

Flow-electrode capacitive deionization enables continuous and energy-efficient brine concentration

Alexandra Rommerskirchen^{a,b}, Christian J. Linnartz^{a,b}, Franziska Egidi^{a,b},
Sefkan Kendir^b, Matthias Wessling^{a,b,*}

^a*DWI - Leibniz-Institute for Interactive Materials e.V., Forckenbeckstraße 50, 52074
Aachen, Germany*

^b*RWTH Aachen University, Aachener Verfahrenstechnik-Chemical Process Engineering,
Forckenbeckstraße 51, 52074 Aachen, Germany*

Abstract

Many industrial and agricultural applications require the treatment of water streams containing high concentrations of ionic species for closing material cycles. High concentration factors are often desired, but hard to achieve with established thermal or membrane-based water treatment technologies at low energy consumptions. Capacitive deionization processes are normally assumed as relevant for the treatment of low salinity solutions only. Flow-electrode capacitive deionization (FCDI), on the other hand, is an upcoming electrically driven water desalination technology, which allows the continuous desalination and concentration of saline water streams even at elevated salinities. Ions are adsorbed electrostatically in pumpable carbon flow electrodes, which enable a range of new process designs.

In this article, it is shown that continuously operated FCDI systems can be applied for the treatment of salt brines. Concentrations of up to 291.5 g/L

*Phone: +49-241-8095470, Fax: +49-241-8092252, Manuscripts.cvt@avt.rwth-aachen.de, Forckenbeckstraße 51, 52074 Aachen, Germany

NaCl were reached in the concentrate product stream. Based on this, FCDI is a promising technology for brine treatment and salt recovery. Additionally, a reduction of the energy demand by more than 70% is demonstrated by introducing multiple cell pairs into a continuous FCDI system. While the economic feasibility is not investigated here, the results show that FCDI systems may compete with established technologies regarding their energy demand.

Keywords: Water desalination, Brine treatment, Capacitive deionization, Flow-electrode capacitive deionization, Energy efficiency

1. Introduction and motivation

Water treatment technologies should be energy efficient, reliable and economical. While the technologies available for water treatment, such as desalination and concentration have been improved significantly over the last decades, there is no viable water treatment technology available in some application cases, while in many other cases there is still room for improvement [1, 2, 3].

Significant attention has been focused on capacitive deionization (CDI) technologies in the last decade. In CDI processes, an applied electrochemical potential gradient leads to the transport of dissolved ions towards the oppositely charged electrodes, where the ions are bound via electrostatic adsorption at the electrode-solution interface. High surface areas, and hence high ion adsorption capacities, are usually achieved by employing solid, porous carbon electrodes. CDI processes can be operated in a variety of configu-

16 rations. The use of ion-exchange membranes (IEM) can improve the per-
 17 formance of CDI processes regarding their desalination performance and
 18 energy efficiency, when placed in between electrodes and treated solution
 19 [2, 3, 4, 5, 6, 7]. Most CDI processes are based on static carbon-based elec-
 20 trodes. In this case, the application is limited to the treatment of brackish
 21 water feed streams. Higher feed salinities would lead to a fast saturation of
 22 the electrode material with ions, making a discontinuous CDI process op-
 23 erated in charge-discharge cycles inefficient due to back-mixing withing the
 24 tubing and modules.

25
 26 An upcoming CDI technology suitable for the treatment of higher salin-
 27 ities is flow-electrode capacitive deionization (FCDI) [8]. In case of FCDI,
 28 flow electrodes consisting of pumpable carbon suspensions replace the static
 29 CDI electrodes, in which charge percolation leads to a utilization of the sus-
 30 pended carbon particles as electrode material [9, 10]. Flow electrodes can be
 31 regenerated via mixing [11] or in a separate module or compartment, and en-
 32 able a fully continuous operation. By now, various continuous FCDI process
 33 layouts have been proposed, including a continuous two-module configuration
 34 [12], single-module configuration [13], a mixer-settler configuration [14], and
 35 a two-step regeneration configuration [15]. In all of these configurations, the
 36 electrodes are continuously regenerated and a diluate and concentrate stream
 37 is produced continuously with more or less constant salt concentrations.

38 FCDI technologies are a promising research field due to the high salt ad-
 39 sorption capacities [5, 12, 16, 17], good desalination performance, the ability
 40 to desalinate high salinity solutions [8], and the possibility of fully contin-

uous operation [12, 13, 14, 18]. A great strength of the FCDI technology is its versatility. The use of suspension-based flow electrodes for desalination and water treatment in general can be seen as a platform technology, which can be operated in many different process layouts for many different applications [19, 20]. Lab-scale FCDI studies published until now were, for example, aimed at salt metathesis [21], ammonia recovery from wastewaters [22, 23, 24], nitrogen and phosphorous recovery [25], nitrate removal [26], copper removal [27], and uranium removal [28]. Apart from a multitude of pure FCDI processes, many combinations with established processes are imaginable, such as the combination of FCDI with nanofiltration [29]. However, most of the prior work focuses on low ionic concentration applications due to the limited adsorption capacity of the carbon electrodes in discontinuous or semi-continuous operation.

Several characteristics make FCDI a promising candidate for the treatment of high salinity solutions. Compared to most established thermal or membrane-based water treatment processes, FCDI processes may enable the selective removal of charged species from water streams in the future, and may at the same time become more energy-efficient for many application cases. Even in comparison to other electrically driven processes [30], FCDI has its advantages: Unlike electrodialysis processes, FCDI relies on the capacitive adsorption of ions in the electrodes at low voltages, and does not require electrochemical reactions in the electrodes. Hence, gas evolution and the use of acids in the electrode compartments is avoided. The elimination of electrochemical reactions in the electrode compartments may also be ad-

66 vantageous for the treatment of sensitive chemicals, which may be altered by
67 the high potentials and side products in case of electrodialysis processes.

68 As shown in our previous article [15], the values regarding the energy de-
69 mand of FCDI processes cannot yet compete with literature values regarding
70 existing technologies. However, a target-oriented advancement of the FCDI
71 technology may lead to a new alternative solution for many water treatment
72 applications.

73 This article demonstrates the possibility of concentrating brines in a con-
74 tinuous process based on a single module using FCDI technology. Addition-
75 ally, it is shown that a significant reduction of the energy demand and an
76 improved productivity can be achieved by using several cell pairs. This ap-
77 proach is similar to the approach recently presented by Ma et al. [31], who
78 presented an FCDI configuration with stacked membranes, which leads to
79 significant productivity improvements, but only enables a semi-continuous
80 water treatment. In our work, we demonstrate the continuous treatment of
81 saline brine using FCDI modules with one or more cell pairs, and therefore
82 an even number of water compartments. While the experiments presented
83 are specifically aimed at the treatment and concentration of high salinity
84 solutions (brines) using FCDI processes, the findings can be transferred to
85 other potential application areas of FCDI processes.

86 *1.1. Reducing the resistance losses in FCDI processes: An analysis*

87 For a better understanding of the contribution of individual electrical re-
88 sistances in an FCDI cell, theoretical estimations of the individual resistances
89 were made.

90 The results are plotted in Figure 1, which shows the electrical resistance

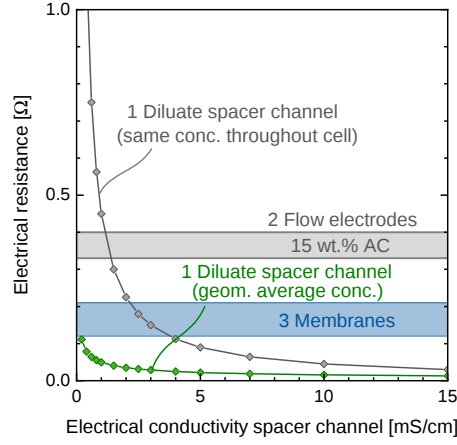


Figure 1: Results of theoretical calculations regarding the influence of the NaCl concentration/ electrical conductivity of the diluate stream on the electrical resistances in an FCDI cell. Assumptions: Constant diluate flow rate of 1 mL/min, diluate concentration constant throughout cell (overestimated resistances/cell voltage), no consideration of laminar boundary layers, desalination up to the required concentration (varied electrical current).

of specific parts of an FCDI cell depending on the electrical conductivity of the diluate product stream. The calculations are based on the following assumptions:

- NaCl feed: 60 g/L NaCl at a diluate feed flow rate of 1 mL/min.
- Resistance of membranes and flow electrodes constant throughout cell.
- The required electrical current is calculated based on the desalination down to the respective diluate concentration, leading to lower energy demands at higher diluate concentrations even at constant resistance.
- (Depleted) laminar boundary layers are not considered.
- Ideal pumping energy: Pump efficiency is not considered.

- 101 • Diluate channel resistance: Geometric average between inlet and outlet
102 concentrations.
- 103 • A current efficiency of one is assumed.
- 104 • Flow-electrode resistance R_{Fe} : based on total resistance R_{total} and com-
105 bined solution/ membrane resistance R_S from EIS measurements pre-
106 sented in [32], $R_{Fe} = R_{total} - R_S$.

107 The resistance of the flow electrodes is 0.33-0.4 Ω for an AC content of
108 15 wt.%, which presents a large fraction of the overall cell resistance. This is
109 in agreement with our previous study [32], in which we observed a significant
110 influence of the carbon slurry quality on the desalination performance.

