# Capacitive Deionization (CDI) Cell Fabrication with *Voltera V-One* Paste Dispenser

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## Contents

# 1    Introduction

Almost four billion people live in areas of severe water scarcity, where twice as much water is withdrawn as is sustainably available for at least one month per year.[1] To meet the increase in demand for potable water in global markets, this project proposes to advance capacitive deionization (CDI) technology. CDI is an emergent, energy efficient water desalination technique in which brackish (i.e. medium salinity, 20 mM) water is flown through a channel with charged, porous electrodes on opposite sides. These electrodes trap charged ionic species in the water and the result is clean, drinkable water. Specifically, we leverage state-of-the-art microfabrication techniques to enhance three critical aspects of CDI: (1) energy efficiency; (2) understanding of ion transport processes; and (3) flow-by cell design. A key aspect of our cell assembly is the preparation of an activated carbon (AC) powder suspension, or AC slurry, which is accurately deposited by a *Voltera V-One* paste dispenser. The performance of this CDI cell is measured and described against the criteria listed above. Finally, this report provides an in-depth focus on the performance of the *V-One* with an emphasis on custom inks.

## 1.1    Broader Context

In the CDI community, there is great interest in the goals described above. Contact resistance between the current collector and the porous electrodes (typically rigid AC structures) is the major contributor of series resistance in CDI cells.[2] A separate investigation, also pursued in this report, is the visualization of local pH variations within a CDI cell. Previously, only stopped-flow visualizations have been reported.[3] Other potential applications of an AC slurry, microfabricated CDI cell include geometry optimization and roll-to-roll fabrication on flexible substrates.[4] Typical cell assemblies (including those made in our own lab) are comprised of thick acrylic slabs pressed against a titanium current collector, rigid AC structure such as PACMM or HCAM, and a ~1 mm thick silicone gasket.
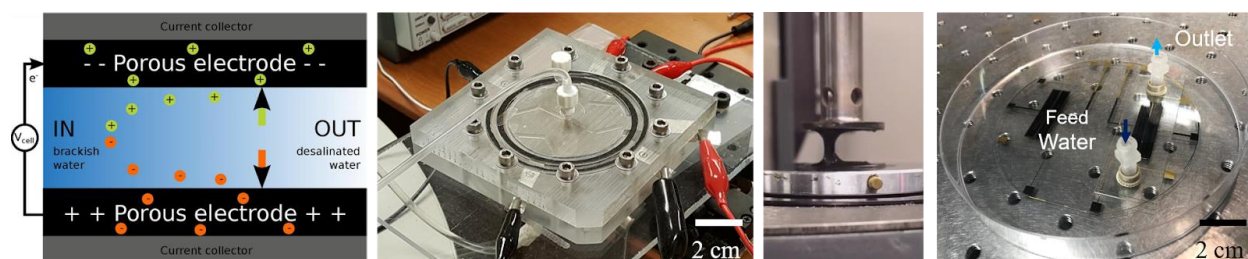


**Figure 1**  (a) In typical CDI architectures, salt ions are electrosoped into a porous electrode.[5] (b) Typical CDI cell. (c) AC slurry in ARES G-2 rheometer. (d) Microfabricated CDI cell.

## 2    *Voltera V-One*

The *Voltera V-One* is a flexible desktop PCB printer, solder paste dispenser, and CNC tool. *Voltera* is a Canadian start-up based out of Toronto with an active online community and resources. Their customer service is responsive and helpful (they offered to receive our sample and conduct deposition tests). Regardless the *V-One* has a handful of issues that show the product is still in its early stages.
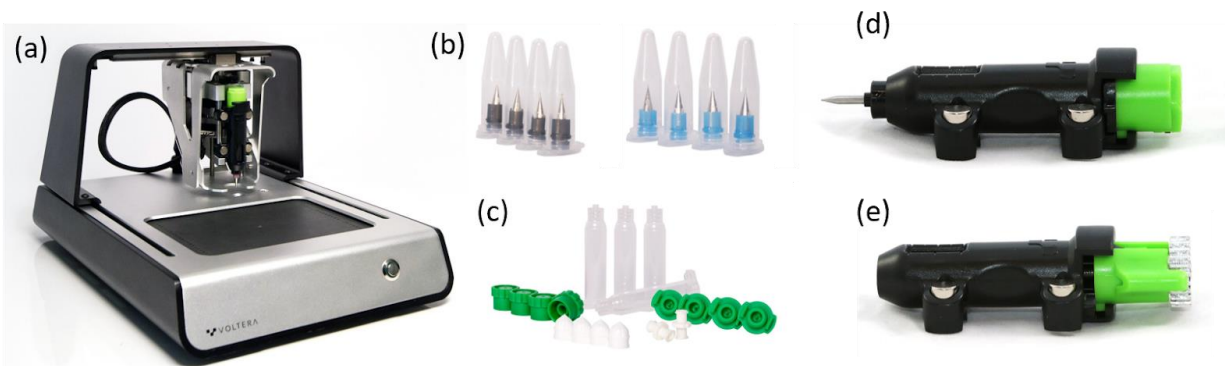
**Figure 2** (a) *Voltera V-One*. (b) 225 and 150 um diameter nozzles. (c) Empty cartridge pack kit the syringes hold 5 cc. (d) Probe for measuring X-Y-Z coordinates of substrate. (e) Dispenser and sheath.

