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Effects of Pore Size on Na/Ca Ion Selectivity Using Flow Through Electrode Capacitive Deionization

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Paper Abstract

In flow through electrode capacitive deionization (fte-CDI), low salinity brackish water flows through two porous carbon electrodes. When an electrical potential difference is applied over the electrodes, ions migrate towards micropores, cleaning the water. Ion selectivity can be controlled by taking advantage of charge and ionic radius differences as well as the applied potential and pore size of the electrodes. The research outlined in this paper consists primarily of running fte-CDI cells with electrodes of varying pore size distributions to experimentally determine the parameters for optimal total salt removal and sodium/calcium ion selectivity. Five fte-CDI cells of different activation were fabricated using microporous hierarchical carbon aerogel materials (HCAMs) as electrodes. For each cell, cyclic voltammetry using 20 mM NaCl solution and 10 mM $CaCl_2$ solution was performed at a scan rate of 0.5, 0.75, and 1 mV/s with a potential window from -0.8 V to +0.8 V. The same pure salts were desalinated in hourly charge/discharge cycles at ±1 V. A mixture of 5 mM NaCl and 2.5 mM $CaCl_2$ was desalinated at 0.6, 0.8, 1.0, and 1.2 V. The collected charge and discharge streams were analyzed with ion chromatography (IC). The IC data for the two least activated cells showed minimal calcium adsorption compared to sodium. All cells adsorbed sodium, regardless of activation, while only highly activated cells removed calcium. This data indicates a tradeoff between more total salt removed at high voltages and selectivity of sodium over calcium at low voltages. Future research with nitrogen porosimetry could provide a quantitative value for the optimal pore size distribution.

General Audience Abstract

In flow through electrode capacitive deionization (fte-CDI), salt water flows through pores in electrodes held at constant voltage, which traps salt ions and cleans the water. Selective ion removal can be controlled by using ion's charge and size. This research is focused on finding the best experimental conditions for selectivity of calcium over sodium. Four fte-CDI cells of differing pore size distributions were made using microporous hierarchical carbon aerogel materials (HCAMs) as electrodes. For each cell, cyclic voltammetry (CV) was run with NaCl and $CaCl_2$. The same pure salts were desalinated for 6 hours of fte-CDI at 1 V. A mixture of NaCl & $CaCl_2$ was desalinated at 0.6, 0.8, 1.0, and 1.2 V, and its purified water was analyzed with ion chromatography (IC). The IC data showed less sodium removal and no calcium removal at low voltages. Around 1 mM of sodium ions was removed by all cells during desalination. The IC data shows a tradeoff between total salt removal and sodium selective. Based on the results, cells with narrower pores were sodium selective over calcium.

I. INTRODUCTION

A. Flow Through Electrode Capacitive Deionization

Capacitive deionization (CDI) is a technique in which an aqueous salt solution is decontaminated by holding a potential between a pair of porous electrodes. Dissociated anions and cations in the solution become attracted to the charges on the electrode plates, migrate towards them, and get captured in pores. After collecting the deionized water, one can regenerate the electrodes by removing the potential and washing off trapped ions into a waste stream, enabling cyclic operation. There are two operation modes for CDI cells, the most common one being flow between (fb), where water moves in parallel with the electrodes and contacts them only on their surface. This work will examine the less common flow through electrode (fte) configuration. For fte-CDI, the water enters the pores and flows inside of the electrodes, allowing continuous contact with the electrode. This removes the diffusion timescale limitations of flow between CDI.

B. Microporous HCAM Selectivity

If a less hydrated, monovalent ion like Na^+ is desired for removal, one can use narrow pores to take advantage of atomic radius variations and screen out more hydrated molecules like Ca^{2+}. On the other hand, should the divalent ion be the target species, wider pores will permit both ions to enter. Microporous hierarchical carbon aerogel material (HCAMs) were chosen as the electrode since their pore size distribution is tunable during synthesis. In order to examine the selectivity of HCAM electrodes, this report examines 5 CDI cells containing electrodes of different activation (degree of pore widening determined by mass loss percentage). These cells were tested for their ability to remove pure $CaCl_2$, pure NaCl, or a mixture of both salts.

