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Scale-Up of flow-electrode capacitive deionization method for hard water softening

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Scale-up of flow-electrode capacitive deionization method for
water softening

4200:497

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March 18th, 2022

Abstract

This study's purpose is to further document a capacitive deionization design that could be capable of purifying H₂O at a household scale where clean water is otherwise unobtainable in applicable regions of the world. The hypothesis behind this study was continuously larger scaled electrochemical cell-units would increase their water softening capabilities in sustainable fashion. The trend at which performance will scale is currently unknown. The units studied were constructed using graphite plates, anion exchange membranes, cation exchange membranes, and Teflon channels. Three streams, two being CaCl₂ solutions in DI H₂O (one being concentrated with CaCl₂ and the other purified of it) and one being an iron/sodium electrolyte, were fed through the unit via peristaltic pumps. Observations were recorded using a conductivity probe and voltammetry equipment. In this study, a 4-cell and a 5-cell unit were observed. When a voltage of 1 V/cell was applied to the 4-cell unit, conductivity of the softened stream dropped by 60 μS/cm. Raising voltage to 2 V/cell, conductivity dropped by 98 μS/cm. The 5-cell unit showed conductivity drops of 120 μS/cm and 269 μS/cm when 1 V/cell and 2 V/cell were applied, respectively. Studies are recommended to continue with larger units to work towards household-scale.

Executive Summary

Fresh water scarcity has been an increasing concern over the last few decades ^[1]. The increased concern stems from industrial and agricultural expansion, climate change, and dramatic population increase ^[1]. Thus, it is imperative that extensive work into cheap and efficient water desalination techniques is conducted to aid humanitarian efforts globally as fresh water becomes increasingly difficult to obtain by regular means in many parts of the world ^[1].

The purpose of this study was to build upon a previous study by The University of Akron in which a single-cell unit was constructed with the intention of creating drinkable water from a stream concentrated with hard water ions, such as calcium or magnesium ^[2]. This current study was an attempt to create increasingly scaled-up versions of this unit in which there would be not one, but multiple cells within the unit. Prior to this study, not much was known about how unit performance would scale with voltage or cell count. It was only known that these properties would increase effectiveness through increased electrical force and the number of passes the streams will take through the unit, but these exact relations are unknown. The goal of this study is to gather data that will aid future efforts in developing models and equations to accurately predict cell performance.

The performance of these units was observed in various ways to measure their efficiency and overall effectiveness. Tests were performed to observe the rapidness of ion migration away from the softened stream, the behavior/response of the unit to a change in electrical potential, and a comparison of total ion concentrations before and after running the tests. The tests conducted in this study observed these aspects of a 4-cell unit and a 5-cell unit over a constant period of 5 minutes.

The tests were conducted sequentially with a hand-constructed unit made from layers of anion exchange membrane, cation exchange membrane, graphite plates, and Teflon channels all sealed together via waterproof silicone sealant. The unit was then fed three separate streams via peristaltic pumps: two hard water streams and a single electrolyte stream. The full explanation of this apparatus can be found in the body of this report.

Upon conclusion of the experiments, it was determined that, at this current scale, water softening performance scales adequately. Applying a voltage of 1 V/cell across the 4-cell unit resulted in a change in conductivity ($\Delta\sigma$) of approximately 60 $\mu\text{S}/\text{cm}$ in the softened stream. When 2 V/cell was applied, the 4-cell unit yielded a $\Delta\sigma$ of 98 $\mu\text{S}/\text{cm}$. Further scaling to the 5-cell unit continued to raise ion migration efficiency. When 1 V/cell was applied to the 5-cell unit, the softened stream showed a $\Delta\sigma$ of 120 $\mu\text{S}/\text{cm}$. Even further, the 5-cell unit increased its effectiveness of $\Delta\sigma$ to 269 $\mu\text{S}/\text{cm}$ over the allotted 5 minute period. It was also noted that electrical current through the cell would drop off dramatically from the beginning of the test until approximately 30 seconds into each trial – where the current flattens to a constant approximate value. This behavior shows that ion migration intensity begins very high relative to the steady-state level seen shortly after startup, then sharply decreases until a fairly constant rate is observed.