111 The second largest resistance in the cell at most diluate concentrations
112 is presented by the membranes. Three ion-exchange membranes of the type
113 fumatech FAB/FKB with PEEK reinforcements, which we currently use in
114 FCDI systems for the treatment of high salinity solutions, account for around
115 0.12-0.21 Ω of the total cell resistance, based on the manufacturers data. The
116 resistance of the diluate channel varies significantly depending on the outlet
117 concentration, ranging between 0.02-0.1 Ω . The sum of the membrane resis-
118 tance and the resistance of the diluate spacer channel should be equal to the
119 resistance R_S from the equivalent circuit model presented in our previous ar-
120 ticle [32]. In this, R_S was usually found to be in the range of 0.2-0.27 Ω , which
121 is in good agreement with the estimations presented here. In case of most
122 diluate concentrations, the membrane resistance dominates over the solution
123 resistance, especially when considering three membranes in an FCDI single
124 module configuration with one cell pair. At very low concentrations, the so-
125 lution resistance is in a similar range as the membrane resistance. However,

126 the solution resistance in this case is likely underestimated, as the laminar
127 boundary layers are not considered.

128

129 Based on this analysis, the reduction of resistances in FCDI cells should
130 be prioritized in the following order: (1) flow electrodes, (2) membranes and
131 (3) diluate channel. Depending on the aimed-at diluate product concentra-
132 tion and the depletion of the diluate boundary layers, the reduction of the
133 diluate channel resistance should be prioritized over the membrane resistance
134 in specific cases.

135

136 Many studies have been published in CDI and FCDI literature, which
137 focus on the selection of the active material and the overall flow-electrode
138 composition to achieve a reduction of the flow-electrode resistance [19, 33,
139 34, 35, 36, 37]. Here, we present a different approach aiming at the module
140 design, based on the use of multiple cell pairs. The hypothesis is that the
141 number of desalination units per unit flow electrode should be increased in
142 order to reduce the relative contribution of the flow electrodes to the total
143 resistance.

144 1.2. Concept: FCDI with multiple cell pairs

145 The motivation for introducing additional cell pairs into an FCDI module
146 is illustrated in Figure 2 (a). By introducing one or more additional cell
147 pairs (each one diluate and one concentrate channel, two membranes), the
148 influence of the voltage drop over the electrodes is reduced. The flow rate of
149 the feed stream is multiplied by the number of cell pairs, to achieve similar
150 flow conditions within the FCDI module. While the overall ohmic resistance

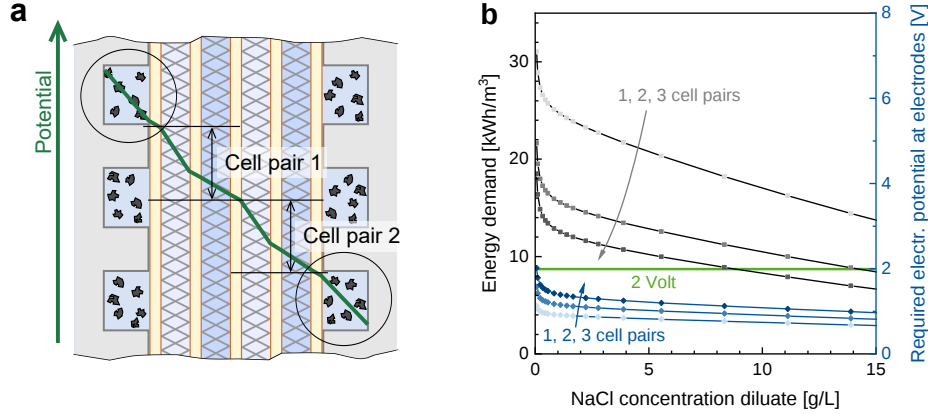


Figure 2: Concept of using multiple cell pairs for reducing the energy demand of continuous FCDI processes. (a) Illustration of the concept. The division of the flow-electrode voltage drop by the number of cell pairs leads to a reduced average voltage drop per cell pair. (b) Results of theoretical calculations regarding the influence of the NaCl concentration/electrical conductivity of the diluate stream on the energy demand and required cell potential in an FCDI cell with 1, 2 and 3 cell pairs. Assumptions: Constant diluate flow rate of 1 mL/min, diluate concentration constant throughout cell (overestimated resistances/cell voltage), no consideration of laminar boundary layers, desalination up to the required concentration (varied electrical current).

151 of the FCDI module increases with increasing number of cell pairs, there
 152 is only one pair of flow electrodes required. Hence, the ohmic resistance of
 153 the flow electrodes is divided by the number of cell pairs, and the overall
 154 impact of the electrode resistance is reduced. The theoretical estimations
 155 plotted in Figure 2 (b) show results regarding the energy demand and the
 156 expected required cell voltage for the desalination down to the desired diluate
 157 concentration (x-axis) in an FCDI system with one, two and three cell pairs.
 158 The calculations are based on the same assumptions as described above.

159 The calculations predict a steep decrease in the energy demand with

160 increasing number of cell pairs, the most significant decrease being expected
161 when introducing the second cell pair. Limitation for the number of cell pairs
162 is the voltage applied to the graphite current collectors. At high voltages,
163 unwanted faradaic reactions (e.g. carbon oxidation) may occur. In this work,
164 a maximum of 2 V was applied in longer lasting experiments, indicated by
165 the green line in Figure 2 (b). At this voltage, no visible deterioration of
166 the graphite plates or other indicators of undesired faradaic reactions were
167 observed.

168 Apart from the voltage drop, the use of multiple cell pairs will also reduce
169 the specific pumping energy required. In this case, the absolute pumping
170 energy for the flow electrodes will stay the same, while the amount of product
171 stream is multiplied by the number of cell pairs.

172 Based on these estimations, the use of multiple cell pairs seems to be
173 a promising approach for FCDI processes, which is in agreement with the
174 observations presented by Ma et al. [31]) regarding a comparable FCDI stack,
175 which is operable in a semi-continuous manner. In the following, the concept
176 of single-module FCDI with multiple cell pairs is implemented, tested, and
177 its performance evaluated.

178 **2. Materials and methods**

179 The FCDI experiments were performed in cross-flow mode, as illustrated
180 in Figure 3. This module design enables the addition of one or more cell
181 pairs into an FCDI module in single-module configuration [13]. Otherwise,
182 the design of the FCDI cells applied in this study is identical to the design
183 described in recent FCDI-related publications by our workgroup [15, 32].

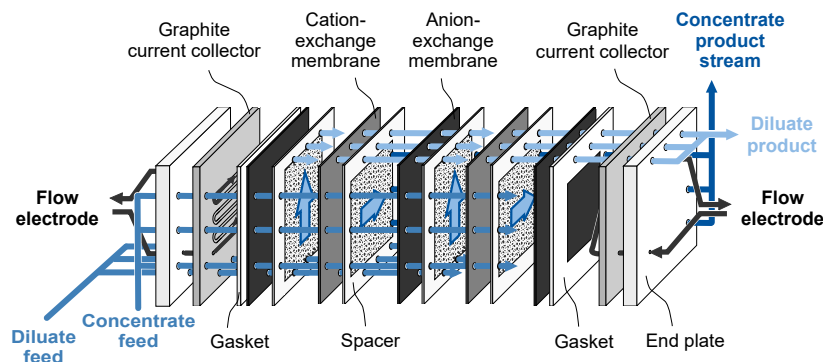


Figure 3: Illustration of the cross-flow module layout applied for multiple cell pair experiments. In this example, a module with two cell pairs is illustrated.

184 The FCDI cells consisted of polyethylene end plates, flat gaskets, epoxy-
 185 impregnated graphite electrodes (Müller & Rössner GmbH & Co. KG,
 186 180x180x10 mm) with flow channels for the flow electrodes (3 mm width,
 187 2 mm depth, 200 cm overall length), two anion-exchange membranes and
 188 one cation-exchange membrane in the configuration with one cell pair (Fu-
 189 masep FAB-PK-130/ED-100 and Fumasep FKB-PK-130/ED-100, Fumatech
 190 BWT GmbH) with an effective surface area of 121 cm², and a 0.5 mm mesh
 191 spacer (Fumatech BWT GmbH, ED-100). For each added cell pair, two net
 192 spacers (ED-100, Fumatech BWT GmbH), one anion-exchange membrane
 193 (AEM) (Fumasep FAB-PK-130, ED-100, Fumatech BWT GmbH) and one
 194 cation-exchange membrane (CEM) (Fumasep FKB-PK-130, ED-100, Fumat-
 195 ech BWT GmbH) were added between the central CEM and the AEM adja-
 196 cent to the flow electrode on the concentrate side, as illustrated in Figure 4.

197 The experiments were performed with two Keysight power supplies (Keysight
 198 Technologies Inc., E3466A). A digital multimeter (Votcraft, VC270 Green-
 199 Line) was used to verify the actual voltage applied to the graphite current

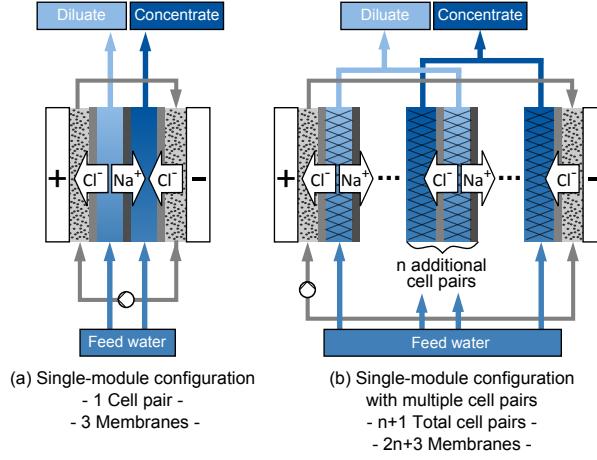


Figure 4: Layout of continuous single module FCDI systems with (a) one cell pair (standard layout), (b) multiple cell pairs (1 cell pair + n additional cell pairs).

collectors. The flow electrodes were recirculated through the FCDI systems using a peristaltic pump (Ismatec MCP process drive, Masterflex two-channel pump head Easy-Load II, Norprene tubing). The feed water was supplied by a second peristaltic pump (Ismatec Reglo ICC peristaltic pump with two independent channels). The pumps, power supplies and conductivity sensors (LTC 0,35/23; Sensortechnik Meinsberg) were connected to a custom-made measuring system "ZUMO-FUMS" (ZUMOLab GbR, Wesseling, Germany), which was used to control the pumps and power supplies as well as record the experimental data. Whenever an FCDI module was newly assembled, fixed amounts of water were recirculated separately through each flow electrode, diluate and concentrate compartment for several hours to rule out internal and external leakages.

