tradeoffs between operational requirements (e.g. throughput vs. energy efficiency). We also provide relations for the investigated CDI cell identifying regimes of charging current and maximum cell voltage which allow a balance between cell throughput and energy efficiency as quantified by the product of salt removal rate and salt removed per unit energy.

2. Materials and methods

2.1. CDI cell design

Fig. 1a shows a schematic of our radial flow-between CDI (fbCDI) cell. We fabricated the cell using five pairs of activated carbon electrodes (two of which are shown here) with 6 cm diameter and 270 μm thickness and total dry mass of 4.3 g. The electrode material (Materials & Methods, PACMM™ 203, Irvine, CA) has been used and characterized for CDI applications extensively and is well described (Biesheuvel et al., 2016; Dykstra et al., 2016; Zhao et al., 2012a,b). We stacked the electrodes between 130 μm thick circular shaped titanium sheets, which acted as current collectors (total of six sheets). Each current collector had a tab section (1 x 5 cm) for connection to external wires (c.f. Fig. 1a). All the electrodes and

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{in}$</td>
<td>Energy input to the cell during charging (J)</td>
</tr>
<tr>
<td>$E_{out}$</td>
<td>Energy recovered during discharging (J)</td>
</tr>
<tr>
<td>$P_{R_{in}}$</td>
<td>Resistive energy loss during charging (J)</td>
</tr>
<tr>
<td>$P_{R_{out}}$</td>
<td>Resistive energy loss during discharging (J)</td>
</tr>
<tr>
<td>$P_{NS_{in}}$</td>
<td>Resistive loss due to series resistances during charging (J)</td>
</tr>
<tr>
<td>$P_{NS_{out}}$</td>
<td>Resistive loss due to series resistances during discharging (J)</td>
</tr>
<tr>
<td>$P_{P_{in}}$</td>
<td>Parasitic energy loss during charging (J)</td>
</tr>
<tr>
<td>$P_{P_{out}}$</td>
<td>Parasitic energy loss during discharging (J)</td>
</tr>
<tr>
<td>$E_{cap}$</td>
<td>Stored energy in the cell (J)</td>
</tr>
<tr>
<td>$V_{ext}$</td>
<td>External voltage measured via sourcemeter (V)</td>
</tr>
<tr>
<td>$V_{max}$</td>
<td>Maximum allowable external voltage (V)</td>
</tr>
<tr>
<td>$V_{cap}$</td>
<td>Equivalent capacitance voltage, $V_{ext} + l_0 R(t)$ (V)</td>
</tr>
<tr>
<td>$\Delta V_{cap}$</td>
<td>Maximum range of $V_{cap}$, defined as $V_{cap,max} - V_{cap,min}$ (V)</td>
</tr>
<tr>
<td>$l_0$</td>
<td>External current magnitude applied to the cell (mA)</td>
</tr>
<tr>
<td>$C$</td>
<td>CDI cell capacitance (F)</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Series resistance, including wires, interfacial electrode-current collector resistance, and solution resistance in spacer and pores (Ω)</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Parallel resistance responsible for parasitic losses (Ω)</td>
</tr>
<tr>
<td>$t_{charge}$</td>
<td>Charging time (s)</td>
</tr>
<tr>
<td>$t_{cycle}$</td>
<td>Cycle time (s)</td>
</tr>
<tr>
<td>$\tau_{RC}$</td>
<td>RC time scale of the cell (s)</td>
</tr>
<tr>
<td>$c_0$</td>
<td>Influent salt concentration (mM)</td>
</tr>
<tr>
<td>$Q$</td>
<td>Flow rate (ml min⁻¹)</td>
</tr>
<tr>
<td>$I_{ads}$</td>
<td>Salt adsorption during charging (μmole)</td>
</tr>
<tr>
<td>ASAR</td>
<td>Average salt adsorption rate ($I_{ads}/N_A t_{cycle}$) (μmole cm⁻² min⁻¹)</td>
</tr>
<tr>
<td>ENAS</td>
<td>Energy-normalized adsorbed salt ($I_{ads}/(E_{in}−E_{out})$) (μmole J⁻¹)</td>
</tr>
</tbody>
</table>
current collectors (except the “book end” electrode and current collector on top of the stack) had a 5 mm diameter opening at their center for the flow passage. We used 420 μm thick non-conductive polypropylene mesh (McMaster-Carr, Los Angeles, CA) between each electrode pair as spacers. We cut the spacers in circles slightly larger (~4 mm) than electrodes and current collectors to prevent electrical short circuit. This assembly was then housed inside a CNC-machined acrylic clamshell structure and sealed with O-ring gaskets and fasteners (not shown here). Flow paths are indicated with arrows in Fig. 1a. Feed water enters the cell via a 5 mm diameter inlet port in the upper clamshell and is radially distributed to the outer surfaces of the stack within the header. Feed solution then flows radially inward (toward the center of the stack) through the spacers and between the electrodes. This radial flow empties down into the vertical flow channel and exits via an outlet port in the lower clamshell.