It is recommended to continue scaling the unit with increasing cells for as long as necessary to reach a capacity that can provide clean water to an entire household. During this study, the near-linear increase of $\Delta\sigma$ over all 4 tests has shown to be promising. From these results, it is hypothesized that this behavior will continue with the addition of more cells and higher voltage over time until internal electrical resistance begins to show an effect. It is also

recommended to seek an alternative to the silicone sealant used for the construction of this unit. The sealant's purpose is to prevent skewed results via chamber leakage or chamber mixing. However, the sealant utilized proved difficult to work with in the given setting. If the recommendations are taken, it is hypothesized that this multi-cell unit design can be scaled large enough to become an economically feasible household water purification device for communities in need of consumable water.

Over the course of this study, many skills have either been strengthened or newly developed. My knowledge and clarity on capacitive deionization methods have significantly increased, alongside my ability to adequately manage time under short timetables while still producing meaningful results. Project management skills and confidence were also strengthened, as the project maintained its predicted timeline. Moving forward, the results of this project prove that this cost-effective water purification technique is feasible at scales larger than just a single cell. If studies continue, society will have an opportunity to reap the benefits of this method – drastically improving the quality of life for communities around the world in which drinkable water is inaccessible.

Introduction & Background

Fresh water scarcity has been an increasing concern over the last few decades due to ever-increasing populations, expanding industrialization, agriculture, and climate change ^[1]. In previous studies ^[2], a new low-cost, efficient, and safe electrochemical process has been created that allows for the desalination of hard water. The overall goal of this new study is to scale-up the version of the cell created in the previous study and observe its performance. Scaled-up chemical processes have been observed to behave in ways differentiating from a small-scale experiment as certain phenomena become more impactful as the process grows in magnitude. If the performance of the larger cell unit maintains or shows comparable efficiency to the single cell studied previously, the outcome could result in the future distribution of this cell unit to homes and communities in places where fresh drinking water is not adequately accessible. The main motivation behind this project is a humanitarian effort to provide a means of creating fresh water to those who are unable to easily obtain it. This study attempts to build on the research that precedes it ^[2]. The methodology of this project is, in short, to construct a larger-scale cell unit and observe its performance so it's efficiency can be later compared to that of its single cell counterpart. The tests and observations taken are to be as similar as possible to those conducted with the previous study to maintain consistency throughout the project. It is believed that applying larger voltages will lead to better performance due to a stronger electrical force – inducing stronger ion migration. It is also believed that increasing cell count within the unit will increase performance by increasing the number of passes the water takes through the unit. However, as cell count increases, it is anticipated that internal electrical resistance can begin to have a negative effect on performance. An actual trend has not yet been observed. This study is

an effort to gather more data to help identify trends in scaling and help develop equations that can relate unit performance to these characteristics.

Experimental Methods

The preparation of the cell unit involves iron (III) chloride, iron (II) chloride tetrahydrate, sodium chloride (NaCl), anion exchange membrane (AEM, Fumasep FAS-PET-130), cation exchange membrane (CEM, Fumasep FKS-PET-130), and carbon cloth (ELAT, hydrophilic). The redox couple was prepared by one simple electrochemical method utilizing a self-designed redox generation battery cell. The cell itself was comprised of an anode and a cathode, which were comprised of a current collector (graphite plate and carbon cloth) and a liquid electrolyte. The liquid electrolyte contained 20 mL deionized water, 50 mM FeCl₃, 50mM FeCl₂, and 200 mM NaCl fully dissolved. The anode and cathode were separated by membranes of varying quantity – forming 4 total chambers. The initial tests involved a chamber sequence as follows: Anode Plate (for electrolyte), Chamber 1, Cation Exchange Membrane (CEM) #1, Chamber 2, Anion Exchange Membrane (AEM), Chamber 3, CEM #2, and Cathode Plate (for electrolyte). This is the organization of a single-cell unit. Each layer of the design is sealed together using a waterproof silicone sealant. The tests conducted in this study involved multiple cells within the unit, meaning that Chambers 2 and 3 make multiple passes along an increasing number of exchange membranes. However, the concept of the cell unit is consistent throughout and can be observed in Figures 1 and 2.