Experiments were performed with one, two and three cell pairs, as indicated in Table 1. In case of the experiments with several cell pairs, the feed

flow rates were multiplied by the number of cell pairs, to achieve comparable hydrodynamic conditions within the cell. Hence, overall flow rates of 1, 2 and 3 mL/min were applied for the diluate feed and 0.04, 0.08 and 0.12 mL/min were applied for the concentrate feed.

Table 1: Overview of parameter settings for desalination experiments.

Number of cell pairs	Cell	Slurry		Feed water	
	Voltage	NaCl	Flow rate	NaCl	Flow rate
	V	g/L	mL/min	g/L	per cell pair mL/min
1 CP	1.2	60	150	60	D:1/C:0.04
1 CP	1.2 & 1.4	120	150	120	D:1/C:0.04
2 CP	1.2	60	150	60	D:1/C:0.04
2 CP	1.2&1.4&1.8	120	150	120	D:1/C:0.04
3 CP	1.2	60	150	60	D:1/C:0.04
3 CP	1.4 & 1.8	120	150	120	D:1/C:0.04

The experiments were conducted at constant voltage. While the addition of additional cell pairs leads to an increased overall cell resistance, only a moderate desalination was chosen. The concentrations in the diluate product stream did not fall below 29.5 g/L. Hence, the cell resistance for additional cell pairs was similar in all experiments with the same NaCl feed concentration, although the diluate concentration varied. In this range (e.g. 29.5 g/L in case of one cell pair and 33.5 g/L in case of three cell pairs), the differences in electrical resistance arising from concentration differences in the diluate stream have a negligible influence of around 0.002 Ω , which

227 ensures the comparability of the experiments.

228 All experiments described in this section were performed with activated
229 carbon slurries used as flow electrodes, which were prepared from 15 wt.%
230 Carbopal SC11PG (Donau Carbon GmbH) in a NaCl solution with a con-
231 centration equaling the feed concentration, either 60 g/L or 120 g/L (Sodium
232 chloride $\geq 99.8\%$, VWR Chemicals). The slurries were stirred overnight be-
233 fore use. For each flow-electrode circuit the slurry was recirculated through
234 the system at a flow rate of 150 mL/min. The slurry storage beakers were con-
235 tinuously stirred using magnetic stirrers. The overall flow rates used for the
236 diluate feed (1 mL/min per cell pair) and the concentrate feed (0.04 mL/min
237 per cell pair) were multiplied by the number of cell pairs to achieve compara-
238 ble flow conditions within the flow channel. During steady-state operation,
239 several samples of the diluate and concentrate stream were taken and the
240 density measured to confirm the NaCl concentration.

241 *Current-voltage characteristics.* The current-voltage characteristics ("IV-curves")
242 of the different systems were investigated by a step-wise change of the applied
243 voltage in a range between 0 V and 2.5 V in steps of 0.1 V. After each change
244 in voltage, the voltage was kept constant for 10 minutes, which corresponds
245 to about two times the residence time. The steady-state electrical current
246 was measured for each step.

247 During the measurements, the diluate feed flow rate was kept constant at
248 1 mL/min. To shorten the time until equilibrium is reached, the concentrate
249 flow rate was set to 1 mL/min. To test the influence of the concentrate feed
250 flow rate on the current-voltage characteristics of the system, one experiment
251 was performed at a concentrate feed flow rate of 0.04 mL/min. The activated

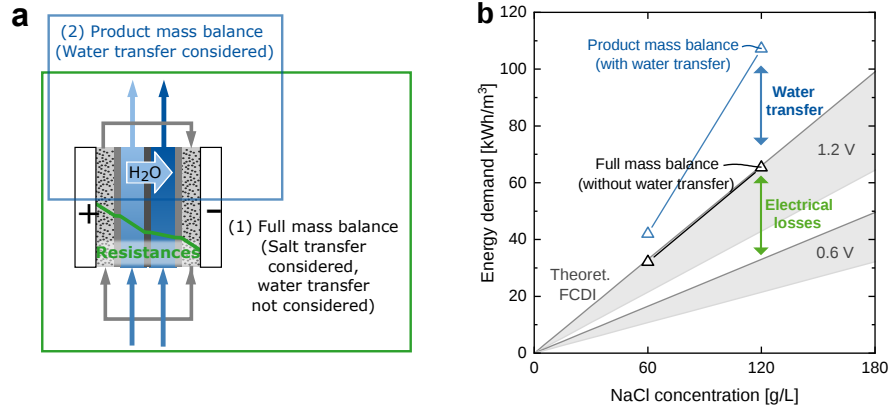


Figure 5: Illustration of (a) the key factors increasing the energy demand in an FCDI process: Water crossover and resistances, which increase the overall cell voltage, and (b) their impact on the electrical energy demand. It depends on the chosen mass balance, as illustrated in (a), whether the water transfer is considered, which leads to a salination of the diluate and a dilution of the concentrate.

252 carbon content in the flow electrodes was 15 wt.% in most cases. In one case,
 253 the activated carbon content was increased to 18 wt.%.

254 3. Assumptions and terminology: Influence of the system bound- 255 aries on the energy demand

256 The choice of the system boundary is crucial when analyzing the energy
 257 demand of FCDI systems. Two possible approaches are illustrated in Fig-
 258 ure 5 (a).

259 In the first approach, the salt transfer is calculated based on the flow
 260 rates and salt concentrations of feed and product water streams, indicated
 261 by the green system boundary in Figure 5 (a). In this case, the actual,
 262 overall salt transfer is considered. This system boundary is useful for the

263 analysis of the salt transfer and the back diffusion of salt, as expressed in
 264 the current efficiency. This means, the energy demand for overcoming the
 265 electrical losses/ resistances in the system is considered. However, due to
 266 the additional transfer of water molecules with the ions as well as the os-
 267 motic transfer, the dilution of the diluate stream and concentration of the
 268 concentration stream is not as high as expected when purely considering
 269 the salt transfer. Hence, the system performance is overestimated and the
 270 energy demand underestimated in case of the first approach. The energy
 271 demand calculated in $\text{Wh}/g_{\text{salt}}$ is, of course, correct in this case. However,
 272 the amount of salt transferred in the system should not be used to calculate
 273 the energy demand in kWh/m^3 product stream, as in this case the energy
 274 demand would be significantly underestimated, as illustrated in Figure 5 (b),
 275 due to the diluate concentration and concentrate dilution.

276 In case of the second option, marked by the system boundary in blue in Fig-
 277 ure 5 (a), only the product water flow rates are considered in combination
 278 with the feed and product salt concentrations. It is assumed that the volu-
 279 metric flow rate of the water streams stays constant when passing the cell.
 280 This way, the actually applied electrical power, calculated from the applied
 281 voltage and the measured current, can be set in relation to the product water
 282 streams. Thus, the negative effect of diluate concentration and concentrate
 283 dilution due to water crossover is considered in the energy demand, as illus-
 284 trated in Figure 5 (b).

285

286 Due to the influence of the chosen system boundaries, the assumptions
 287 and terminology chosen in this article regarding the energy demand and

current efficiencies are elucidated in the following.

3.1. Energy demand per m^3 diluate product stream

There are several ways to calculate the energy demand for the desalination of one cubic meter of salt water, as indicated above. In addition to the differences between product and full mass balance, disparities between the mass balances around the diluate and around the concentrate stream were observed.

Neglect of water transfer, $E_{dil,noWT}$. When calculating the energy demand based on the full salt mass balance, the water transfer is neglected. The salt stream which is transferred from the diluate stream to the concentrate stream can be calculated in two ways: (1) via the salt mass balance around the diluate stream, which results in Equation 1 for the energy demand $E_{dil,D,noWT}$, and (2) via the salt mass balance around the concentrate stream, which results in Equation 2 for the energy demand $E_{dil,C,noWT}$. The average between the two energy demands $E_{dil,D,noWT}$ and $E_{dil,C,noWT}$ is in the following termed $E_{dil,noWT}$ (Equation 3).

$$E_{dil,D,noWT} = \frac{c_{Feed} \cdot I \cdot V}{n_{cp} \cdot (c_{Feed,D} \cdot \dot{V}_{Feed,D} - c_{Diluate} \cdot \dot{V}_{Diluate})} \quad (1)$$

$$E_{dil,C,noWT} = \frac{c_{Feed} \cdot I \cdot V}{n_{cp} \cdot (c_{Conc} \cdot \dot{V}_{Conc} - c_{Feed,C} \cdot \dot{V}_{Feed,C})} \quad (2)$$

$$E_{dil,noWT} = \frac{E_{dil,D,noWT} + E_{dil,C,noWT}}{2} \quad (3)$$

In these equations, I stands for the electric current and V for the cell voltage. c_{Feed} and $\dot{V}_{Feed}$ are the NaCl concentration and volumetric flow rate

of the feed stream, in which the subscripts D and C stand for the diluate and concentrate stream, respectively. n_{cp} stands for the number of cell pairs.

The consideration of the full salt mass balance allows the calculation of the actually transferred salt amount. However, the additional transfer of water due to hydration shells and osmotic effects leads to a reduction of the actual desalination and concentration performance. The concentrate is diluted and the diluate stream concentrated due to the transfer of water. This effect is not considered when calculating the energy demand via the full salt mass balance.