2.2. Energy pathway in CDI

The schematic of Fig. 1b shows the energy pathway in a typical CDI cell. To understand this, we first note that the goal in any CDI system is to increase the potential energy of electrode stack from its base level, and consequently, attract ionic species to the electrodes with electrostatic forces. This is done by transferring electrons to the cell through an external voltage and/or current source. This input energy is denoted as $E_{in}$ in Fig. 1b. However, not all transferred potential energy is used for ionic charge storage (capacitive energy, or $E_{cap}$), as there are various loss mechanisms during the charging process. Namely, resistive and parasitic energy losses, denoted respectively as $E_{in}^{R}$ and $E_{in}^{P}$ in Fig. 1b. The charging process continues until one or more charging criteria are met, such as a specified maximum cell voltage or a pre-set amount of transferred electronic charge. Then the regeneration or discharge process starts and gradually lowers the stack’s potential energy level to its base level. The extractable or recoverable energy ($E_{out}$), however, is smaller than $E_{cap}$, as there are resistive and parasitic energy losses in discharge process as well ($E_{out}^{R}$ and $E_{out}^{P}$ respectively).

We emphasize that $E_{in}$ is the total electrical energy input during charging. We measure $E_{in}$ as the (unsigned) magnitude area under the voltage versus time curve during charging multiplied by the current during charging. As we shall describe, we measure $E_{out}$ as the (unsigned) magnitude area under the voltage versus time curve during discharge multiplied by the current during discharge. A portion of $E_{in}$ is dissipated (by internal resistance and parasitic reaction losses) and the rest of $E_{in}$ is stored as capacitive energy. The energy loss in the entire charge and discharge phase is thus equal to $E_{in} - E_{out}$. The following two equations can then describe the energy pathway in CDI systems.

$$E_{in} - E_{out} = (E_{in}^{R} + E_{in}^{P}) + (E_{in}^{P} + E_{out}^{P})$$  \hspace{1cm} (1)

$$E_{cap} = E_{in} - (E_{in}^{R} + E_{in}^{P})$$  \hspace{1cm} (2)

We further define resistive loss during charging and discharging as

$$E_{in}^{R} = E_{in}^{R,NS} + E_{in}^{R,S} = E_{in}^{R,NS} + \int_{0}^{t_{charge}} I^{2}R_{s}(t) \, dt,$$  \hspace{1cm} (3)

$$E_{out}^{R} = E_{out}^{R,NS} + E_{out}^{R,S} = E_{out}^{R,NS} + \int_{t_{charge}}^{T} I^{2}R_{s}(t) \, dt,$$  \hspace{1cm} (4)

where $E_{in}^{R,NS}$ and $E_{in}^{R,S}$ are series resistive loss during charging and discharging, respectively. Series resistance here corresponds to contact resistance, ionic resistance of solution in separators, and resistance of wires. Similarly, $E_{out}^{R,NS}$ and $E_{out}^{R,S}$ are energy loss due to network of distributed ionic resistance of solution inside the electrode pores during charging and discharging. Superscript NS stands for non-series resistance. We here will neglect the resistances of the electrode matrix as this tends to be negligible in CDI (e.g., compared to ionic resistance in electrodes) (Dykstra et al., 2016; Qu et al., 2015).

We separated resistive loss contributions into series and non-series resistances because of their distinct behavior, as described in the following. The equivalent circuit of a CDI cell can be described as a network of resistors and non-linear capacitors (Qu et al., 2015; Suss et al., 2013). Some of these resistors are electrically in series and others are parallel to capacitors. The series resistors include the external lead resistances, the current collector, and the non-series resistance associated with the electrolyte inside the pores of the (porous dielectric) spacers. The voltage (current) response of these series resistors to rapid changes in current (voltage) can be assumed to be instantaneous. In contrast, the distributed resistor/capacitor network of the porous CDI cell electrodes have significant characteristic RC (resistance-capacitance) time delays associated with charging (order 10's of seconds or greater for significant penetration of charge into the electrode). As a result, due to its fast time response, series resistances can be measured at each time during charging and discharging (c.f. Section 3.2), while it is not feasible to directly measure values of $E_{in}^{R,NS}$ and $E_{out}^{R,NS}$ in situ and independently. We therefore directly measure series resistive loss (c.f. Section 3.2) and also quantify parasitic loss with a separate experiment. We then use Eq. (1) to calculate the sum of non-series resistive loss for the charging and discharge phases ($E_{in}^{P} + E_{out}^{P}$). In this paper, we perform a series of experiments to distinguish contribution of different loss mechanisms (resistive and parasitic mechanisms) and study energetic performance in CDI.

2.3. Experimental procedure

The experimental setup consisted of our fBCDI cell (c.f. Section 2.1.), a 3 L reservoir filled with 50 mM potassium chloride (KCl) solution, a peristaltic pump (Watson Marlow 120U/DV, Falmouth, Cornwall, UK), a sourcemeeter (Keithley 2400, Cleveland, OH), and a
flow-through conductivity sensor (eDAQ, Denistone East, Australia). We used KCl to approximate a univalent, binary, and symmetric solution. We operated our cell at constant current (CC) charging and discharging to study the energy budget introduced in Section 2.2. We used a fixed flow rate of 2 mL min⁻¹ with closed-loop circulation in all of our experiments (flow from reservoir to cell and back to reservoir). This is equivalent to normalized loop circulation in all of our experiments (condition, in which salt adsorption during charging is equal to discharge cycles). This ensured the dynamic steady state (DSS) working voltage because of considerable resistive voltage drop. For each current, we charged the cell to 0 V. Higher currents had necessarily narrower discharge current and limit voltage of \(3.1\). Voltage profile and energy breakdown