## 2.1 Overview of *V-One* and Performance Characterization

The *V-One* is best described as a controlled paste dispenser, similar to a fused deposition modeling (FDM) 3D printer without a significant vertical component. Its main functional mechanism is a carriage mounted syringe that can travel anywhere in X or Y (and a bit in Z) on its print bed (128 x 105 mm^2). On its carriage, it contains a magnetically removable syringe holder with a small gear and lead screw which pushes the end of the fit piston and extrudes the paste. At the end of the syringe is a custom *Voltera* nozzle tip which is available in 225, 150 and 100 um diameters. The nozzle tips break or clog often and as such it is often necessary to purchase extra. To use the *V-One* with a custom ink it is necessary to buy an empty syringe kit but this kit is mostly reusable since the components do not get damaged during normal use. We have found that extruding IPA through the nozzle (using a separate syringe), as well as submerging the nozzle in IPA, can fix clogging in certain occasions.

The deposition operating procedure for the *V-One* is the same across inks while the subsequent ink curing procedure varies. The *V-One* software is good at providing clear instructions and videos of the procedure. Firstly, the substrate is secured on the print bed using the appropriate clamps and thumbscrews. A Z-height measured probe then measures the position/height of the substrate. Finally, the ink is primed by manually turning the lead screw gear and placed on the carriage to deposit. Please refer to "Custom Ink Printing on the Voltera V-One" video for a demonstration.
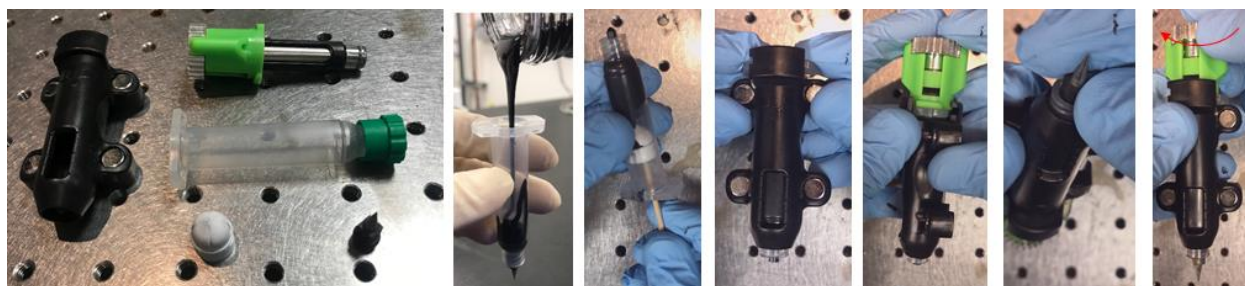


**Figure 3** Components required and loading process for custom paste deposition

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At first, the deposition of ink must be calibrated. Although *Voltera* inks are mostly well characterized, many parameter perturbations e.g. temperature of paste, motor wear, nozzle conditions, etc., may affect the print quality. This is true for custom inks as well. Therefore, the *V-One* undergoes a minor calibration step in which a quick pattern is deposited. The user controls two parameters: E and Z which are the relative travel position of the lead screw and the Z distance from the nozzle tip to the substrate, respectively. In practice, 2-3 calibration runs are sufficient to achieve clear lines with appropriate gaps between depositions.
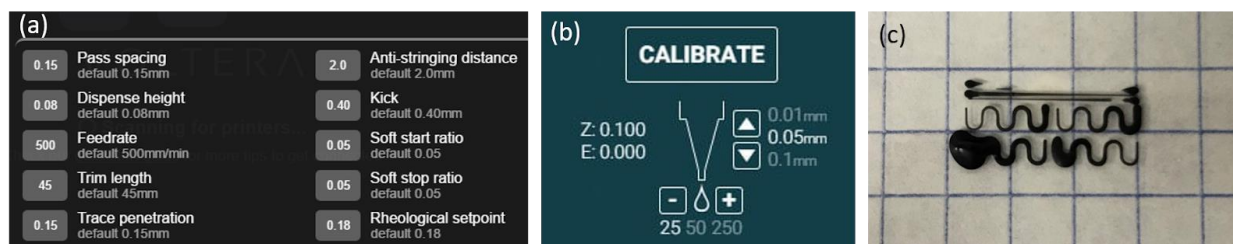