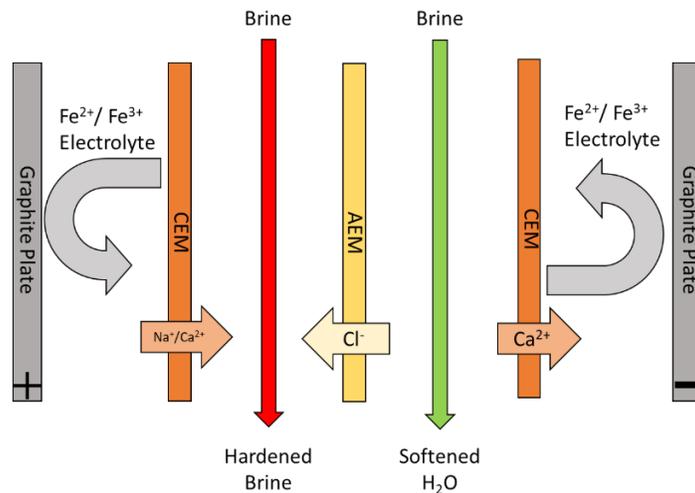


Figure 1 – Simplified illustration of a single unit cell.

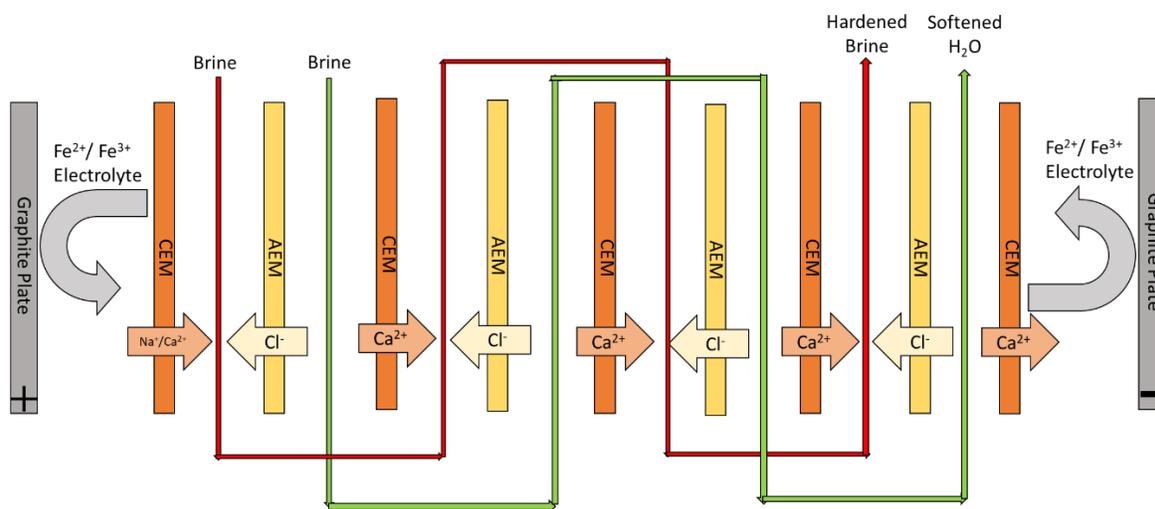


Figure 2 – Illustration of 4-cell unit.

The electrolyte redox couple was circulated between the electrodes in Chamber 1 and Chamber 4. Two 5 mM Calcium chloride (CaCl_2) in DI H_2O solutions were circulated separately via two peristaltic pumps in Chamber 2 and Chamber 3. Chamber 2 was considered the desalinated stream whereas Chamber 3 was considered the brine stream (to be salinized). The schematic of an individual cell is illustrated in Figure 3, and the design of this unit was inspired

by previous studies ^[3]. All tests conducted as a function of time were held at a constant $t_{\max} = 300$ s (5 min).