II. EXPERIMENTAL METHODS

A. Cell Construction

The HCAM electrodes were cut with a laser cutter to 4 cm by 6 cm. The thickness of the electrodes varied from 0.25 to 0.5 mm. Cells consisted of a pair of electrodes from the same batch separated by a 90 µm thick non-conductive polyester rectangular mesh. Two 25 µm graph foil current collectors were placed in contact with each of the electrodes on the sides opposite the mesh. These current collectors had copper wires glued on with silver paint that allowed direct connection to instrumentation. The electrodes were held between by two custom produced acrylic header plates that were then glued together with a UV curing epoxy. Five differently activated HCAM-electrode cells were made by this method: AB-01 (18.0%), AB-02 (24.6%), MC-27 (31.7%), MC-28 (37.4%), and MC-29 (75.1%). In this work, both cells made of electrode materials below 30.0% will be referred to as lower activation cells, while all 3 cells higher than 30.0% will be called the higher activation cells.

B. CV and EIS

1. Cyclic Voltammetry

Cyclic voltammetry (CV) experiments were conducted at room temperature to measure gravimetric capacitance of the cells using pure sodium or calcium aqueous solutions. All CV was performed on a Biologic VSP-300 Multi potentiostat, with a four-wire setup and a positive terminal to downstream current collector configuration. Feed solution (either 20 mM NaCl or 10 mM $CaCl_2$) was pumped through Tygon tubing to the cell at 15 rpm on a Watson Marlow 120U Benchtop Pump, equivalent to a flow rate of 2 mL/min. The conditions used to produce the data reported in the results section were a scan rate of 0.5 mV/s, in a 1.6 V potential window (from 0.8 V to -0.8 V), and 4 cycles per experiment. Only the last cycle is shown in the results section.

2. *Electrochemical Impedance Spectroscopy*

After the CV experiment, constant voltage chronoamperometry (CA) discharged the cells for 30 minutes at 0 V. Then, electrochemical impedance spectroscopy (EIS) was measured to obtain frequency response analysis curves over the frequencies 5mHz to 700kHz. The full impedance readouts are included in Appendix A.

C. Constant Voltage Desalination Experiments

1. *Desalination of Pure Salts*

In addition, constant voltage charge/discharge experiments were performed with pure 20 mM NaCl and 10 mM $CaCl_2$ solutions. A Keithley 2602B System Sourcemeter held the cell at a constant 1 V charge for 20 minutes, followed by a constant 0 V discharge for20 minutes. The cells were charged and discharged a total of 6 times (with alternating positive and negative charge potentials), while a constant flow rate of 1 mL/min of feed solution flowed through the cell. Four-wire positive terminal to downstream current collectors was also used here. The downstream feed was run through a Laqua Sensor that collected conductivity data. A LabView program was used to input all collected data and output time vs conductivity plots as well as each charge/discharge cycle's total concentration of salt removed (ΔC) in mM, charge efficiency, and coulombic efficiency. After flowing past the sensor, the downstream solution was added back to the feed source. This instrumentation and cell configuration were used for the mixed salt constant voltage charge/discharge experiments, as well as cell washing and conditioning.

2. *Desalination and Collection of Salt Mixtures*

The final test for the cells was constant voltage charge/discharge experiments using a mixture of 5 mM NaCl and 2.5 mM $CaCl_2$. In order to test the effect of voltage on selectivity, four different charge voltages were run on each cell with 1 mL/min flow rate: 0.6, 0.8, 1.0, and 1.2 V. The downstream desalinated solution was collected in a 30 mL plastic bottle after it exited the sensor. After discharging the cell at 0 V the brine stream was also collected. Similar to the previous experiments, the charging potential alternated between positive and negative every cycle. A total of 6 charge/discharge cycles were run for each cell at each voltage. Then, 1 mL of each sample was diluted in 9 mL of deionized water to analyze using ion chromatography.

3. Cell Preparation: Washing and Conditioning

When any cell was disconnected from its feed solution and needed to be connected to a new feed of different species or concentration, it was washed first with deionized water. The cell cycled 4 times at a ±1 V charge and 0 V discharge for 5 minutes each. The contaminated stream that this washing step produced was discarded. If the sensor still detected salt after the 4 cycles were finished, the full washing process was repeated.

Before a collection experiment could be conducted, the cell was prepared by a constant voltage charge/discharge conditioning with 5 mM NaCl + 2.5 mM $CaCl_2$ solution at a 0.6 V charge, 0 V discharge, and 1 mL/min flow rate. Conditioning consisted of 6 charge/discharge cycles, each for 30 minutes. No data was collected for conditioning or washing.