Consideration of water transfer, $E_{dil,withWT}$. When calculating the energy demand based on the product salt mass balance, however, the water transfer is considered. By using only the volumetric flow rate of the product streams, the actual energy demand for the production of a specific volume of product (diluate or concentrate) of a certain desired concentration can be calculated, as given in Equation 4 for the energy demand $E_{dil,D,withWT}$, and in Equation 5 for the energy demand $E_{dil,C,withWT}$. The average between the two energy demands $E_{dil,D,withWT}$ and $E_{dil,C,withWT}$ is in the following termed $E_{dil,withWT}$ (Equation 6).

$$E_{dil,D,withWT} = \frac{c_{Feed} \cdot I \cdot V}{(c_{Feed,D} - c_{Diluate}) \cdot n_{cp} \cdot \dot{V}_{Diluate}} \quad (4)$$

$$E_{dil,C,withWT} = \frac{c_{Feed} \cdot I \cdot V}{(c_{Conc} - c_{Feed,C}) \cdot n_{cp} \cdot \dot{V}_{Conc}} \quad (5)$$

$$E_{dil,withWT} = \frac{E_{dil,D,withWT} + E_{dil,C,withWT}}{2} \quad (6)$$

324 By using the above described equations, the additional electrical current
 325 required to reach exactly the concentration of 0 g/L NaCl in the diluate
 326 product stream is considered. Additional resistances within the desalination
 327 cell, especially due to the change of the diluate stream conductivity and the
 328 additional resistance of depleted laminar boundary layers at the membrane
 329 surface, are not considered by this. This means the values for "full desalina-
 330 tion" given in this article are not completely realistic and mostly serve as a
 331 base for comparing the different module layouts.

332 A full desalination is likely not possible using a single cell and single pass
 333 FCDI system at feed concentrations of 60 g/L NaCl. A (nearly) full desali-
 334 nation may be achieved when using an optimized cell design, for example by
 335 using ion-conductive spacers, similar to continuous electrodeionization sys-
 336 tems. However, a desalination to a low concentration of <1 g/L is possible.
 337 For practical applications, the actual energy demand for a specific separation
 338 task should be determined by an experiment in which the desired concentra-
 339 tions are reached. Only this way, or by applying a process model, it can be
 340 ensured that interlocking physical and chemical effects are considered.

341 *Mass balances diluate vs. concentrate.* Example results for the four different
 342 ways to calculate the energy demand are plotted in Figure 6 (a). The results
 343 for the average energy demand per cubic meter diluate without consideration
 344 of the water transfer, $E_{dil,noWT}$, and with consideration of the water transfer,
 345 $E_{dil,withWT}$, are plotted in Figure 6 (b).

346 When considering the different curves in Figure 6 (a), it is striking that in
 347 all cases of this example the energy demand was higher when calculated for
 348 the diluate stream, compared to the calculation via the concentrate stream.

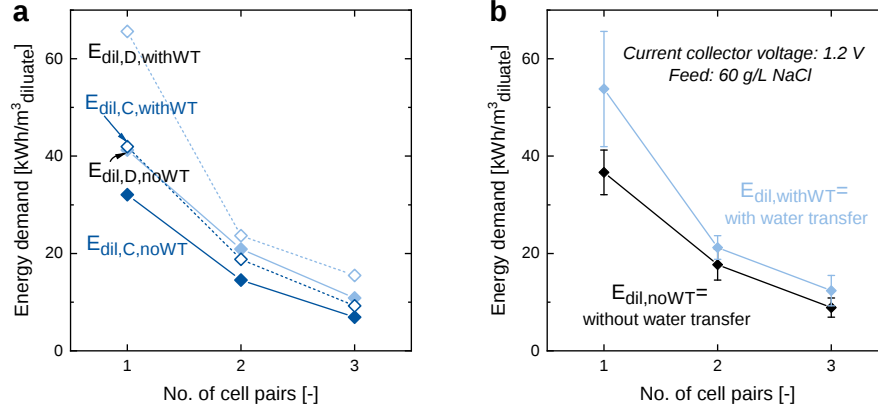


Figure 6: Illustration of the averaging regarding the energy demand calculations in this article. The sample graphs show results of desalination experiments comparing modules with one, two and three cell pairs with a NaCl feed concentration of 60 g/L and a cell voltage of 1.2 V. The graphs show the energy demand calculated per diluate product stream, based on (a) the results for the individual mass balances of diluate and concentrate stream and (b) the average of the two mass balances. The values are recalculated to represent full desalination. Values do not account for pumping energy.

349 However, a sighting of data collected over a longer period of time revealed
 350 experiments in which also the opposite was the case. The reason for these
 351 deviations are most probably experimental and/or measurement errors. An
 352 example for a possible systematic error in the data, which leads to a higher
 353 tendency of the energy demand being higher when calculated via the diluate
 354 mass balance, may for example be the evaporation of water from the water
 355 samples during or after the collection of water samples. This would lead to
 356 a concentration of the concentrate (and hence a performance improvement),
 357 as well as a concentration of the diluate (and hence a performance reduction
 358 and an increased energy demand).

359 In the following, only the average results between diluate and concentrate
 360 mass balance are plotted, similar to Figure 6 (b). This averaging based
 361 on two mass balances within the same experiment reduces the impact of
 362 experimental and measurement errors and allows a more reliable estimation
 363 of the energy demand required per cubic meter diluate product stream.

364 3.2. Energy demand per m^3 concentrate product stream

365 The results are more realistic when determining the energy demand based
 366 on the product mass balance including the water transfer. Due to this, the
 367 energy demand per cubic meter concentrate product stream is only plotted
 368 including the water transfer in the following sections. To ensure a compara-
 369 bility between the experimental results, the energy demand was recalculated
 370 for a concentration up to 260 g/L NaCl concentration in the concentrate,
 371 according to the following equation:

$$E_{conc260} = \frac{(260 \text{ g/L} - c_{Feed,C}) \cdot I \cdot V}{(c_{Conc} - c_{Feed,C}) \cdot n_{cp} \cdot \dot{V}_{Conc}} \quad (7)$$

372 By using this equation, the additional/ reduced current required to reach
 373 exactly the concentration of 260 g/L NaCl in the concentrate is considered.
 374 The change in resistances and back diffusion due to changes in the concen-
 375 tration gradients are not considered. To identify the actual energy demand
 376 for this specific task, an experiment in which these actual concentrations
 377 are reached would be required, due to the many interlocking physical and
 378 chemical effects.

379 3.3. Current efficiency

380 Similar to the energy demand, also the current efficiency (CE) can be
 381 calculated based on different mass balances. In case of FCDI processes, the
 382 current efficiency brings the transferred salt into relation with the required
 383 electric current:

$$CE = \frac{F \cdot \dot{n}_{Salttransfer}}{I} \quad (8)$$

384 In Equation 8, F stands for the Faraday constant, $\dot{n}_{Salttransfer}$ for the
 385 molar amount of salt transferred from the diluate to the concentrate stream,
 386 and I stands for the electric current. The salt flux $\dot{n}_{Salttransfer}$, and hence
 387 the current efficiency, can be calculated based on the full mass balance:

$$CE = \frac{F \cdot (c_{Feed,D} \cdot \dot{V}_{Feed,D} - c_{Diluate} \cdot \dot{V}_{Diluate})}{I \cdot M_{NaCl}} \quad (9)$$

388 Or based on the product mass balance:

$$CE_{eff} = \frac{F \cdot \dot{V}_{Diluate} \cdot (c_{Feed,D} - c_{Diluate})}{I \cdot M_{NaCl}} \quad (10)$$

389 In Equations 9 and 10, M_{NaCl} represents the molar mass of the transferred
 390 salt, which in this case is NaCl. The first version of the current efficiency,
 391 based on the full mass balance, represents the physically correct current
 392 efficiency. The full salt mass balance gives information on how much salt was
 393 actually transferred. The CE based on the full mass balance hence represents
 394 the actual number of ion pairs transferred per electron and allows conclusions
 395 regarding the membrane selectivity. However, as discussed before, this does
 396 not represent the apparent current efficiency observed in a real application. In

397 reality, the apparent current efficiency will also be reduced by water transfer,
 398 which is why the term "effective current efficiency", CE_{eff} , is introduced
 399 here for the cases when the CE has been calculated based on the product
 400 mass balance.

401 4. Results and discussion

402 4.1. Current-voltage characteristics

403 For an initial comparison of the performance of different energy demand
 404 reduction concepts, the current-voltage characteristics were investigated, as
 405 described above. The results for NaCl concentrations of 60 and 120 g/L in
 406 feed and flow electrodes are plotted in Figure 7 in form of IV-curves.

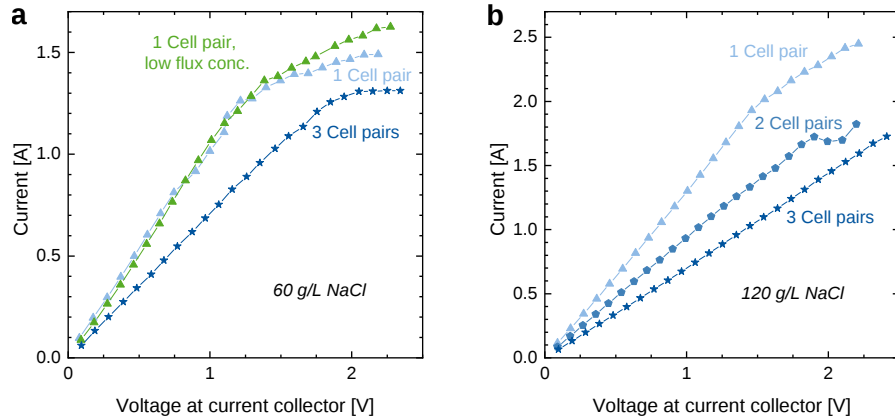


Figure 7: IV-curves of FCDI systems at (a) 60 g/L NaCl, comparing the standard system to a system operated at a low concentrate flux and a system with three cell pairs, and at (b) 120 g/L NaCl, comparing the standard system to systems with two and three cell pairs.