### 3. Results and discussion

#### 3.1. Voltage profile and energy breakdown

Fig. 2a shows voltage profiles of our cell vs. time with 200 mA charge/discharge current and limit voltage of \(V_{\text{max}} = 1.2\) V and 2 mL min⁻¹ flow rate (under DSS condition). Solid curve shows voltage measured by the sourcemeter and denoted as \(V_{\text{ext}}\). Dashed curve corresponds to underlying “equivalent capacitance” voltage \(V_{\text{cap}}\), the total voltage difference across the electrodes excluding voltage drop across the series resistance. We term this \(V_{\text{cap}}\) as an analogy to the equivalent RC circuit shown as an inset in Fig. 2a and we define it as \(V_{\text{ext}} - I_0 R_{\text{p}}\) or \(V_{\text{ext}} - I_0 R_{\text{p}}\), respectively during charging and discharging \((R_{\text{p}}\) and \(I_0\) being series resistance and external current magnitude). The instantaneous rise/drop in \(V_{\text{cap}}\) shown in Fig. 2a is because of series resistance and is equal to \(2 R_{\text{p}} I_0\). The prefactor 2 is consistent with the reversal of current at the start of charging or discharging. \(V_{\text{cap}}\) also exhibits a small, abrupt drop after current reversal as well. We hypothesize the latter effect is due to charge redistribution in the porous carbon electrodes, which has been observed in transmission line (Black and Andreas, 2010, 2009) and high-fidelity models (Hemmatifar et al., 2015; Rica et al., 2013) of CDI as well as in experiments (Drugojecki and van der Wal, 2013; Pell et al., 2000). We refer the reader to Fig. S.1 of the SI for plots of voltage measurements at other experimental conditions.

In Fig. 2b, we show power input/generation of our fbCDI cell under the same conditions as those of Fig. 2a. This plot is generated by multiplying \(V_{\text{ext}}\) and \(V_{\text{cap}}\) by external current \(I_0\). Positive \(I_0\) \(V_{\text{ext}}\) values correspond to power transferred to the cell and negative \(-I_0\) \(V_{\text{ext}}\) values are power generated by the cell—power which can ideally (in the limit of perfect transfer efficiency) be stored or used. Shaded regions show total input \((E_{\text{in}}^P)\) and output (recovered) energy \((E_{\text{out}})\) of the cell. Diagonal and vertical hatched areas are respectively measured series resistive loss \((E_{\text{RS}}^P\) and \(E_{\text{RS}}^o\)) and parasitic loss \((E_{\text{IP}}^P\) and \(E_{\text{IP}}^o\)) during charging and discharging. We calculated series resistive loss using in-situ, in-line measurement of series resistance (c.f. Section 3.2 for more information). Further, we measured parasitic energy loss through an independent set of constant voltage experiments. We hypothesize that the parasitic loss is primarily due to leakage currents associated with Faradaic reactions at electrodes. To this end, we charged the cell to fixed external voltage between 0.1 and 1.2 V (with 0.1 V increments) for 25 min each and monitored the current via sourcemeter. We attribute the remaining current at 25 min \((>10\) \(I_{\text{RC}}\) with \(I_{\text{RC}}\) being the RC time scale of our cell at the beginning of charging phase) mainly to the parasitic current \(I_{\text{p}}\) at that voltage. We show the parasitic current vs. capacitance voltage \((V_{\text{cap}})\) in the inset of Fig. 2b. We further made the assumption that parasitic
current is only a function of voltage (not applied current) and used the relations below to calculate parasitic energy loss.

\[ E_{in}^{p} = \int_{0}^{t_{charge}} I_{p} V_{cap} \, dt \text{ and } E_{out}^{p} = \int_{0}^{t_{cycle}} I_{p} V_{cap} \, dt \]  
(5)

Note, as a visual aid, we have exaggerated the magnitudes of \( E_{in}^{p} \) and \( E_{out}^{p} \) in Fig. 2b (although Fig. 2a is actual experimental data to scale).

3.2. In-situ series resistance measurement

We performed in-situ, on-the-fly measurement of series resistance of the cell \( R_s \) by sampling voltage response to a mid-frequency (~10 Hz), small-amplitude (2 mA) AC current signal on top of the charging or discharging DC current \( I_0 \). We measured \( R_s \) by dividing the measured voltage amplitude by current amplitude (c.f. Fig. S.4 of the SI). \( R_s \), as mentioned before, includes interfacial contact resistance and resistance of solution in spacers as well as external wires. For more information about resistance characterization refer to Section 3.3 of the SI.

In Fig. 3, we show the results of series resistance measurements vs. capacitance voltage difference \( \Delta V_{cap} \) for currents of 25–300 mA and fixed limit voltage of \( V_{max} = 1.2 \) V. We define capacitance voltage difference as maximum variation of capacitance voltage during a full cycle. \( \Delta V_{cap} \) is defined as \( V_{cap, max} - V_{cap, min} \). Each data point in each loop is an average of at least two measurements in two consecutive cycles under DSS conditions. The upper (lower) half of the loops corresponds to series resistance in the charging (discharging) process (see arrows in Fig. 3). As can be seen here, \( R_s \) in the charging step is greater than that in the discharging step. This is because salt is removed from the spacers during charging. Cell operation under high currents therefore leads to greater asymmetry in resistance plots. This is expected, as charging with high currents removes a considerable portion of influent salt, which in turn, increases solution resistance in the spacer. As an example, Fig. S.2 of the SI shows more than 80% salt removal at 100, 150, 200, and 300 mA currents and \( V_{max} = 1.2 \) V (each loop corresponds to a fixed current). At low currents, \( R_s \) does not vary considerably throughout the cycle, while it varies more strongly at high currents due to significant salt removal. The inset presents series resistance data vs. time (normalized by cycle time \( t_{cycle} \)) for one cycle.