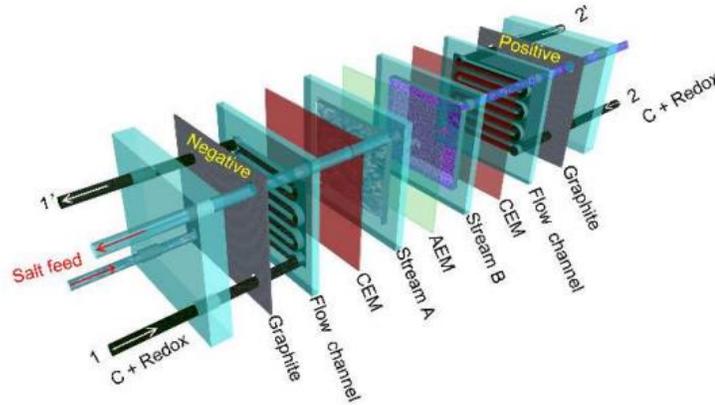
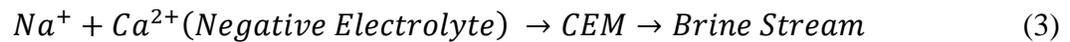
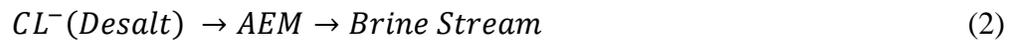


Figure 3 – Detailed schematic of single unit cell. ^[3]

The movement of ions away from the desalination stream into the redox and brine chambers are as follows ^[2]:



This ion migration allows for the constant replenishment of the redox couple, allowing the cell unit to desalinate a stream until a desired conductivity is reached. Methods of observation for desalination performance remained the same as the previous study. To obtain quantitative data, the conductivity of the $CaCl_2$ solution flowing through Chamber 2 and Chamber 3 were monitored using a conductivity meter. Observing the conductivity change of the desalinated stream will show the overall change in Ca^{2+} and Cl^{-} ion concentration over the allotted time period – proving the unit's degree of effectiveness.

The current through the cell and electrolyte (both as a function of electrical potential and time) were recorded via the use of voltammetry equipment. The current density through the cell directly corresponds to ion migration intensity. Observing this quantity over time allowed for further assessment of the unit's effectiveness. Monitoring current density as a function of electrical potential had shown the cell can react to voltage change. This change proved that the current through the cell is caused by ion migration and that applying voltage to the cell was the trigger to said ion migration – resulting in a desalinated water stream. Regarding the redox couple, measuring the current through it while changing electrical potential was meant to find evidence of necessary redox reactions ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$, $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$) that allowed ion migration to continue. Peaks in the redox curve are signals of successful redox reactions.

In the previous study^[2] observing a single cell, its performance was measured by calculating the average salt removal rate (ASRR in $\text{g}_{\text{CaCl}_2}/(\text{mol}_{\text{Electrolyte}}\text{-hr})$), the salt removal capacity (SRC in $\text{g}_{\text{CaCl}_2}/(\text{mol}_{\text{Electrolyte}})$), and the overall energy consumption (E in kJ/mol). Their respective values were calculated using the equations below^[2]. However, due to time constraints and experimental limitations, the unit cell's performance was observed via raw data from tests measuring conductivity vs. time, current vs. electrical potential, and current vs. time.

$$ASRR = \frac{(C-C_0)*V_{\text{CaCl}_2}*M_{\text{CaCl}_2}}{C_{\text{electrolyte}}*V_{\text{electrolyte}}*t} \quad (4)$$

$$SRC = \frac{(C-C_0)*V_{\text{CaCl}_2}*M_{\text{CaCl}_2}}{C_{\text{electrolyte}}*V_{\text{electrolyte}}} \quad (5)$$

$$E = \frac{I*V*t}{(C-C_0)*V_{CaCl_2}} \quad (6)$$

In the above equations, C and C₀ are the final and initial concentrations (mol/L) of the stream in Chamber 2, V_{CaCl₂} is the total volume of the stream inside of Chamber 2, M_{CaCl₂} is the molar mass of CaCl₂, C_{electrolyte} is the molar concentration (mol/L) of electrolyte, V_{electrolyte} is the total volume of the flowing electrolyte, t is the time, I and V is the current and voltage, respectively, which can be obtained directly from the electrochemical tools used. All concentration data for each test was derived from all conductivity measurements taken throughout the trial.

Data & Results

The study began with observing the behavior of a 4-cell unit utilizing all components mentioned above. When applying 1 V/Cell, the magnitude of change in conductivity, Δσ, of the CaCl₂ solution in the desalinated stream was approximately 60 μS/cm over the 5 minute duration of the test and can be seen in Figure 4. The magnitude of Δσ increased to approximately 98 μS/cm with a voltage increase to 2 V/Cell and can be seen in Figure 5.