III. RESULTS AND DISCUSSION

A. Cyclic Voltammogram

With the cyclic voltammetry raw data (potential vs current), the gravimetric capacitance of the cells was determined by taking the current in mA divided by the scan rate of 0.5 mV/s, multiplied by two (on account of the cell's second electrode), and divided by the average mass of both electrodes. The 20 mM NaCl and 10 mM $CaCl_2$ cyclic voltammograms for the five cells are plotted in Figure 1.

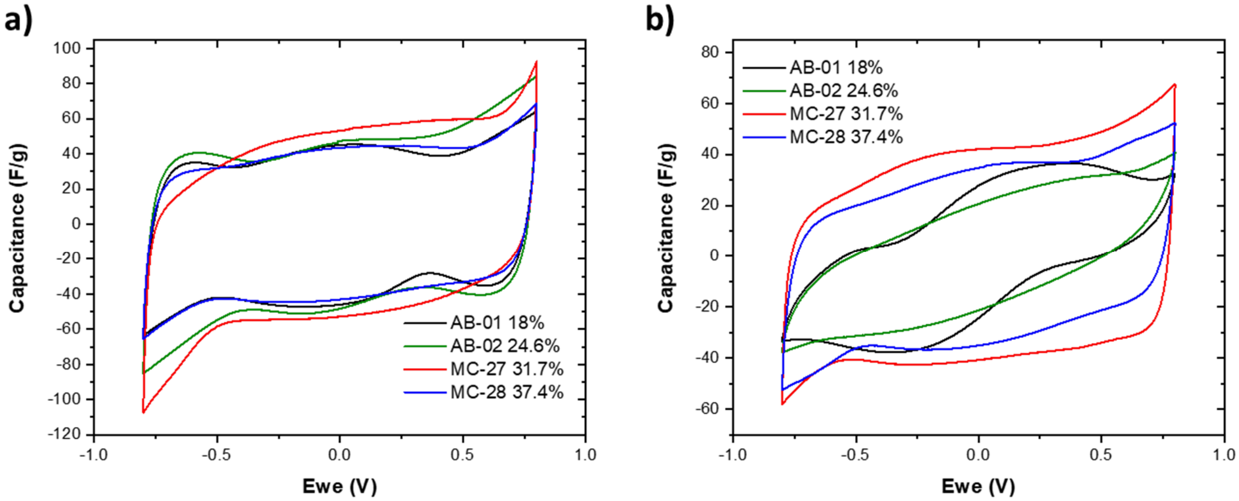


FIG. 1. Potential vs gravimetric capacitance from cyclic voltammetry for (a) 20 mM NaCl and (b) 10 mM $CaCl_2$.

Gravimetric capacitance is a metric to compare the desalinating efficiency of a given material. A higher capacitance indicates that the potential is effectively being applied to salt removal. Therefore, it is expected and generally observed that greater activation manifests as increased capacitance. Voltammograms are ideally shaped like a box with pointed edges (similar to the higher activation cell's shape in the NaCl plot). Figure 1-B shows a deviation from this ideal shape with the lower activation cells in $CaCl_2$ solutions. This indicates that these cells have not been activated to obtain the ideal pore size for the effective capture of calcium ions, especially at lower potentials. The higher activated cells display no such curvature deformation in either salt.

B. Pure Salt Desalination Results

The data compiled by LabView during the pure salt desalination includes the concentration change (ΔC), charge efficiency, and coulombic efficiency. These values are presented in Table 1. All cells regardless of activation seem to be able to remove millimolar quantities of sodium chloride, and the higher activation cells showed greater charge efficiency. On the other hand, there is a large divide between lower and higher activation cells in their ability to desalinate calcium chloride. Based on the data, it would seem 31% is the minimum activation percentage required to adsorb calcium ions on the same order of magnitude as sodium; below this threshold, only trivial amounts of salt are removed. LabView also generated time vs conductivity plots, whose last positive and negative charge cycle is presented in Appendix B.