**Figure 4** (a) *V-One* deposition parameters for *Voltera* Conductor ink. A thorough description of the parameters is available online.[6] (b) On-the-fly parameters for calibration. © (c) AC slurry deposited (poorly) in calibration pattern. The user should adjust either the print settings or on-the-fly parameters.

## 2.2 Commercially Available and Custom Inks

*Voltera* sells a handful of custom inks suited for various uses and substrates. They are listed on their web store below.[7] In addition, the *V-One* has the option of loading a custom ink which requires the tweaking of deposition parameters. For this, it is necessary to obtain an empty 5 cc syringe (similar to a standard BD 6 mL syringe) and a sealing component, called a fit piston. For this reason, the *V-One* may be thought of as a useful, quick-to-learn alternative to the Dimatix and Optomec.

The viscosity of the *Voltera* conductor ink (with reported dynamic viscosity at room temperature of > 200 Pa s)[8] and the AC carbon slurry were measured on a ARES G-2 rheometer. A flow step test which varied the shear rate applied on both pastes from 2 to 20 $s^{-1}$ was used to experimentally determine the viscosity. Plots of the of the shear rate vs shear stress are shown below:
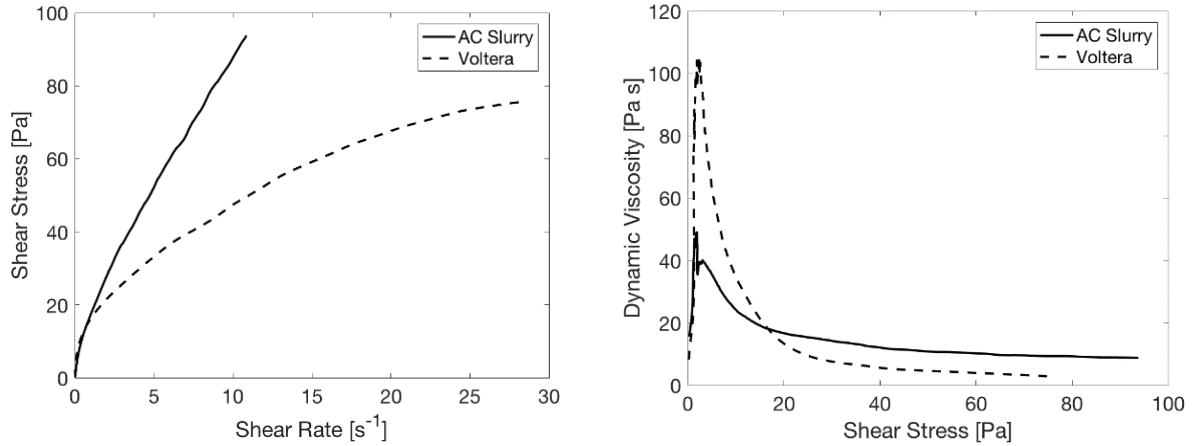
**Figure 5** Results of ARES G-2 flow step test. (a) Shear stress versus shear rate for the activated carbon (AC) powder and *Voltera* conductive ink at room temperature. Both of these inks become less viscous with increasing shear stress which indicates that they are non-Newtonian and exhibit shear-thinning behavior. (b) *Voltera* reported viscosity at room temperature is > 200 Pa s, while the peak here is 100 Pa s at low shear stress.

## 2.3   *V-One* Characterization

The *V-One*'s repeatability, +/- 20 μm, is comparable to the Fujifilm Dimatix DMP 2831 or Optomec Aerosol Jet (AJ) 300 printer, with repeatabilities of +/- 25 and +/- 1 μm, respectively.[9]–[11] However it is still a good candidate for controlled deposition of many Newtonian and non-Newtonian pastes since setup and calibration are relatively easy. For example, the AJ 300 requires extensive preparation, setup, and calibration before deposition. A secondary, and arguably more important, benefit is the much larger viscosity range, assuming your ink is already highly viscous (i.e. > 40,000), of the *V-One* against the DMP 2381's and AJ 300's of 2 - 30 cP and 1 - 1000 cP, respectively. A summary is below in Table 1. For these reasons, the *V-One* was chosen for the fabrication of our CDI cells.