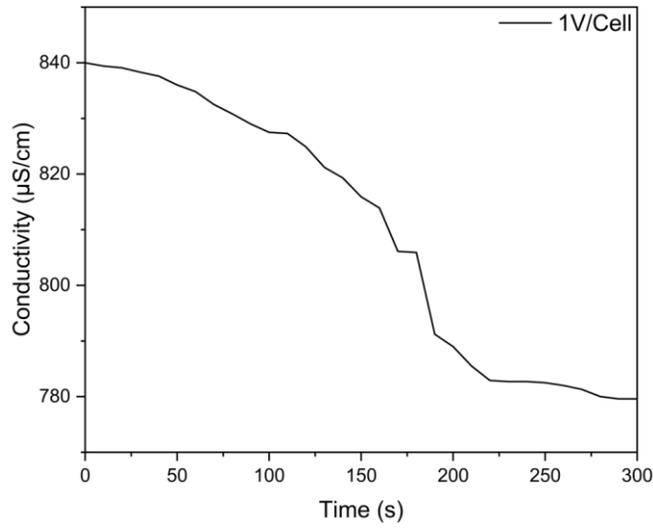


Figure 4 - Conductivity vs. Time for 4-Cell Unit with an applied voltage of 1 V/Cell.

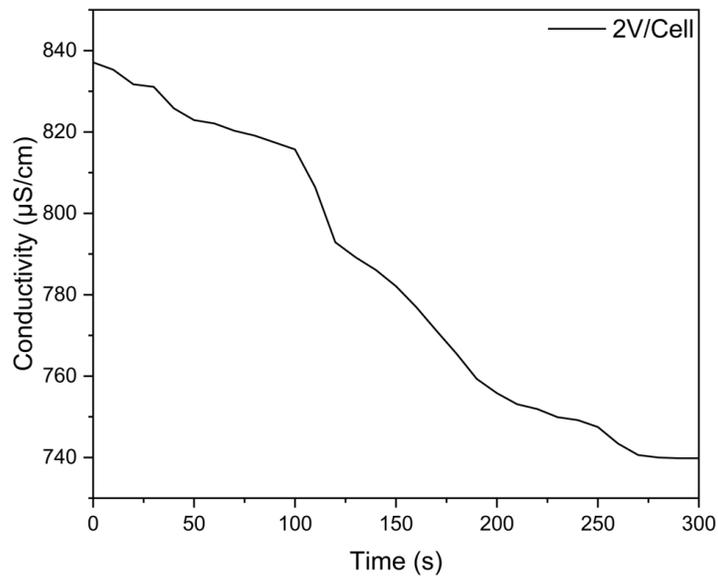


Figure 5 - Conductivity vs. Time for 4-Cell Unit with an applied voltage of 2 V/Cell.

The unit was then lengthened to a total of 5 cells in which the tests were repeated. When a voltage of 1 V/Cell was applied to the larger unit, $\Delta\sigma$ was approximately 120 $\mu\text{S}/\text{cm}$. When

voltage was raised to 2 V/Cell, $\Delta\sigma$ was approximately 269 $\mu\text{S}/\text{cm}$. The data for both of these tests can be observed below in Figures 6 and 7.

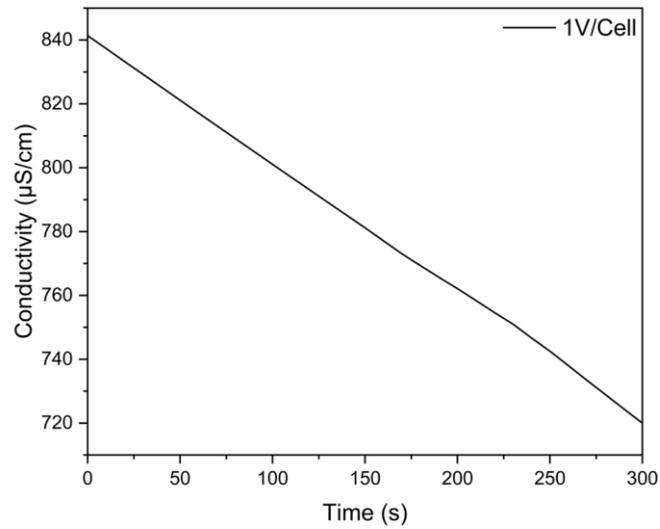


Figure 6 - Conductivity vs. Time for 5-Cell Unit with an applied voltage of 1 V/Cell.