Given MC-29's low ΔC during pure $CaCl_2$ desalination and, it seems likely the pores of its electrodes (75.1%) are not big enough to adsorb calcium ions. Activation percentage is determined by the percentage change of electrode mass after their activation process with CO_2. Thus, it is possible that MC-29's high activation comes from nonuniform activation of the electrodes etching away material only from the surface and the edges. This theory is supported by measurements of the electrode's thickness, which varied from 0.5 mm to 0.68 mm depending on the site of measurement. An alternative explanation is the loss of mass via chipping or cracking during preparation. Either way, data from MC-29 may be an inaccurate representation of a higher activation cell, and no further experiments were performed.

C. Mixed Salt Desalination and Collection Results

The LabView data from the mixed salt desalination experiments is shown in Table 2. Ion chromatography provided the concentration of each salt in both the desalinated and brine streams. With this data, the calcium and sodium molar adsorbed quantities were calculated for the lower activation cells and are presented in Figure 2. The higher activation cells' ion chromatography data could not be collected in time to be included in this report.

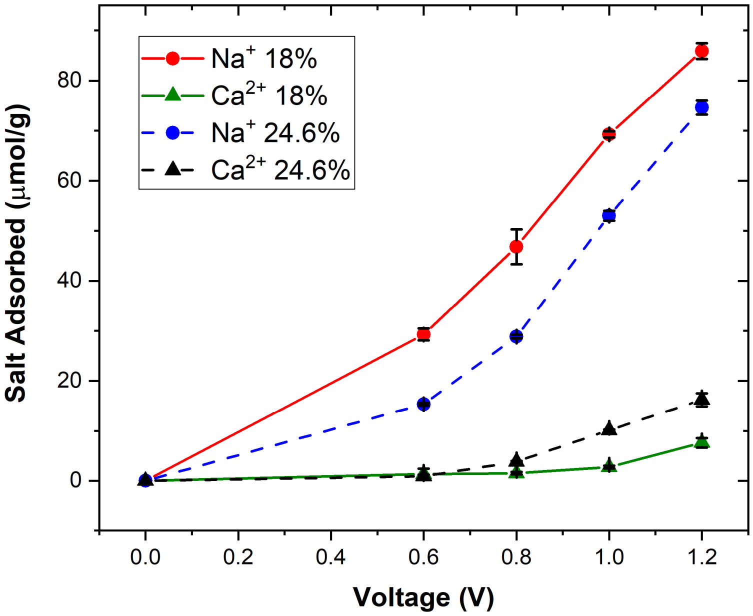


FIG 2. Results of ion chromatography for constant voltage charge/discharge of 2.5 mM $CaCl_2$ *+ 5 mM NaCl by lower activation cells. This data represents how much salt has been removed at each of the four voltages examined, as well as a zero voltage for reference.*

As the voltage increased, the total salt adsorbed for both species increased, the selectivity of sodium over calcium decreases with higher potentials. An inherent tradeoff occurs between desalination capacity and ion selectivity.

IV. CONCLUSION

A. Summary of Findings

This report presented research regarding flow through electrode capacitive deionization cells made with HCAMs to analyze the effects of pore size and applied potential over the selectivity of Na^+/Ca^{2+} cation removal. The cyclic voltammograms confirmed the current theory – smaller pores are less likely to capture more hydrated divalent ions. 31.7% was the cutoff below which mainly sodium cations were adsorbed on a millimolar magnitude, based on pure salt desalination experiments. Furthermore, these two pure salt experiments also found that a cell of supposed 75.1% activation was more similar to the lower activation cells in its ability to remove calcium. Mixed salt desalination and ion chromatography of the streams it produced displayed a trend relating increasing voltage to increasing salt removal, but also to decreasing sodium selectivity.