![Fig. 3. Measured series resistance vs. \( \Delta V_{cap} \) during charging and discharging for 25, 50, 100, 150, 200, and 300 mA currents and \( V_{max} = 1.2 \) V (each loop corresponds to a fixed current). At low currents, \( R_s \) does not vary considerably throughout the cycle, while it varies more strongly at high currents due to significant salt removal. The inset presents series resistance data vs. time (normalized by cycle time \( t_{cycle} \)) for one cycle.](image)

3.3. Energy losses in CDI

In Fig. 4a, we show total energy loss per cycle \( (E_{in} - E_{out}) \) vs. \( \Delta V_{cap} \) for currents between 25 and 300 mA. At a fixed current, energy loss monotonically increases with \( \Delta V_{cap} \) (or equivalently, with cycle time). In Fig. S.7 of the SI, we show that cycle time increases almost linearly with \( \Delta V_{cap} \). We also include \( E_{in} \) and \( E_{out} \) vs. \( \Delta V_{cap} \) in Fig. S.7. Fig. 4a further shows that energy loss is generally greater at higher charging currents. We attribute this to the importance of the resistive loss which is approximately linearly proportional to current (for fixed charge transferred), and dominates the total loss at higher charging currents. We will discuss this in more detail below.

Fig. 4b shows calculated parasitic loss \( (E_{in}^{p} + E_{out}^{p}) \) vs. \( \Delta V_{cap} \). Reduction of dissolved oxygen at 0.69 V (vs. SHE) and oxidation of carbon electrode at 0.7–0.9 V are considered as two main sources of parasitic reactions at voltages below electrolysis potential in CDI (He et al., 2016; Lee et al., 2010). We observe an exponential relation between parasitic loss and \( \Delta V_{cap} \) (in the inset of this figure we plot the data on a logarithmic scale). This exponential growth is consistent with power loss due to parasitic reactions on the carbon surface. As given by the Butler-Volmer equation, the currents for these reactions (e.g. oxidation of surface groups and dissolved gasses in solution such as oxygen) are usually exponential with respect to surface potential. For example, Biesheuvel et al. (2012) used generalized Frumkin-Butler-Volmer model to derive an exponential relation between rate of redox reactions and Stern potential. Our results further show that parasitic loss is smaller at higher charging currents. For example, at \( \Delta V_{cap} \approx 1.2 \) V, parasitic loss at 100 mA is about 5 times smaller than the 25 mA case. We attribute this to the effect of series resistance voltage drop and cycle time. At high currents, cycle time is shorter and voltage drop across series resistances can be significant (c.f. Fig. S.1 of the SI). So, the electrodes experience lower voltages (compared to low current cases) for a shorter period of time.

We show calculated resistive loss per cycle vs. \( \Delta V_{cap} \) for 25–300 mA currents in Fig. 4c. As discussed in Section 2.2, to arrive at resistive loss, we first independently measured energy loss \( (E_{in} - E_{out}) \), series resistive loss \( (E_{in}^{s} + E_{out}^{s}) \), and parasitic loss \( (E_{in}^{p} + E_{out}^{p}) \). We then used Eq. (1) to estimate energy loss due to non-series resistances \( (E_{in}^{NS} + E_{out}^{NS}) \). We finally used Eqs. (3) and...
308 mA currents. Energy loss increases with both \( \Delta V_{\text{cap}} \) and \( I_{\text{c}} \). At low currents, energy loss varies approximately exponential with \( \Delta V_{\text{cap}} \), while it is almost linear at high currents. (b) Measured parasitic loss per cycle vs. \( \Delta V_{\text{cap}} \). Parasitic losses (likely associated with Faradaic reactions) vary exponentially with \( \Delta V_{\text{cap}} \) (see inset). (c) Resistive loss (series and non-series) in one cycle for experimental conditions identical to those of (a). Resistive loss increases almost linearly with both \( \Delta V_{\text{cap}} \) and \( I_{\text{c}} \). (d) Calculated stored energy is well described as the square of \( \Delta V_{\text{cap}} \).

Resistive loss increases proportionally with charging current. With charging time (c.f. Fig. S.7 of the SI). Fig. 4c also shows that resistive loss increases almost linearly with both \( \Delta V_{\text{cap}} \) and \( I_{\text{c}} \). The shaded and white areas correspond to parasitic dominant (>50% parasitic) and resistive dominant (>50% resistive) conditions. The results show that the resistive energy loss dominates the total loss at high charging current and small \( \Delta V_{\text{cap}} \) cases. Both resistive and parasitic losses decrease with decreasing \( \Delta V_{\text{cap}} \), but the exponential dependence of parasitic loss on \( \Delta V_{\text{cap}} \) makes it negligible at low \( \Delta V_{\text{cap}} \). Parasitic loss, however, is dominant at low current and high \( \Delta V_{\text{cap}} \) (see shaded area where parasitic >50% of total loss). This is because, as Figs. 4b and 4c suggest, resistive loss linearly increases with current, while parasitic loss generally decreases with charging current.

In Fig. 5b, we show the ratio of capacitor energy, \( E_{\text{cap}} \), over total energy loss in a cycle vs. \( \Delta V_{\text{cap}} \) for the applied current values of Fig. 5a. This ratio is essentially an energy transfer coefficient and reflects the efficiency of energy storage in the cell. As a visual aid, the shaded region is plotted to be consistent with Fig. 5a. Results show that this ratio is generally greater at lower charging currents. However, in the lowest charging currents (i.e. 25 and 50 mA), we observe a maximum at a voltage in which parasitic and resistive losses are comparable. We hypothesize that this optimum operating point balancing resistive and parasitic losses may hold for other CDI systems, at least for low to moderate applied current densities, although more evidence is needed before we can confirm this.