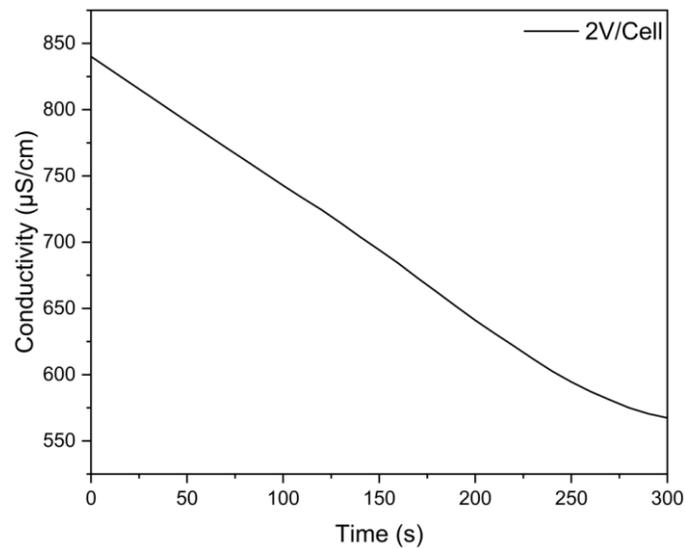


Figure 7 - Conductivity vs. Time for 5-Cell Unit with an applied voltage of 2 V/Cell.

A table compiling the results of the 4 tests can be observed below in Table 1.

Table 1 - Compilation of all conductivity vs. time tests. The voltage change between the 5-cell unit tests is significantly greater than the 4-cell tests.

# of Cells	Voltage (V/Cell)	Total Voltage (V)	$\Delta\sigma$ ($\mu\text{S}/\text{cm}$)
4	1	4	60
4	2	8	98
5	1	5	120
5	2	10	269

The conductivity tests described above were observed simultaneously with a test observing current through the unit over a fixed time period of 5 minutes. The 4-cell unit showed a sharp exponential decay for about 30 seconds when both 1 V/cell and 2 V/cell were applied to the unit and can be observed in Figures 8 and 9.

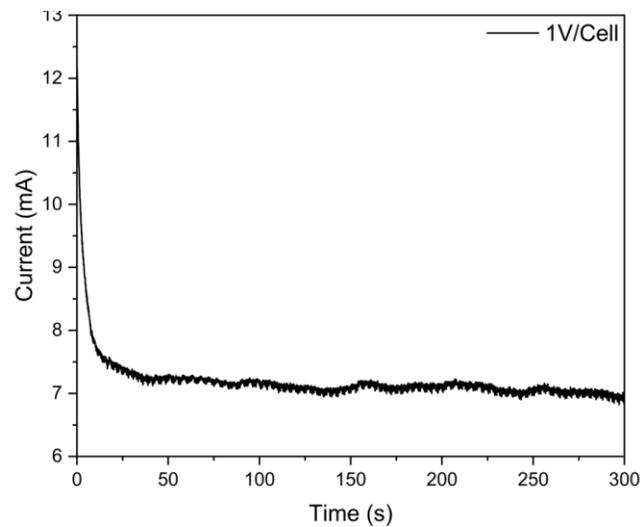


Figure 8 - Current through the 4-cell unit vs. time with an applied voltage of 1 V/cell. The current decays exponentially until it levels out at approx. 7 mA.

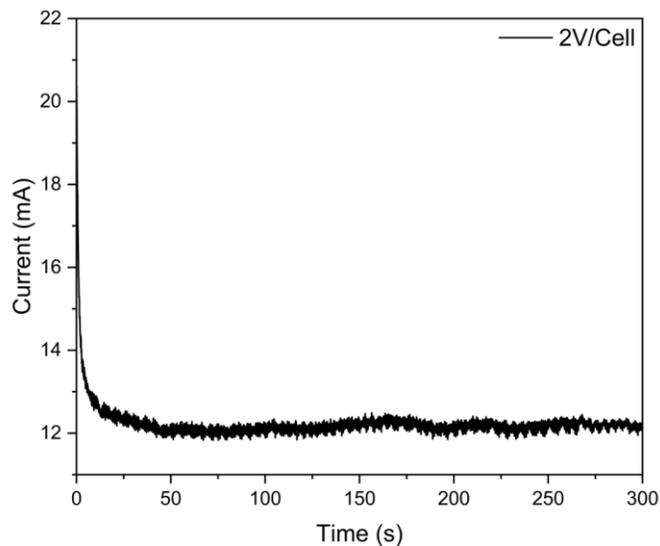


Figure 9 - Current through the 4-cell unit vs. time with an applied voltage of 2 V/cell. The current decays exponentially until it reaches approx. 12 mA, then plateaus.