407 Similar to IV-curves of electrodialysis systems, the FCDI IV-curves show
 408 an ohmic region at low voltages, in which the electrical current increases lin-

early with increasing potential. At higher potentials, in case of the curves at hand usually around 1-2 V, the curves transcend to a limiting current region. The ohmic resistances and limiting currents differ significantly between the different systems. The resulting ohmic resistance determined from the IV-curves are listed in Table 2.

Table 2: Overview of the ohmic resistances derived from the IV-curves.

Description	<i>Experimental parameters</i>		<i>Analysis results</i>
	Slurry wt.% AC	Feed water mL/min	Ohmic resistances Ω
<i>IV-curves with 60 g/L NaCl in Feed and Slurry</i>			
1 CP, Standard	15	D:1/C:1	0.927
1 CP, low flux concentr.	15	D:1/C:0.04	0.994
3 CP	15	D:1/C:1	1.411
<i>IV-curves with 120 g/L NaCl in Feed and Slurry</i>			
1 CP, Standard	15	D:1/C:1	0.789
2 CP	15	D:1/C:1	1.056
3 CP	15	D:1/C:1	1.447

The standard FCDI system with three ion-exchange membranes (AEM, CEM, AEM) in cross-flow mode has an ohmic resistance of 0.927 Ω . At around 1.2 V, the system starts to transcend to a limiting region, reaching a limiting current ranging around 1.4-1.5 A. The same system operated at a low concentrate flux, which would enable a high concentration factor in a desalination experiment, exhibits a very similar current-voltage behaviour. The two curves and ohmic resistances are very comparable. Only a small difference can be observed in the limiting region, in which the current of the low concentrate flux curve has a slightly steeper slope, reaching currents of close to 1.6 A in the same voltage range. This insignificant difference may

424 be caused by an increasing conductivity in the concentrate channel due to
425 the reduced flow rate.

426 In case of the standard FCDI system with one cell pair at 120 g/L, the
427 overall behaviour is similar to the system at 60 g/L, while the increased con-
428 ductivity of the 120 g/L feed solution and flow-electrode electrolyte concen-
429 tration leads to a significantly lower ohmic resistance ($0.789\ \Omega$). Additionally,
430 the limiting current and the voltage at which the limiting region sets in are
431 increased significantly.

432 Striking is the unusually flat "limiting current region" in case of many
433 IV-curves plotted here. The reason for this is probably that unlike in IV-
434 curves of electrodialysis processes, the effect causing the "limiting current"
435 region is a different one in case of these FCDI IV-curves. The electric current
436 required for the full desalination of a 60 g/L NaCl solution at a feed flow rate
437 of 1 mL/min, assuming a CE of 1, is 1.65 A. The maximum current achieved
438 in an FCDI IV-curve with a 60 g/L feed is exactly in this range. This
439 indicates that the limiting current observed here is close to the maximum
440 current reachable at the applied flow rate and feed salinity, based on the salt
441 ions available in the feed stream. Having this in mind, the IV-curves can be
442 discussed under a different light.

443 The introduction of additional cell pairs into an FCDI cell leads, as is to
444 be expected, to an increased ohmic resistance. In case of the 60 g/L NaCl
445 concentration, the resistance increases from $0.927\ \Omega$ (1 cell pair) to $1.411\ \Omega$ (3
446 cell pairs). This would be equal to around $0.242\ \Omega$ per cell pair. The limiting
447 current decreases slightly with increasing numbers of cell pairs, while the
448 voltage at which the limiting current is reached increases significantly, due to

the increased cell resistance. Presuming the reason for the observed "limiting current" is really the maximum desalination, as described above, the cause for the reduced limiting current density in this case may be a maldistribution of the flow between the different cell pairs. In case of small differences in the volumetric flow rate between the different cell pairs the cell pair with the lowest flow rate would reach full desalination at the lowest current density. Hence, the lowest flow rate would limit the further desalination of the other cell pairs. This hypothesis should be investigated further in future works.

The trends at a NaCl concentration of 120 g/L are similar to the trends observed at NaCl concentrations of 60 g/L in the feed solution. In case of the 120 g/L concentration, however, the ohmic resistance increases more significantly with the addition of the second cell pair (which results in a three cell pair system). The reason for this is not clear, a possible explanation may be measurement inaccuracies or an unproportional increase of the resistance when bordered with salt solutions of significantly different concentrations [38].

4.2. Desalination and concentration performance

Figure 8 shows results of desalination experiments performed with the experimental conditions given in Table 1. Figure 8 (a) shows a plot of the NaCl concentrations of the diluate and concentrate product streams at a feed concentration of 60 g/L and a constant potential of 1.2 V applied to the graphite plates. The grey line indicates the feed concentration c_0 . Figure 8 (b) shows the results of desalination/concentration experiments at a feed concentration of 120 g/L. In this case, the constant potential applied to the graphite plates was varied between 1.2 V and 1.8 V.

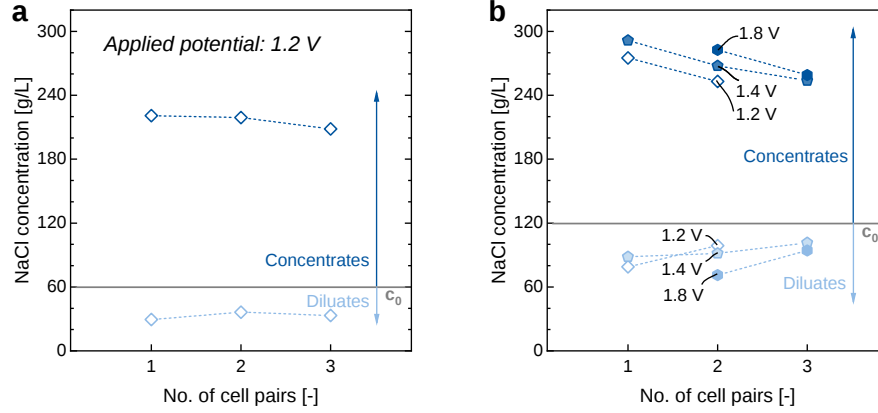


Figure 8: Results of desalination experiments comparing modules with one, two and three cell pairs. The graphs show the NaCl concentrations of feed, diluate and concentrate streams depending on the number of cell pairs at NaCl feed concentrations of (a) 60 g/L and (b) 120 g/L. The potential applied to the current collectors was 1.2 V in case of the 60 g/L experiments and was varied between 1.2 V and 1.8 V in case of the 120 g/L experiments.

474 In case of all experimental results plotted in Figure 8, the NaCl concen-
 475 tration achieved in the concentrate stream was higher than 200 g/L NaCl.
 476 The maximum NaCl concentration achieved in this study was 291.5 g/L.
 477 The water recovery in the experiments presented here ranges from 70 % to
 478 92 % at NaCl feed concentrations of 60 and 120 g/L NaCl. This is a very
 479 promising result regarding the use of FCDI as a potential brine concentration
 480 technology.

481 In case of both 60 and 120 g/L NaCl as feed concentration, the NaCl con-
 482 centration was reduced by about 30 g/L when applying the same feed flow
 483 rate in the FCDI system. This leads to a diluate product stream concen-
 484 tration of around 30 g/L NaCl in case of the 60 g/L feed stream and about

485 90 g/L NaCl in the diluate product stream in case of the 120 g/L feed stream
486 at 1.2 V. The NaCl transfer rates in g NaCl/min calculated for these exper-
487 iments are in a similar range for both feed concentrations. It is likely that
488 in this concentration range, meaning high salinities of 60-120 g/L NaCl, the
489 additional increase in conductivity has only a small effect. This corresponds
490 well with results presented by Yang et al. [39]. The small effect it has is
491 probably countered by a decreasing membrane selectivity at increasing salt
492 concentrations, which results in a decreasing current efficiency and higher
493 back diffusion rates.

494 In case of both feed concentrations, the desalination and concentration
495 performance decreases when adding additional cell pairs, due to the increased
496 resistance with increasing number of cell pairs. This trend can be avoided to
497 a certain extent by increasing the applied voltage, as shown in Figure 8 (b).
498 However, as faradaic reactions such as carbon oxidation are to be avoided in
499 FCDI, the applicable voltage is limited. Due to this, the maximum voltage
500 applied in this work did not exceed 2 V in longer experiments and up to
501 2.5 V in shorter experiments such as the measurement of IV-curves.

502 *4.3. Energy demand*

503 The energy demand corresponding to the results regarding the desalina-
504 tion performance at 60 g/L NaCl in the feedstream, shown in Figure 8 (a),
505 is plotted in Figure 9.

506 The energy demand is normalized per cubic metre diluate product stream,
507 determined according to the equations described above. The energy demand
508 with and without consideration of the water transfer decreases significantly
509 with increasing number of cell pairs. When comparing these results to the

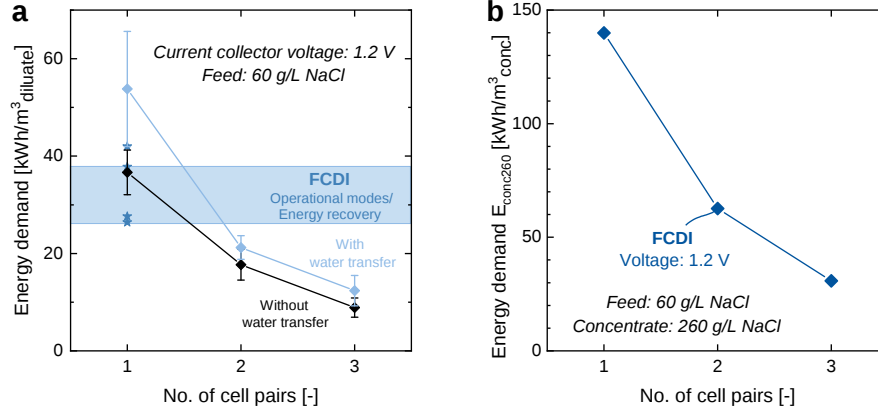


Figure 9: Results of desalination experiments comparing modules with one, two and three cell pairs with a NaCl feed concentration of 60 g/L and a cell voltage of 1.2 V. The graphs show the energy demand calculated (a) per diluate product stream, compared to the value range achieved in our previous article [15], and (b) per concentrate stream. The values are recalculated to represent full desalination in case of (a) and concentration up to 260 g/L NaCl in case of (b). Values do not account for pumping energy.