### 3.4. Energy and salt adsorption performance in CDI

We here present two performance FOMs for our cell. The first metric is average salt adsorption rate (ASAR) in units of moles of salt per total electrode area per time and can be defined as (Suss et al., 2015)

\[
\text{ASAR} = \frac{I_{\text{ads}}}{N A t_{\text{cycle}}} = \frac{Q}{N A t_{\text{cycle}}} \int_0^{t_{\text{charge}}} (c_0 - c) \, dt.
\]

where \( I_{\text{ads}} \) is amount of salt adsorbed during charging (in units of moles), \( N=5 \) is number for electrode pairs, \( A=28 \) cm\(^2\) is single electrode area, \( t_{\text{cycle}} \) is cycle time, \( t_{\text{charge}} \) is charging time, \( Q \) is flow rate, and \( c_0 \) and \( c \) are effluent and influent salt concentrations, respectively. This metric quantifies the throughput of the

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**Fig. 4.** (a) Measured energy loss per cycle vs. \( \Delta V_{\text{cap}} \) for 25, 50, 100, 150, 200, and 300 mA currents. Energy loss increases with both \( \Delta V_{\text{cap}} \) and \( I_{\text{c}} \). At low currents, energy loss varies approximately exponential with \( \Delta V_{\text{cap}} \), while it is almost linear at high currents. (b) Measured parasitic loss per cycle vs. \( \Delta V_{\text{cap}} \). Parasitic losses (likely associated with Faradaic reactions) vary exponentially with \( \Delta V_{\text{cap}} \) (see inset). (c) Resistive loss (series and non-series) in one cycle for experimental conditions identical to those of (a). Resistive loss increases almost linearly with both \( \Delta V_{\text{cap}} \) and \( I_{\text{c}} \). (d) Calculated stored energy is well described as the square of \( \Delta V_{\text{cap}} \).

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**Fig. 5.** (a) Ratio of resistive to total energy loss in one cycle vs. \( \Delta V_{\text{cap}} \) for 25–300 mA currents. Resistive loss dominates total loss at high charging current and small \( \Delta V_{\text{cap}} \) cases. Parasitic loss, however, is dominant at low current and high \( \Delta V_{\text{cap}} \) (see shaded area where parasitic >50% of total loss). (b) Ratio of stored charge to total energy loss in one cycle vs. \( \Delta V_{\text{cap}} \) for the same data as in (a). This ratio quantifies the effectiveness of energy storage in the cell and is generally greater at lower currents. Results show this ratio has an optimum at small currents (25 and 50 mA), and this optimum coincides with \( \Delta V_{\text{cap}} \) at which (series plus non-series) resistive loss and parasitic loss are comparable.
desalination process. Second is energy normalized adsorbed salt (ENAS) in units of moles of salt per joules of energy lost and is defined as

$$ENAS = \frac{Q}{E_{in} - E_{out}} \int_{0}^{t_{charge}} (c_0 - c) \, dt,$$

(7)

which quantifies the energetic efficiency of the desalination process. In Fig. 6, we show values of $\Gamma_{ads}$ (in units of $\mu$mol cm$^{-2}$ and mg g$^{-1}$), ASAR (in units of $\mu$mol cm$^{-2}$ min$^{-1}$ and mg g$^{-1}$ min$^{-1}$), and ENAS (in units of $\mu$mol J$^{-1}$ and mg J$^{-1}$) as functions of $\Delta V_{cap}$ for various currents mentioned before. The conversion between our two forms of normalization can be performed by using a total mass of the ten individual electrodes of 4.3 g, an area of $A = 28$ cm$^2$ per electrode, and the KCl atomic mass of 74.55 g mole$^{-1}$. We have here normalized $\Gamma_{ads}$ and ASAR by stack electrode area (NA) and total electrode mass. Fig. 6a shows that charging the cell with higher $\Delta V_{cap}$ leads to greater salt adsorption. Operating at lower charging current generally has the same effect. Salt adsorption, however, can decrease for very low currents of 25 mA and high $\Delta V_{cap}$ (where parasitic loss dominates). For example, at fixed $\Delta V_{cap} = 1.2$ V, salt adsorption at 25 mA current results in significant charge consumed by parasitic losses, and this results in less salt adsorbed than the 50 mA case.

ASAR and ENAS are shown in Figs. 6b and 6c. Regions with dominant parasitic loss are indicated by grey shading. In resistive dominant regimes, both ASAR and ENAS increase with $\Delta V_{cap}$; however, as parasitic loss becomes dominant, ASAR and ENAS can decrease with $\Delta V_{cap}$. An important observation in Fig. 6a is the inefficiency of salt adsorption at high currents. That is, ASAR does not noticeably improve from 200 to 300 mA current. We attribute this retardation of salt removal rate to the relative magnitude of cell time constant (defined as ratio of cell volume to flow rate) and charging time ($t_{charge}$). In Appendix A, we develop a simple transport model for effluent salt concentration under CC charging condition and show that the time scale for concentration to reach a plateau can be well described by a simple cell time constant of the form $t_{cell} = V_{cell}/Q$ ($V_{cell}$ and $Q$ being cell volume and flow rate, respectively). At high currents (beyond 200 mA), the charging time $t_{charge}$ is so short (on the order of a few minutes) that it becomes comparable to $t_{cell}$. As a result, the charging phase finishes “pre-maturely” (discharge phase starts before effluent concentration reaches its plateau level). This is evident for the case of 300 mA.
charging current and limit voltage of \( V_{\text{ext}} = 1.2 \text{ V} \), where the shape of the effluent concentration profile has no clear plateau region (c.f. Fig. S.2 of the SI and Fig. A.1 below). Another possible reason is the effect of re-adsorption of desorbed salt from previous discharging phase. This is specifically problematic at high currents, as the flush time and charging time are on the same order.