When the 5-cell unit was tested, the current passing through it exhibited a much more gradual decline and can be observed in Figures 10 and 11.

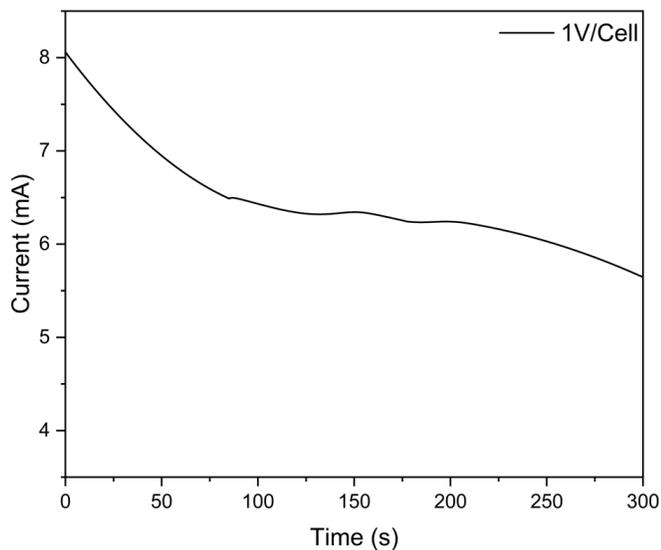


Figure 10 - Current through the 5-cell unit vs. time with an applied voltage of 1 V/cell. The change in current resembles the shape of a 3rd-order polynomial.

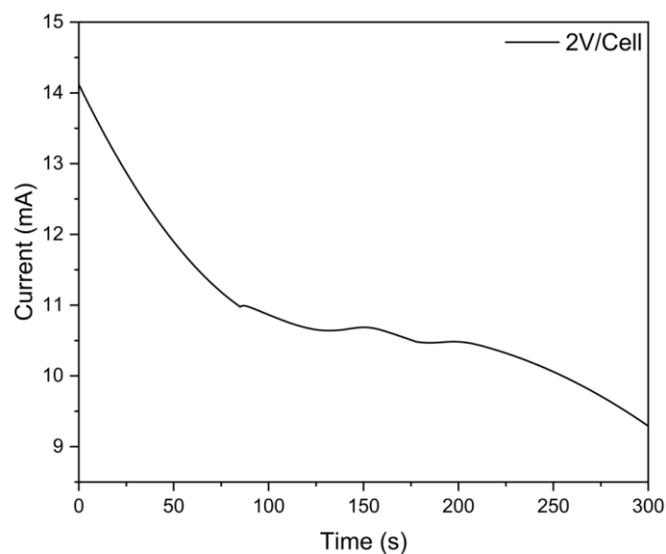


Figure 11 - Current through the 5-cell unit vs. time with an applied voltage of 2 V/cell. The change in current resembles the shape of a 3rd-order polynomial - more defined than 1 V/cell.

The current travelling through the redox couple (electrolyte) appeared to exhibit behavior consistent with previous studies when compared to changing the cell's electrical potential and can be observed Figure 12.