510 results presented in our previous article [15], indicated by the blue area in
 511 Figure 9 (a), it becomes clear that the use of multiple cell pairs can reduce the
 512 energy demand of an FCDI process more efficiently than the partial energy
 513 recovery achievable using a second regeneration module. With energy recov-
 514 ery, the energy demand for the desalination of a 60 g/L NaCl solution was
 515 reduced to around 25 kWh/m³ diluate, while a value of only 15.5 kWh/m³
 516 diluate was reached using an FCDI module with three cell pairs.

517 The same trend is visible in Figure 9 (b), which shows the energy demand
 518 per cubic metre concentrate product stream. In this figure, all values con-
 519 sider the water transfer, which leads to a dilution of the concentrate. The
 520 use of three cell pairs leads to a reduction of the energy demand by more

521 than 70 %, compared to using only a single cell pair.

522

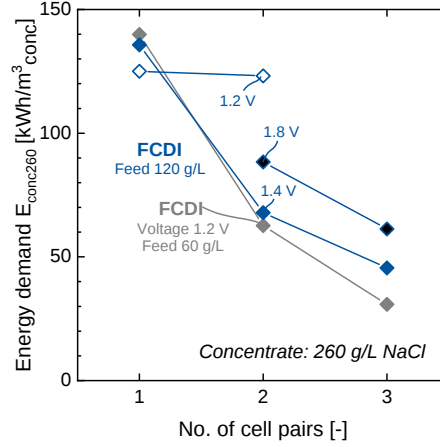


Figure 10: Results of desalination experiments comparing modules with one, two and three cell pairs with a NaCl feed concentration of 120 g/L and a constant cell voltage, which was varied between 1.2 V and 1.8 V. The graphs show the energy demand calculated per cubic meter concentrate product stream. The values are recalculated to represent concentration up to 260 g/L NaCl. Values do not account for pumping energy.

523 Figure 10 shows the energy demand per cubic metre concentrate product
524 stream, which corresponds to the desalination performances plotted in Fig-
525 ure 8 (b). The results for the concentration of a 120 g/L NaCl solution at
526 varied cell voltages are compared to the results achieved for the concentra-
527 tion of a 60 g/L NaCl solution. All in all, the desalination and concentration
528 of a 120 g/L NaCl solution at a cell voltage of 1.2 V worked well when using
529 a single cell pair. However, when increasing the number of cell pairs to two,
530 the energy demand hardly decreased when applying a voltage of 1.2 V. When
531 applying a voltage of 1.4 V or higher, the energy demand decreases signifi-

cantly with increasing number of cell pairs, similar to the results observed for a feed concentration of 60 g/L NaCl. A reason for this is possibly a strong back diffusion and increased resistance, which requires the application of a higher voltage. Whether this is a reproducible trend should be investigated further in the future. When the applied voltage is increased further to 1.8 V, the desalination performance improves while at the same time the energy demand increases. However, the overall energy demand is still low compared to a single cell pair system. The right choice of the applied voltage will be an optimization task when designing an FCDI system for an actual application. While increasing the voltage leads to higher current densities, and hence reduced capital cost, it also leads to a higher energy demand and increased operation costs.

Surprising is that at a constant voltage of 1.4 V, the energy demand for the concentration up to 260 g/L NaCl is nearly the same for a for a 120 g/L feed solution as for a 60 g/L feed solution at 1.2 V. This is a distinct difference to thermally driven processes, in which the feed concentration has a major effect on the energy demand when aiming at the same concentrate concentration. Hence, an advantage of FCDI processes compared to thermally driven processes may be the ability to bridge this wide concentration range with a moderate energy demand.

4.4. *Cell pair resistances and pumping energy*

The use of multiple cell pairs in an FCDI module has several potential advantages, as described above. The theoretical calculations presented above in Figure 2 illustrate the expected advantages. The results presented in Figure 11 are based on the same calculations and illustrate the fractions of

the energy demand caused by the different resistances in comparison to the required pumping energy in case of one and three cell pairs. The energy demand calculated for pumping the flow electrodes is based on pressure drop measurements in flow electrodes continuously pumped by a peristaltic pump through a circuit with a dampening vessel to even out pressure fluctuations, and was determined analogue to measurements presented in our previous publication [15]. In Figure 11, the theoretical estimations are compared to actual experimental results.

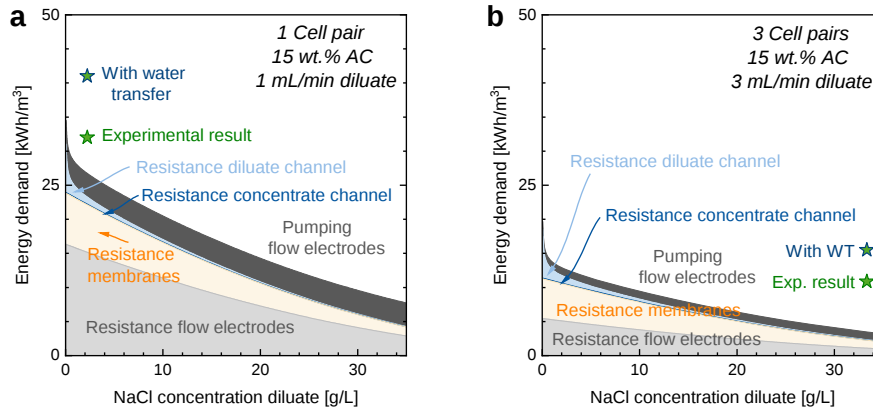


Figure 11: Results of theoretical calculations regarding the influence of the NaCl concentration of the diluate stream on the energy demand and its causes in an FCDI cell with (a) 1 cell pair and (b) 3 cell pairs. Assumptions as described above: Constant diluate flow rate of 1 mL/min, diluate concentration constant throughout cell (overestimated resistances/cell voltage), no consideration of laminar boundary layers, desalination up to the required concentration (varied electrical current).

As can be seen from the calculation results plotted in Figure 11 (a), the resistance of the flow electrodes is a major driver of the energy demand in case of a single cell pair. Depending on the required diluate concentration,

568 either the membrane resistance or the flow-electrode pumping energy make
569 up a larger part of the total energy demand. By introducing multiple cell
570 pairs, here represented by the example of three cell pairs, the fraction of the
571 flow-electrode resistance and pumping energy, which are two major drivers of
572 the energy demand, can be reduced significantly. This makes the membrane
573 resistance a key factor to reduce the energy demand further in case of an
574 FCDI system with more than one cell pair. Hence, in the following sections
575 the influence of the membranes is investigated in more detail.

576 When considering the results of practical experiments to the theoretical
577 calculations, the energy demand in the experiments is significantly higher
578 than the estimations. This indicates that not all phenomena are accounted
579 for. Some of these, of course, lie in the nature of the estimation itself: non-
580 ideal behaviour is not considered, such as a reduced current efficiency and
581 back-diffusion. These lead to increased currents in reality. Additionally,
582 laminar boundary layers are not considered, which may increase the required
583 voltage. Studies published by Geise et al. [38]) and Galama et al. [40]) also
584 indicate a more than ten times increased membrane resistance at high con-
585 centration gradients across the membrane, which may be an explanation for
586 increased cell resistances. The absolute concentration difference across the
587 membrane is in this case at least 170 g/L NaCl. The question is, whether
588 this increased resistance only occurs when one of the bordering concentra-
589 tions is very low, as described in the study by Geise et al. [38], or when
590 there is generally a large concentration gradient. The combination of these
591 phenomena may explain why the deviation between experimental and the-
592 oretical results is especially significant in case of the three cell pair system.

593 The higher number of membranes in the system may increase the overall
594 effect of the non-idealities which are not considered in this calculation.

595 *4.5. Effective current efficiency and diluate concentration*

596 In some cases, extreme concentration gradients occur over a single ion-
597 exchange membrane in the above described experiments. In literature, in-
598 creased membrane resistances were observed for high concentration gradients
599 [38, 40]. Such concentration gradients are rarely reached in electrodialysis
600 processes, due to the choice of higher flow rates and the treatment of lower
601 salinities in most cases. A remaining question is how such high concentration
602 gradients affect the membrane performance and selectivity. Does the current
603 efficiency, for example, mainly depend on the concentration of the diluate
604 stream ("low concentration") or the concentration of the concentrate stream
605 ("high concentration")? The NaCl concentrations measured in diluate and
606 concentrate product streams over the measured current efficiency, obtained
607 from a number of experiments performed in the context of this study, are
608 plotted in Figure 12. The experiments were performed with high salinity
609 feeds and various continuous FCDI process and cell configurations.

610 There is no clear trend visible for the NaCl concentration in the concen-
611 trate streams and the current efficiency. This is surprising, as one may expect
612 a relation due to reduced membrane selectivities at high salinities. However,
613 a very clear trend is visible for the NaCl concentration in the diluate streams
614 and the current efficiency. Low salinities in the diluate stream are clearly
615 associated with high current efficiencies. There are two explanations for this,
616 which may also occur in combination: (1) The low concentrations in the
617 diluate product streams lead to a significant improvement of the membrane

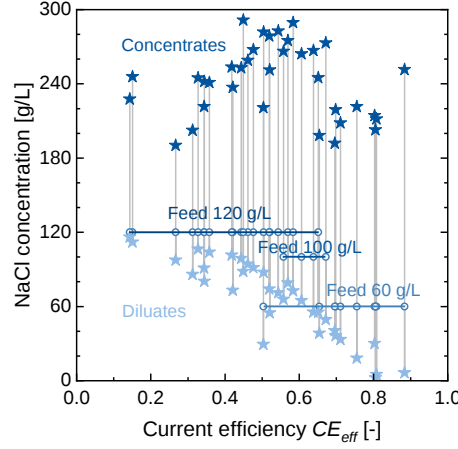


Figure 12: Results for the NaCl concentration in diluate and concentrate product stream plotted over the effective current efficiency, CE_{eff} , which considers the water transfer within the system. The plot shows results from a high number of experiments performed with high salinity feeds and various continuous FCDI process and cell configurations.