For a better representation of ASAR and ENAS results, in Figs. 7a and 7b, we show interpolated contour plots of these two metrics as functions of \( \Delta V_{\text{cap}} \) and external current for the same data as in Figs. 6b and 6c. The markers overlaid on the contour plots are the corresponding measurement points (at each current and voltage). The dashed curves are consistent with those of Figs. 5 and 6 and indicate the locus of equal resistive and parasitic losses. As discussed earlier, ASAR increases as either current or \( \Delta V_{\text{cap}} \) increases. However, as current exceeds ~200 mA, ASAR remains constant or even decreases at low \( \Delta V_{\text{cap}} \). ASAR results, therefore, show the best removal rate performance at mid-level currents (~200 mA) and highest possible \( \Delta V_{\text{cap}} \) (~1.1 V). In contrast, Fig. 7b shows that ENAS (indicator of energetic performance) is maximized at lower currents and mid-level voltage (~0.6 V). Note that, similar to our observations of the data of Fig. 6c, ENAS rapidly drops with increasing \( \Delta V_{\text{cap}} \) as parasitic losses begin to dominate the energy loss. This suggests that the data points at high current and high \( \Delta V_{\text{cap}} \) correspond to a point that simultaneously favors the two performance requirements considered, namely, removal rate and low energy cost. To elaborate this, we plot ENAS versus ASAR for different external currents in Fig. 7c. Data points in each curve correspond to a variation in the value of \( \Delta V_{\text{cap}} \) (as shown in Figs. 6b and 6c). The results clearly show a tradeoff between removal rate and energy efficiency of desalination process (ASAR and ENAS respectively quantify desalination speed and energetic performance of the cell). For example, small charging currents are generally more favorable in terms of energy performance (higher ENAS), while large currents have higher adsorption rate (higher ASAR). It is possible, however, to combine ASAR and ENAS into a new metric (or user-defined cost function) and optimize the resulting metric. In Section S.5 of the SI, we introduce an energetic operational metric (EOM) as the product of ASAR and ENAS and seek a combination of current and \( \Delta V_{\text{cap}} \) which maximizes our EOM. Interestingly, we show that the location of maximum EOM approximately coincides with the locus of operational points where (series plus non-series) resistive loss and parasitic loss are comparable.

4. Conclusions

We have quantified individual loss mechanisms operative during CDI charging and discharging, and characterized their dependence on the parameters of charging current and maximum cell voltage. We identified losses dependent on cell voltage attributable to parasitic currents and losses depending on charging rate, which are dominated by cell resistances. We measured series resistance for the cell throughout charge/discharge phases for a range of input solute concentrations and a variety of charging currents and cell voltages. We also used independent experiments to quantify parasitic losses as a function of voltage in double layers. The two categories of loss favor different charging rates, with resistive losses minimized at low charging currents, but parasitic losses (and associated leakage current losses) lessened for higher rates which reduce the time the cell spends at high voltage. We introduced two figures of merit, ASAR and ENAS, which characterize the performance of a CDI cell in terms of throughput and energy efficiency, respectively. We showed that these figures of merit provide a powerful tool for optimizing CDI operation.

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Appendix A. Time scales in fbCDI

We here present a simple transport model for fbCDI systems under constant current and constant flow rate operation and identify relevant time scales. Starting with a one-dimensional transport equation for salt along the flow direction and neglecting diffusion, we have

\[
\frac{\partial c}{\partial t} + \frac{\partial u_{\text{sup}} c}{\partial x} = A i, \tag{A.1}
\]

where \( p_{\text{sp}} \) is porosity of the spacer, \( u_{\text{sup}} \) is superficial (not interstitial) velocity in the spacer (by definition, \( u_{\text{sp}} \) is the ratio of volume flow rate to the spacer area perpendicular to the flow), \( i \) is the volumetric current density, \( \lambda \) is charge efficiency, and \( F \) is Faraday’s constant. We assume a constant inlet concentration \( c_0 \), fixed charge efficiency, and uniform (transverse) current density along the flow. We then integrate Eq. (A.1) in the direction of flow and arrive at

\[
\frac{\partial c_{\text{out}}}{\partial t} = \frac{Q}{v_{\text{cell}}} (c_0 - c_{\text{out}}) - \frac{A}{F v_{\text{cell}}} I_0. \tag{A.2}
\]

where \( v_{\text{cell}} \) is cell volume (volume of spacers), \( c_{\text{out}} \) is effluent concentration, \( Q \) is flow rate, and \( I_0 \) is applied external current. Eq. (A.2) can be written as

\[
\frac{\partial c_{\text{out}}}{\partial t} = Q (1 - c_{\text{out}}) - I_0. \tag{A.3}
\]

where \( \tau_{\text{out}} = c_{\text{out}} / c_0, \tau_{\text{in}} = Q / (p_{\text{sp}} v_{\text{cell}}), \) and \( I_0 = A I_0 / (F p_{\text{sp}} v_{\text{cell}} c_0) \). Effluent concentration can then be solved as

\[
\tau_{\text{out}} = 1 - \frac{I_0}{Q} \left[ 1 - \exp \left( -\frac{Q}{I_0} t \right) \right]. \tag{A.4}
\]