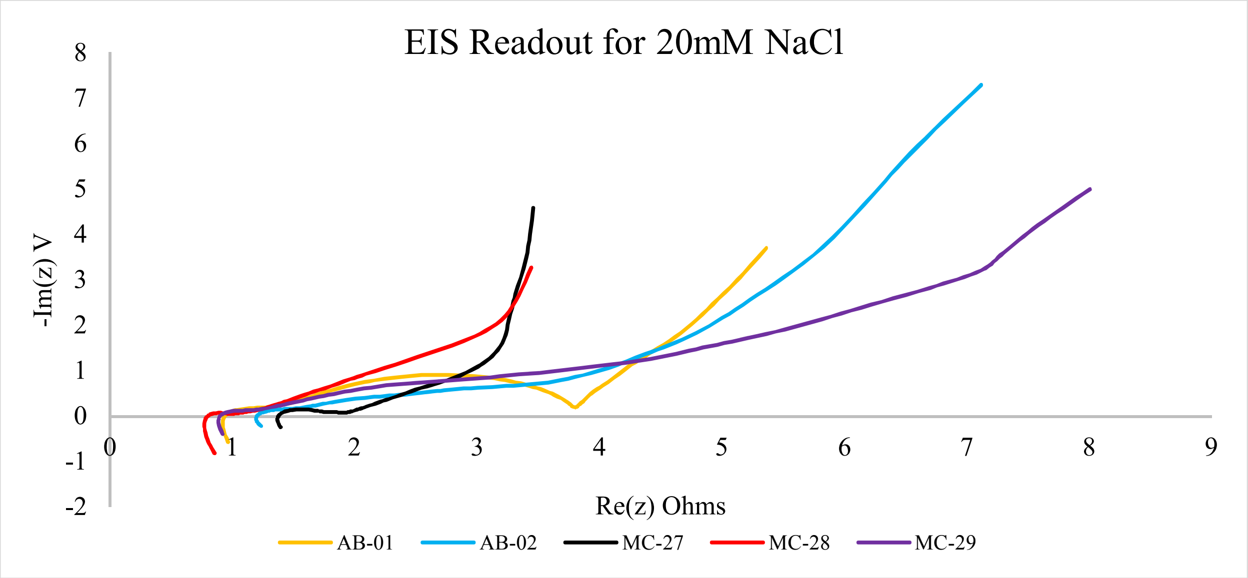
B. Further Research

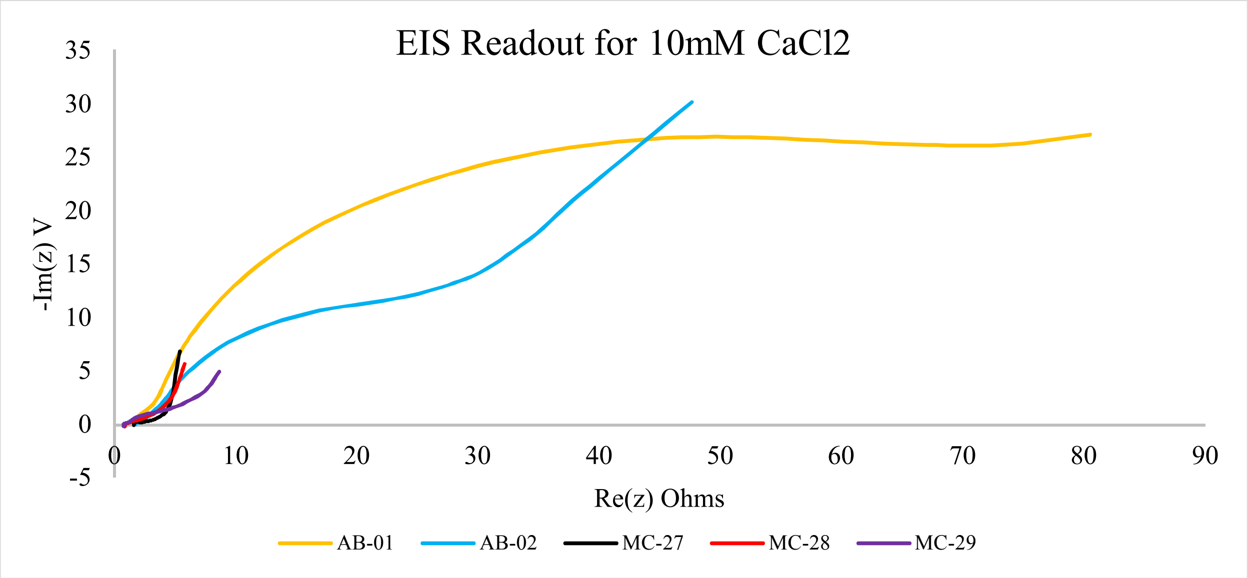
The findings of this report suggest that future work involving more detailed methods of pore width analysis such as BET could provide further insight. In addition, the lower/higher activation dichotomy for calcium cation adsorption could be narrowed down to a more specific value by testing cells between 24% and 31% activation. Testing with other cations of varying size and similar charge (Mg^{2+}, K^+) would also produce important results for the future of CDI, provided those ions are present in salt water at low enough concentration for fte-CDI removal.