618 selectivity and hence the current efficiency. This would mean the lower con-
 619 centration bordering an ion-exchange membrane determines the membrane
 620 selectivity. This would be a possible advantage for ion-exchange membrane
 621 processes aiming at high concentration gradients, in opposition to high dilu-
 622 ate flow rates aiming at the reduction of the impact of concentration polar-
 623 ization. (2) Low concentrations in the diluate are only reachable, when also
 624 a high membrane selectivity and hence a high current efficiency is achieved.
 625 A low membrane selectivity would lead to a stronger back diffusion of salt
 626 into the diluate stream and hence a higher salt concentration in the diluate
 627 product stream.

628 Apart from the scientific interest, the apparent independency of the cur-
 629 rent efficiency on the concentrate product stream concentration is promising

for an application of FCDI processes for brine concentration and brine treatment in general.

4.6. Energy demand of FCDI compared to mechanical vapor compression

The improvements achieved by the use of more than one cell pair are significant and illustrate the extant potential of the FCDI technology. Figure 13 compares the energy demand achieved in FCDI experiments with one, two and three cell pairs to literature values for mechanical vapor compression [41]) and results achieved by FCDI systems with energy recovery presented in our previous article [15].

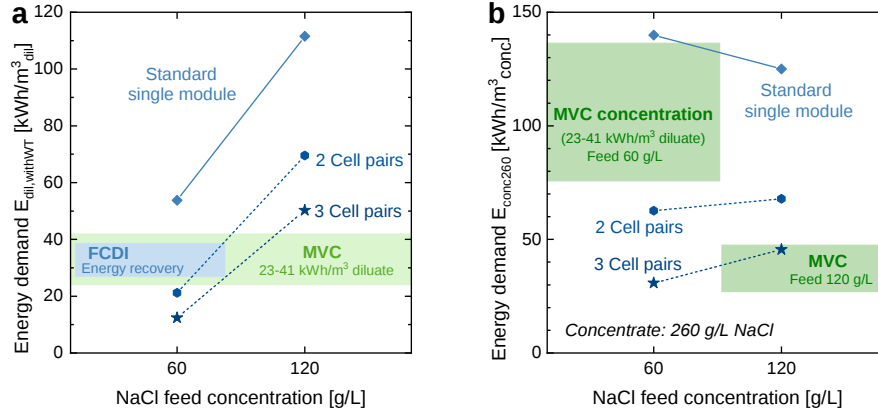


Figure 13: The energy demand of FCDI experiments with one, two and three cell pairs in direct comparison with the energy demand of MVC for a comparable separation task [41]) and FCDI with energy recovery [15].

The energy demand for the production of one cubic meter of desalinated water using the different FCDI systems compared to mechanical vapor compression (MVC) is plotted in Figure 13 (a). Figure 13 (b) shows results for the energy demand when normalized per one cubic meter of produced con-

643 concentrate at 260 g/L NaCl. All values consider the increased energy demand
644 due to water transfer from the diluate to the concentrate channel.

645 The energy demand scales with increasing feed concentration in case of
646 desalination, which is consistent for all desalination technologies driven by
647 an electrical field. However, in case of FCDI, the energy demand for con-
648 centration is fairly independent from the feed concentrations of 60 g/L or
649 120 g/L NaCl.

650 To achieve a reduced energy demand it is vital to reduce the cell voltage.
651 This can be achieved by the use of two or more cell pairs, which leads to a
652 division of the voltage drop over the flow electrode by the number of cell pairs.
653 The electrical current stays more or less constant, while the product volume
654 stream is doubled or tripled, leading to a significant reduction of the energy
655 demand per product volume. Compared to FCDI with energy recovery, the
656 use of multiple cell pairs is a more efficient approach, as it enables (1) a better
657 desalination and concentration performance, (2) a higher current density, is
658 (3) generally more stable and reliable in operation, and (4) enables a stronger
659 reduction of the energy demand.

660 When comparing the lab results regarding FCDI to literature results re-
661 garding MVC [41]-9, FCDI is competitive with MVC at the lower feed salinity
662 of 60 g/L regarding the energy demand. At higher feed salinities, the energy
663 demand for concentration via FCDI is barely able to reach values comparable
664 to MVC. However, considering the given potential of FCDI, this may change
665 in the future. An advantage of FCDI over alternative technologies such as
666 mechanical vapor compression or osmotically assisted reverse osmosis may
667 be the possibility of a selective recovery of ionic components.

668 An open question is, whether FCDI can become competitive with state-of-
669 the-art technologies, such as MVC, regarding the investment and operating
670 costs.

671 5. Conclusions

672 In this article, it is shown that continuously operated FCDI systems can
673 be applied for the concentration of salt brines. Concentrations of up to
674 291.5 g/L NaCl were reached in the concentrate product stream at water
675 recoveries ranging from 70 % to 92 % at NaCl feed concentrations of 60 and
676 120 g/L NaCl. Hence, FCDI is a promising technology for the treatment and
677 recovery of salts from high salinity water streams (brines).

678 So far, the energy demand of FCDI systems tested for brine treatment was
679 comparably high. However, the use of multiple cell pairs in FCDI systems, as
680 presented in this article, is a very promising approach to reduce the overall
681 energy demand of FCDI systems. Advantages of this approach are: (1)
682 Reduced influence of the electrical resistance of the flow electrodes and hence
683 a significantly decreased electrical energy demand, (2) reduced flow-electrode
684 pumping energy per volume product stream and per mass of transferred salt,
685 (3) reduced investment costs compared to stacking of single-cell pair systems.

686 The economic feasibility of FCDI systems still needs to be proven. How-
687 ever, with further application-oriented research, FCDI systems may soon
688 become viable for many industrial and agricultural applications aiming at
689 closing material cycles via salt recovery from waste water streams.

690 **Acknowledgements**

691 This work was supported by the German Federal Ministry of Education
692 and Research (BMBF) under the project ElektroWirbel (FKZ 13XP5008)
693 and by the European Research Council (ERC) under the European Unions
694 Horizon 2020 research and innovation program (694946). The authors thank
695 Fumatech BWT GmbH and Donau Carbon GmbH for the provision of mate-
696 rial samples. The authors thank the ElektroWirbel project partners and all
697 other project partners and colleagues for the valuable discussions. The au-
698 thors are especially grateful for the in-depth discussions with Yuliya Schießer,
699 Matthias Woyciechowski, Tomas Klicpera and Youri Gendel. The authors
700 thank Max Düppenbecker, Jingyu Xie, Zhaowei Zou and Niklas Köller for
701 their constructive effort in this study.

- [1] M. Elimelech, W. A. Phillip, The Future of Seawater and the Environ-
ment: Energy, Technology, and the Environment, *Science* 333 (2011)
712–718. doi:10.1126/science.1200488.
- [2] M. A. Anderson, A. L. Cudero, J. Palma, Capacitive deionization as
an electrochemical means of saving energy and delivering clean water.
Comparison to present desalination practices: Will it compete?, *Elec-
trochimica Acta* (12) 3845–3856. doi:10.1016/j.electacta.2010.02.012.
- [3] S. Porada, R. Zhao, A. van der Wal, V. Presser, P. M. Biesheuvel,
Review on the science and technology of water desalination by ca-
pacitive deionization, *Progress in Materials Science* (8) 1388–1442.
doi:10.1016/j.pmatsci.2013.03.005.

- [4] Y. Oren, Capacitive deionization (CDI) for desalination and water treatment - past, present and future (a review), *Desalination* 228 (1-3) (2008) 10–29. doi:10.1016/j.desal.2007.08.005.
- [5] M. Suss, S. Porada, X. Sun, M. Biesheuvel, J. Yoon, V. Presser, Water desalination via capacitive deionization: what is it and what can we expect from it?, *Energy & Environmental Science* 8 (2015) 2296–2319. doi:10.1039/C5EE00519A.
- [6] F. A. AlMarzooqi, A. A. Al Ghaferi, I. Saadat, N. Hilal, Application of Capacitive Deionisation in water desalination: A review, *Desalination* 3–15doi:10.1016/j.desal.2014.02.031.
- [7] W. Tang, J. Liang, D. He, J. Gong, L. Tang, Z. Liu, D. Wang, G. Zeng, Various cell architectures of capacitive deionization: Recent advances and future trends, *Water Research* 150 (2019) 225–251. doi:10.1016/j.watres.2018.11.064.
- [8] S.-i. Jeon, H.-r. Park, J.-g. Yeo, S. Yang, C. H. Cho, M. H. Han, D. K. Kim, Desalination via a new membrane capacitive deionization process utilizing flow-electrodes, *Energy & Environmental Science* 6 (5) (2013) 1471–1475. doi:Doi 10.1039/C3ee24443a.
- [9] B. Akuzum, P. Singh, D. A. Eichfeld, S. Uzun, Y. Gogotsi, E. C. Kumbur, *Energy , Environmental , and Catalysis Applications Percolation Characteristics of Conductive Additives for Capacitive Flowable (Semi-Solid) Electrodes Percolation Characteristics of Con-*

ductive Additives for Capacitive Flowable (Semi-Solid) Electrodes-
doi:10.1021/acsami.9b19739.