This simplified analysis shows effluent concentration profile should exhibit a time scale of \( \tau_{\text{cell}} = 1 / Q \). We show the result of normalized effluent concentration in Fig. A.1a. Time scale for concentration to reach a plateau level is \( 1 / Q \), and (normalized) concentration change under constant current charging \( I_0 \) condition is \( \Delta c = I_0 / Q \). The second time scale shown in Fig. A.1a is charging time \( \tau_{\text{charge}} \), which can be approximated by the ideal capacitor equation as \( \tau_{\text{charge}} = \Delta V_{\text{cap}} / I_0 \). Equating the two time scales gives a linear relation between current and flow rate as \( Q / I = p_{\text{sp}} v_{\text{cell}} / (\Delta V_{\text{cap}}) \). Fig. A.1b is then a regime map constructed by plotting flow rate versus current (in logarithmic scale). This figure summarizes the two possible regimes based on relative values of \( \tau_{\text{cell}} \) and \( \tau_{\text{charge}} \). The upper-left region corresponds to a “plateau mode” regime, where the effluent concentration reaches a steady level before the charging phase ends. The lower-right regime corresponds to a “triangular-peaked” regime, where the charging phase ends prematurely, and the effluent does not reach to a plateau.
Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.08.020.

References


Supplementary Information for

Energy Breakdown in Capacitive Deionization

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This document contains Supplementary Information and figures describing complete set of experimental data and further discussion on energetic performance of our flow-between CDI (fbCDI) cell.

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S.1. Voltage profile under constant current conditions

As discussed in Section 2.3 of the main text, we performed a series of constant current charging/discharging experiments for a range of applied currents $I_0$ and limit voltages $V_{\text{max}}$. That is, we charged the cell with a constant current until the pre-determined limit voltage was reached. We then discharged the cell with the same current (with reversed direction) until the voltage reached zero. We present voltage profiles for 25-300 mA charging/discharging current ($I_0$) and 0.2-1.2 V limit voltage ($V_{\text{max}}$) in Fig. S.1. Each subplot shows the external voltage measurements for a fixed current $I_0$ and different $V_{\text{max}}$ values. Each profile is an overlay of 2 to 4 successive cycles under dynamic steady state (DSS) condition (to show cycle-to-cycle reproducibility). As mentioned in the main paper, the DSS condition is the operation mode wherein voltage and effluent concentration profiles vary negligibly between cycles; DSS is reached after a few cycles. We observe that this is indeed the case for the results in Fig. S1, as the voltage profiles shown here are very repeatable across cycles.

![Graph showing voltage profile under constant current conditions](image)

Fig. S.1. Measured external voltage versus time for 25-300 mA charging/discharging current ($I_0$) and limit voltages 0.2-1.2 V ($V_{\text{max}}$). Galvanostatic voltage increases until the pre-set limit voltage is reached and current is reversed. The jumps just after current reversals are associated with the fast response associated with purely serial resistive response. Profiles shown here are all under DSS condition and each profile is an overlay of 2 to 4 successive cycles.
S.2. Effluent concentration measurement

We measured effluent salt concentration via a calibrated in-line conductivity meter. To this end, we created a calibration curve relating the known KCl solution concentrations to measured conductivity. In Fig. S.2, we present effluent concentration versus time for experimental conditions identical to those of Fig. S.1. Flow rate was held constant at 2 mL min$^{-1}$. Dashed lines in each subplot show the influent concentration level. Each curve is an overlay of 2 to 4 cycles under DSS condition. Results show very good cycle-to-cycle repeatability for effluent concentration. In Fig. S.3, we show example measured cell voltage and effluent concentration for the case of 200 mA current and 0.8 V maximum external potential from startup until six cycles. Results show establishment of DSS condition after first few cycles.

![Raw measurements of effluent concentration profiles measured via an in-line conductivity meter.](image)

Each curve is an overlay of two or more cycles under DSS condition. Dashed lines show influent concentration level.

![Measured (a) voltage and (b) effluent concentration for $I_0 = 200$ mA and $V_{\text{max}} = 0.8$ V during the first six cycles. DSS condition is established after first few cycles.](image)
S.3. In-situ series resistance measurement

In Section 3.2 of the main text, we briefly introduced the procedure for in-situ series resistance measurement. We here discuss this process in more detail. As mentioned in Section 3.2 of the main paper, we provide galvanostatic control of the cell at specified currents (and pre-set voltage limits) using a sourcemeter (Keithley 2400, Cleveland, OH). We then use the same sourcemeter to probe the CDI cell in real-time to measure its serial resistance response. As mentioned in the main text, we use the strong disparity in time response between series and non-series resistances to real-time sample series resistance component of CDI cells. Namely, we apply a small-amplitude (2 mA) AC current signal with ~10 Hz frequency during small portion of the charging or discharging current steps (within each charging or discharging half-cycle we apply a DC current $I_0$). We apply this 10 Hz probing signal once the external voltage is a multiple of 50 mV (e.g. at $V_{ext} = 0.4, 0.45, 0.5$ V, etc.) and sustain this for order 1 s durations at a time. We initiate such pulse modulated AC currents roughly every 15 s to 4 min during charging and discharging (which last order 4 to 90 min, depending on applied current and set voltage limit). In Figs. S.4a and S.4b, we show example of applied current and corresponding voltage response signals for the case of $I_0 = 200$ mA, $V_{max} = 1$ V, and $V_{ext} = 1$ V during a typical charging step. The applied current profile is a saw-tooth signal with a mean value of $I_0$ and peak-to-peak amplitude $\delta I$ of 2 mA. Voltage is a saw-tooth signal on top of an underlying approximately linear voltage response. The DC current signal ($I_0$) is responsible for charging/discharging the cell and the linear feature in voltage signal. As a result, this underlying voltage feature should be subtracted from the measured signal for correct resistance measurement. We label the voltage signal amplitude about this linear trend as $\delta V$ in Fig. S.4b. Series resistance of the cell can then be calculated simply by the ratio of $\delta V$ to $\delta I$ ($R_s = \delta V/\delta I$).