V. ACKNOWLEDGEMENTS

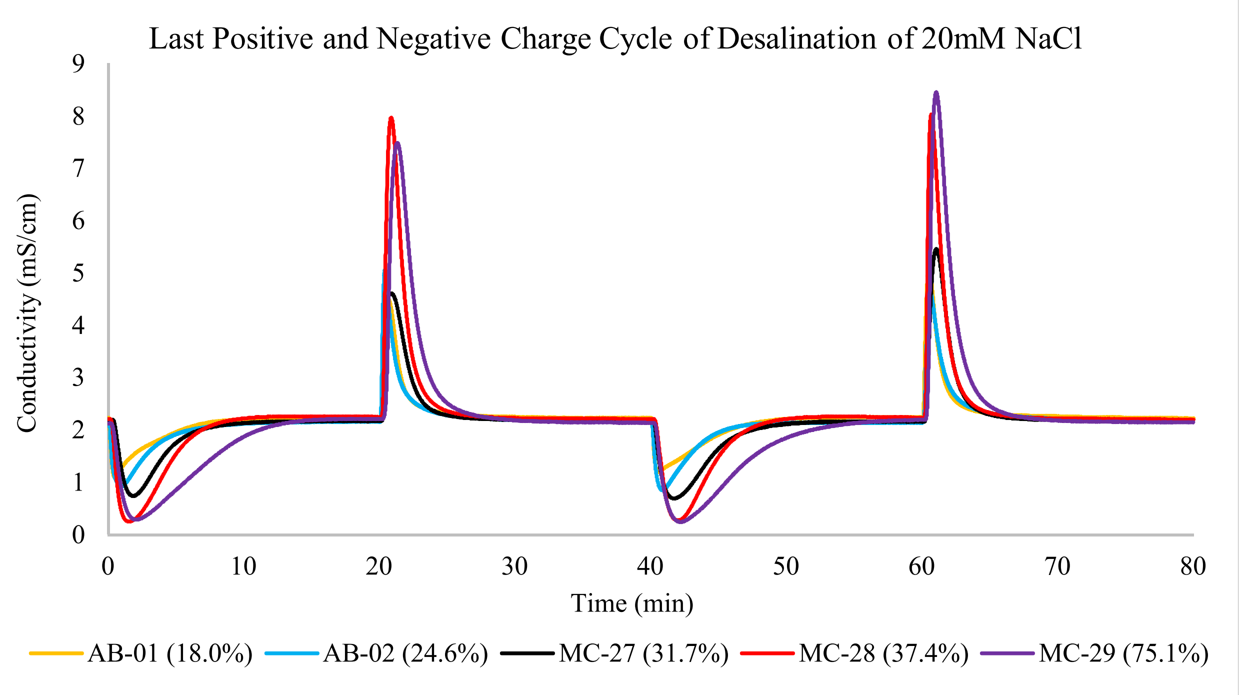
The data was collected with the assistance of Dr. Maira Ceron-Hernandez, Dr. Patrick Campbell, Dr. Steven Hawks, Colin Loeb and Helen Kuo. All research was conducted at the Lawrence Livermore National Laboratory under the Science Undergraduate Laboratory Internship Program.