- [10] G. Shukla, A. A. Franco, Interphases in Electroactive Suspension Systems: Where Chemistry Meets Mesoscale Physics, *Batteries & Supercaps* 2 (7) (2019) 579–590. doi:10.1002/batt.201800152.
- [11] S.-i. Jeon, J.-g. Yeo, S. Yang, J. Choi, D. K. Kim, Ion storage and energy recovery of a flow-electrode capacitive deionization process, *Journal of Materials Chemistry A* 2 (18) (2014) 6378. doi:10.1039/c4ta00377b.
- [12] Y. Gendel, A. K. E. Rommerskirchen, O. David, M. Wessling, Batch mode and continuous desalination of water using flowing carbon deionization (FCDI) technology, *Electrochemistry Communications* 46 (2014) 152–156. doi:10.1016/j.elecom.2014.06.004.
- [13] A. Rommerskirchen, Y. Gendel, M. Wessling, Single module flow-electrode capacitive deionization for continuous water desalination, *Electrochemistry Communications* 60 (2015) 34–37. doi:10.1016/j.elecom.2015.07.018.
- [14] G. J. Doornbusch, J. E. Dykstra, P. M. Biesheuvel, M. E. Suss, Fluidized bed electrodes with high carbon loading applied to water desalination by capacitive deionization, *Journal of Materials Chemistry A* 3642–3647doi:10.1039/C5TA10316A.
- [15] A. Rommerskirchen, C. J. Linnartz, D. Müller, L. K. Willenberg, M. Wessling, Energy Recovery and Process Design in Continuous Flow-Electrode Capacitive Deionization Processes, *ACS Sus-*

- tainable Chemistry and Engineering 6 (10) (2018) 13007–13015. doi:10.1021/acssuschemeng.8b02466.
- [16] S. Shanbhag, J. F. Whitacre, M. S. Mauter, The Origins of Low Efficiency in Electrochemical De-Ionization Systems, *Journal of The Electrochemical Society* (14) E363–E371. doi:10.1149/2.0181614jes.
- [17] K. B. Hatzell, M. Boota, Y. Gogotsi, Materials for suspension (semi-solid) electrodes for energy and water technologies, *Chem. Soc. Rev.* 44 (23) (2015) 8664–8687. doi:10.1039/C5CS00279F.
- [18] S. Dahiya, B. K. Mishra, Enhancing understandability and performance of flow electrode capacitive deionisation by optimizing configurational and operational parameters : A review on recent progress, *Separation and Purification Technology* (November 2019) 116660. doi:10.1016/j.seppur.2020.116660.
- [19] S. Porada, D. Weingarth, H. V. M. Hamelers, M. Bryjak, V. Presser, P. M. Biesheuvel, Carbon flow electrodes for continuous operation of capacitive deionization and capacitive mixing energy generation, *Journal of Materials Chemistry A* 2 (24) (2014) 9313–9321. doi:10.1039/c4ta01783h.
- [20] K. B. Hatzell, E. Iwama, A. Ferris, B. Daffos, K. Urita, T. Tzedakis, F. Chauvet, P. L. Taberna, Y. Gogotsi, P. Simon, Capacitive deionization concept based on suspension electrodes without ion exchange membranes, *Electrochemistry Communications* 18–21doi:10.1016/j.elecom.2014.03.003.

- [21] C. Linnartz, A. Rommerskirchen, M. Wessling, Y. Gendel, Flow-electrode capacitive deionization for double displacement reactions, *ACS Sustainable Chemistry & Engineering* 5 (2017) 3906–3912. doi:10.1021/acssuschemeng.6b03086.
- [22] C. Zhang, J. Ma, D. He, T. D. Waite, Capacitive Membrane Stripping for Ammonia Recovery (CapAmm) from Dilute Wastewaters, *Environmental Science and Technology Letters* 5 (1) (2018) 43–49. doi:10.1021/acs.estlett.7b00534.
- [23] C. Zhang, J. Ma, T. D. Waite, Ammonia-Rich Solution Production from Wastewaters Using Chemical-Free Flow-Electrode Capacitive Deionization, *ACS Sustainable Chemistry and Engineering* 7 (7) (2019) 6480–6485. doi:10.1021/acssuschemeng.9b00314.
- [24] K. Fang, H. Gong, W. He, F. Peng, C. He, K. Wang, Recovering ammonia from municipal wastewater by flow-electrode capacitive deionization, *Chemical Engineering Journal* 348 (2018) 301–309. doi:10.1016/j.cej.2018.04.128.
- [25] Y. Bian, X. Chen, L. Lu, P. Liang, Z. J. Ren, Concurrent Nitrogen and Phosphorus Recovery Using Flow-Electrode Capacitive Deionization, *ACS Sustainable Chemistry and Engineering* 7 (8) (2019) 7844–7850. doi:10.1021/acssuschemeng.9b00065.
- [26] J. Song, J. Ma, C. Zhang, C. He, T. D. Waite, Implication of non-electrostatic contribution to deionization in flow-electrode CDI: Case

- study of nitrate removal from contaminated source waters, *Frontiers in Chemistry* 7 (2019) 1–11. doi:10.3389/fchem.2019.00146.
- [27] X. Zhang, F. Yang, J. Ma, P. Liang, Effective removal and selective capture of copper from salty solution in flow electrode capacitive deionization, *Environmental Science: Water Research & Technology* doi:10.1039/c9ew00467j.
- [28] J. Ma, Y. Zhang, R. N. Collins, S. Tsarev, N. Aoyagi, A. S. Kinsela, A. M. Jones, T. D. Waite, Flow-Electrode CDI Removes the Uncharged Ca-UO₂-CO₃ Ternary Complex from Brackish Potable Groundwater: Complex Dissociation, Transport, and Sorption, *Environmental Science and Technology* 53 (5) (2019) 2739–2747. doi:10.1021/acs.est.8b07157.
- [29] S. Choi, B. Chang, J. H. Kang, M. S. Diallo, J. W. Choi, Energy-efficient hybrid FCDI-NF desalination process with tunable salt rejection and high water recovery, *Journal of Membrane Science* 580–586doi:10.1016/j.memsci.2017.07.043.
- [30] A. Giwa, V. Dufour, F. Al Marzooqi, M. Al Kaabi, S. W. Hasan, Brine management methods: Recent innovations and current status, *Desalination* 1–23doi:10.1016/j.desal.2016.12.008.
- [31] J. Ma, J. Ma, C. Zhang, J. Song, W. Dong, T. D. Waite, Flow-electrode capacitive deionization (FCDI) scale-up using a membrane stack configuration, *Water Research* 115186doi:10.1016/j.watres.2019.115186.
- [32] A. Rommerskirchen, A. Kalde, C. Linnartz, L. Bongers, G. Linz, M. Wessling, Unraveling charge transport in carbon flow-electrodes:

- Performance prediction for desalination applications, *Carbon* 145 (2019) 507–520. doi:10.1016/j.carbon.2019.01.053.
- [33] K. B. Hatzell, M. C. Hatzell, K. M. Cook, M. Boota, G. M. Housel, A. McBride, E. C. Kumbur, Y. Gogotsi, Effect of oxidation of carbon material on suspension electrodes for flow electrode capacitive deionization, *Environmental Science and Technology* 49 (5) (2015) 3040–3047. doi:10.1021/es5055989.
- [34] P. Liang, X. Sun, Y. Bian, H. Zhang, X. Yang, Y. Jiang, P. Liu, X. Huang, Optimized desalination performance of high voltage flow-electrode capacitive deionization by adding carbon black in flow-electrode, *Desalination* 420 (2017) 63–69. doi:10.1016/j.desal.2017.05.023.
- [35] S. Yang, H.-r. Park, J. Yoo, H. Kim, J. Choi, M. H. Han, D. K. Kim, Plate-Shaped Graphite for Improved Performance of Flow-Electrode Capacitive Deionization, *Journal of The Electrochemical Society* 164 (13) (2017) E480–E488. doi:10.1149/2.1551713jes.
- [36] K. Tang, S. Yiacoumi, Y. Li, C. Tsouris, Enhanced Water Desalination by Increasing the Electroconductivity of Carbon Powders for High-Performance Flow-Electrode Capacitive Deionization, *ACS Sustainable Chemistry and Engineering* 7 (1) (2019) 1085–1094. doi:10.1021/acssuschemeng.8b04746.
- [37] Y. Cho, C. Y. Yoo, S. W. Lee, H. Yoon, K. S. Lee, S. C. Yang, D. K. Kim, Flow-electrode capacitive deionization with

- highly enhanced salt removal performance utilizing high-aspect ratio functionalized carbon nanotubes, *Water Research* (2019) 252–259doi:10.1016/j.watres.2018.11.080.
- [38] G. M. Geise, A. J. Curtis, M. C. Hatzell, M. A. Hickner, B. E. Logan, Salt Concentration Differences Alter Membrane Resistance in Reverse Electrodialysis Stacks, *Environmental Science and Technology Letters* 1 (1) (2013) 36–39. doi:10.1021/ez4000719.
- [39] S. Yang, J. Choi, J.-g. Yeo, S.-i. Jeon, H.-r. Park, D. K. Kim, Flow-Electrode Capacitive Deionization Using an Aqueous Electrolyte with a High Salt Concentration, *Environmental Science & Technology* (11) 5892–5899. doi:10.1021/acs.est.5b04640.
- [40] A. H. Galama, D. A. Vermaas, J. Veerman, M. Saakes, H. H. Rijnaarts, J. W. Post, K. Nijmeijer, Membrane resistance: The effect of salinity gradients over a cation exchange membrane, *Journal of Membrane Science* 279–291doi:10.1016/j.memsci.2014.05.046.
- [41] G. P. Thiel, E. W. Tow, L. D. Banchik, H. W. Chung, J. H. Lienhard V, Energy consumption in desalinating produced water from shale oil and gas extraction, *Desalination* 94–112doi:10.1016/j.desal.2014.12.038.