Fig. S.5 shows the results of resistance measurement versus time with the method discussed above for experimental conditions similar to those of Fig. S.1. Each curve is an overlay of 2 to 4 cycles under DSS condition. In Fig. S.6, we present the same resistance data but here plot them as a function of $\Delta V_{cap}$. Both figures show higher (lower) series resistance during charging (discharging), consistent with the respective depletion (enrichment) of ions from (into) the spacer layer. Also, variation of resistance is greater at higher currents as expected.
Fig. S.4. (a) An example of 2 mA amplitude AC current probe signal ($\delta I$) with a fixed 200 mA DC component ($I_0$) used for in-situ resistance measurement of our fbCDI cell. (b) Voltage response of the cell for current signal shown in (a). The response consists of saw-tooth with the underlying linear component associated with the charging of electrodes. To calculate resistance, we subtract the underlying linear signal variation from voltage response and divide the amplitude of resulting signal ($\delta V$) by $\delta I$.

Fig. S.5. Time resolved series resistance for various currents (25-300 mA) and limit voltages (0.2-1.2 V) during cell operation. Each curve is an overlay of resistance measurements for 2 to 4 cycles under DSS condition.
Fig. S.6. Series resistance during cell operation as a function of $\Delta V_{cap}$ for various currents (25-300 mA) and limit voltages (0.2-1.2 V). Resistance values form a closed loop for each experimental condition. The loop becomes wider and more asymmetric under higher currents and higher $\Delta V_{cap}$, which we attribute to the effect of depletion and enrichment of ions from the spacer region (substantial salt removal and enrichment during charging and discharging, respectively).

S.4. Energy and cycle time measurements

As discussed in Section 3.1 of the main text, we measured the input and output energy ($E_{in}$ and $E_{out}$) of the cell operation under a variety of current and voltage conditions by integrating measured instantaneous power over the charging and discharging phases. We present the results as a function of $\Delta V_{cap}$ in Figs. S.7a and S.7b. Both $E_{in}$ and $E_{out}$ monotonically increase with $\Delta V_{cap}$. In contrast, current magnitude has a competing effect on input and output energies. Fig. S.7a shows that energy input $E_{in}$ is generally greater when the cell is operated at higher currents (see arrow in Fig. S.7a). Energy recovered $E_{out}$, however, decreases as discharge current magnitude increases. This leads to greater energy loss ($E_{in} - E_{out}$) at high currents, as shown in Fig. 4a of the main text. We additionally plot the cycle time (in units of min) versus $\Delta V_{cap}$ in Fig. S.7c. This figure shows an approximately linear relation between cycle time $t_{cycle}$ and $\Delta V_{cap}$.
Fig. S.7. (a) Input and (b) recovered electrical energy of our fbCDI cell as a function of $\Delta V_{cap}$ for currents in the range of 25-300 mA. Both energies increase monotonically with $\Delta V_{cap}$, but current magnitude has opposite effects on input and recovered energy (see arrows in (a) and (b)). (c) Cycle time versus $\Delta V_{cap}$ under experimental conditions similar to those of (a) and (b). Cycle time and $\Delta V_{cap}$ are approximately linearly dependent.

S.5. Energetic operational metric (EOM)

To study the combined effect of ENAS and ASAR on desalination performance, we introduce an energetic operational metric (EOM) as the product of average salt adsorption rate ($ASAR$) and energy-normalized adsorbed salt ($ENAS$). We stress that this EOM is just one arbitrary “cost function”, which we use here as an example global optimization used to balance the trade-off between desalination throughput and energy efficiency. Other possibilities include a monomial form $ASAR^\alpha ENAS^\beta$ or linear form $\alpha \cdot ASAR + \beta \cdot ENAS$, where $\alpha$ and $\beta$ are arbitrary positive constants determined by the user and which reflect the relative value the user places on adsorption rate versus energy loss. The EOM we present here ($ASAR \cdot ENAS$) is one example figure of merit describing global performance. We then seek a combination of current and $\Delta V_{cap}$ (or equivalently, current and cycling time) to maximize our EOM. Fig. S.8 shows an interpolated contour plot of the EOM as a function of $\Delta V_{cap}$ and external current. The markers overlaid on the contour plot are the corresponding measurement points (similar to those in Fig. 7 in main text). The dashed curve is the locus of operational points where resistive loss equals parasitic loss. Fig. S.8 shows that the EOM dramatically decreases in the limit of low current and high $\Delta V_{cap}$ (dominant parasitic loss, negligible ASAR) as well as high current, low $\Delta V_{cap}$ (dominant resistive loss, negligible ENAS). EOM, on the other hand, is maximized at moderate values of current and $\Delta V_{cap}$. The location of maximum EOM coincides with comparable resistive and parasitic losses.
Fig. S.8. Contour plot of EOM (defined as $ASAR \cdot ENAS$) as a function of current $I_0$ and $\Delta V_{cap}$. Dashed curve and the associated “parasitic dominant” shaded region are consistent with Fig. 7 of the main text. As with our earlier observations, EOM is maximized roughly in the regions with comparable resistive and parasitic losses.