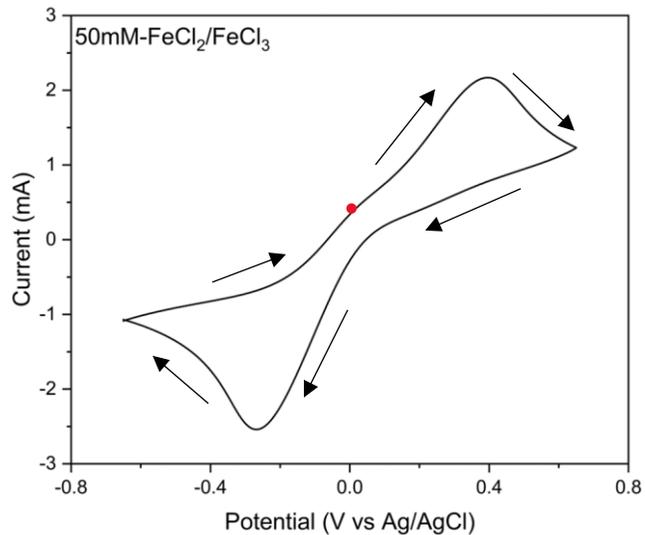


Figure 12 - Plot of electrical potential vs. current passing through the electrolyte. The peaks in the curve denote successful redox reactions. The test starts at 0 V, increases potential to 0.75 V, decreases to -0.75 V, and returns to 0 V at a rate of 0.6 V/min.

The unit itself was finally tested at three separate levels to observe the change in current through the cell with respect to electrical potential. This can be seen below in Figure 13.

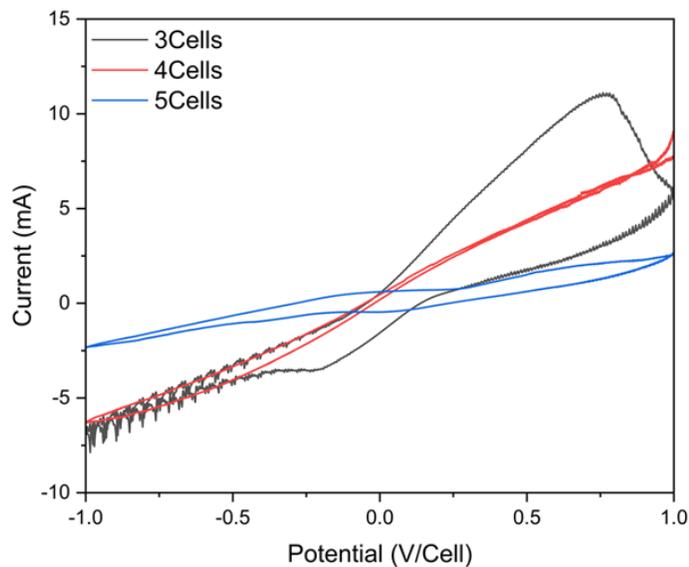


Figure 13 - Current through the cell vs. electrical potential. This test includes a separate 3-cell unit in addition to the 4-cell and 5-cell units mentioned above.

Conclusions & Analysis

The data collected during the first tests, monitoring the change in conductivity over time, shows that the effectiveness of the cell over a standardized time period scales almost linearly over this cell range. It is recommended that studies continue to build larger units to document desalination effectiveness scaling up to and including sizes that can produce enough clean water to supply a household. At the scale of this study, it remains unknown where performance losses begin to appear – if they appear at all.

Monitoring change in current over time between 4-cell and 5-cell units show that the intensity of ion migration begins relatively high and immediately drops in the shape of exponential decay. For the 4-cell unit, this decay seems to plateau, and current maintains a constant level after approximately 30 seconds. This plateau is signifying of the unit's ion migration rate at steady state. When looking at the 5-cell unit, it initially begins with the same behavior. However, it seems that there's an inflection point in both tests around 150 seconds where the current begins to decrease again. Per these results, it is recommended that these tests are continued alongside conductivity tests to determine if any specific pattern can be identified between the number of cells per unit and drops in current.

The tests observing current vs changes in electrical potential had matched observations in the previous study. This test also confirmed that redox reactions were, in fact, occurring within the cell, and confirmed current through the cell is caused by ion migration. It is recommended that any future studies on this subject include this test in their observations to confirm the validity of all other obtained data.

With this study, there were multiple setbacks that limited the scope and sample size over its duration. The main reoccurring issue was chamber leakage and blockage. Over the course of numerous tests, it would become obvious that any of the 4 total chambers in the cell would begin to leak out of the sides between any of the membranes and/or become entirely blocked and inhibit any flow from occurring through the unit itself. This leakage/blockage is likely attributed to the difficult workability of the sealant used. It is recommended to avoid using waterproof silicone sealant in any future tests to adhere layers together, and an alternative should be sought prior to unit construction.

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