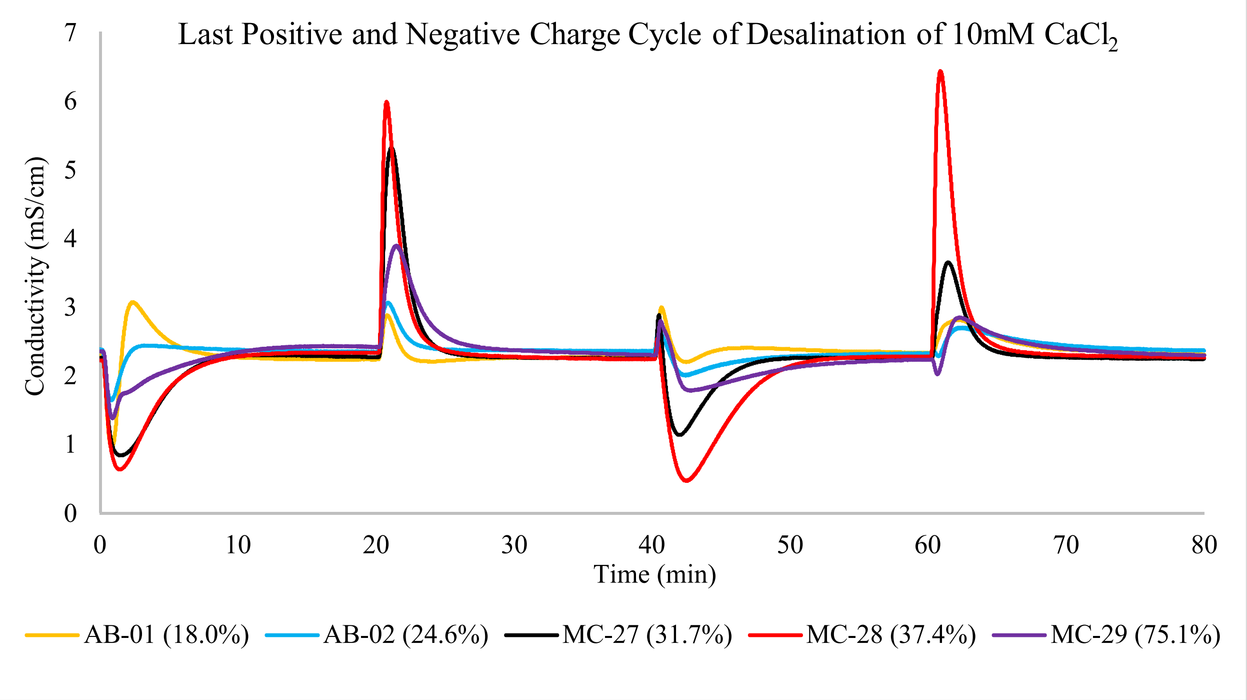
VI. APPENDIX A – ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY DATA





VII. APPENDIX B – PURE SALT DESALINATION TIME VS CONDUCTIVITY PLOTS





VIII. TABLES

A. Table 1

Table 1 – Data collected by LabView during the desalination of pure sodium chloride and calcium chloride, including concentration change, charge efficiency, and coulombic efficiency.

Cell Name and Activation	**AB01 (18%)**	**AB02 (24.6%)**	**MC27 (31.7%)**	**MC28 (37.4%)**	**MC29 (75.1%)**
Average ΔC (mM), 20mM NaCl	2.08	1.72	3.02	2.78	4.74
Average charge efficiency (%), 20mM NaCl	23.30	32.67	55.00	40.02	59.38
Average coulombic efficiency (%), 20mM NaCl	70.97	66.90	58.99	69.52	74.25
Average ΔC (mM), 10mM $CaCl_2$	0.31	0.37	1.63	2.44	0.87
Average charge efficiency (%), 10mM $CaCl_2$	10.40	10.23	23.80	22.66	12.65
Average coulombic efficiency (%), 10mM $CaCl_2$	61.29	68.41	67.04	72.17	70.15

B. Table 2

Table 2 – Data collected by LabView during the desalination and collection of a 5 mM sodium chloride and 2.5 mM calcium chloride mixture, including concentration change, charge efficiency, and coulombic efficiency. No data was collected for MC-29 (75.1%), as its activation may not be an accurate representation of pore size.

Cell Name and Activation	**AB01 (18%)**	**AB02 (24.6%)**	**MC27 (31.7%)**	**MC28 (37.4%)**
Average ΔC (mM), 0.6 V	0.57	0.28	0.45	0.56
Average ΔC (mM), 0.8 V	0.96	0.53	0.66	1.12
Average ΔC (mM), 1.0 V	1.30	0.95	0.85	1.66
Average ΔC (mM), 1.2 V	1.58	1.31	0.83	1.71
Average charge efficiency (%), 0.6 V	48.29	20.04	24.93	27.59
Average charge efficiency (%), 0.8 V	39.28	26.79	33.43	32.88
Average charge efficiency (%), 1.0 V	38.85	30.65	33.42	36.26
Average charge efficiency (%), 1.2 V	34.58	31.78	22.97	25.31
Average coulombic efficiency (%), 0.6 V	64.96	69.67	77.17	78.40
Average coulombic efficiency (%), 0.8 V	67.62	66.46	67.78	72.38
Average coulombic efficiency (%), 1.0 V	62.97	63.97	59.96	66.29
Average coulombic efficiency (%), 1.2 V	58.17	59.25	52.50	60.69