### 2.3.1   Minimum Feature Size

The minimum feature size is here defined as the minimum width characteristic of a print setup. This will be a function of the nozzle selected by the *V-One* user although the only available nozzles are 225, 150, and 100 μm as well as the paste and its deposition parameters. We propose, in a future test, to replace the custom *Voltera* nozzles with standard BD needles of even smaller diameters. Along the same vein, the minimum feature distance is measured. The reported and experimentally found minimum feature sizes are below in Table 1.

### 2.3.2   X-Y Resolution

X-Y resolution may vary based on minimum feature size (if deposited paste 'travels' past the intended geometry), but here will be evaluated by measuring a distance which is much larger than the estimated travel distance of the deposited paste. Table 1 shows the reported X-Y resolutions:

**Table 1** Comparison of the principal characteristics of three paste deposition printers. *Voltera V-One*, Fujifilm Dimatix DMP 2831, and Optomec Aerosol Jet (AJ) 300.

| Reported | *Voltera V-One* | Fujifilm Dimatix DMP 2831 | Optomec Aerosol Jet (AJ) 300 |
|---|---|---|---|
| Printable Area (mm) | 128 x 105 | 210 x 315 | 300 x 300 |
| Minimum Feature Size (μm) | 200 | ~22 | 10 |
| Repeatability (μm) | +/- 20 | +/- 25 | +/- 1 |
| Ink Viscocity (cP) | > 40,000 | 2 - 30 | 1 - 1000 |

### 2.3.3 Alignment with Pre-Existing Features

Alignment of a print job with pre-existing features on any given substrate is often a necessary part of deposition. The *Voltera* desktop application permits placement of the job anywhere on the print bed, such that the user clicks and drags the intended job to a location.

To start the alignment process, a minimum of two alignment marks are required. The simplest geometry to align the *Voltera* probe with the alignment mark on the substrate is a cross or a small circle. If there are no alignment marks on the substrate, it is possible to draw small circles in distinct corners of the geometry. Irrespectively of the chosen type alignment mark, the alignment process consists on a visual alignment of the tip of the *Voltera* probe with the centroid of the alignment mark geometry. After performing this alignment with both of the alignment marks, the system is ready for deposition of the paste.



**Figure 6** Alignment of pre-existing features on a glass substrate. Circles on the corners were used to align the probe with the alignment marks

### 2.4  Deposition of AC Slurry Electrodes

Deposition of an activated carbon (AC) slurry onto pre-existing Au current collector features on a four-inch glass wafer was performed as a method for microfabricating CDI cells. While recipe optimization results are specific to the job, some of the lessons learned should translate well to other custom (or *Voltera*) inks. This section discusses the tuning of the AC slurry for printing, deposition optimization, and the results of our process.

### 2.4.1  Preparation of AC Slurry

The activated carbon slurry was prepared using a straightforward recipe developed in the Stanford Microfluidics Lab. The process for preparation of slurry is demonstrated below in Table 2. For deposition process, the ideal customized ink is one with the capability of changing viscosity by modification of the concentration of the solvent, e.g., in this particular case IPA concentration.

**Table 2** Detailed process for the preparation of the AC slurry

| Step | Process | Notes |
|------|---------|-------|
| 1 | Mix ethyl cellulose (1 g), terpineol (3 mL), 2-propanol (15 mL) in glass container with magnetic stirrer and appropriate cap. | |
| 2 | Place on hotplate-magnetic stirrer with container cap on. | 1 hour @ 100C, 60 rpm |
| 3 | Add activated carbon powder (1 g) and carbon black (0.125 g) | Net mass should be 33.43 g |
| 4 | Place on hotplate-magnetic stirrer with container cap off | Evaporate @ 100C until mass is 24.5 g |
| 5 | Place in ultrasonic bath | 1 hour |

### 2.4.2  Particle Size

Customized inks or slurries require a particle diameter smaller than the *V-One* nozzle and also some method to prevent agglomeration of particles. For example, our initial AC slurry recipe clogged the *V-One* nozzle quickly after only a handful of uses. Our hypothesis for this occurrence is agglomeration in the AC slurry. A cluster of order 100 AC particles that stuck together before introducing the premix may have stuck together even after magnetic stirring. We measured amount (and size) of agglomerations by placing a suspension of AC powder particles in water and captured images using a MicroMax 1300 Y/HS. The images were post-processed using conventional ImageJ software. We investigated three methods for reduction of particle agglomerations and compared the average particle size: (1) ball mill, (2) filter, and (3) ultrasonic bath. Of the three options, we found that the ultrasonic bath was able to eliminate the agglomerations.
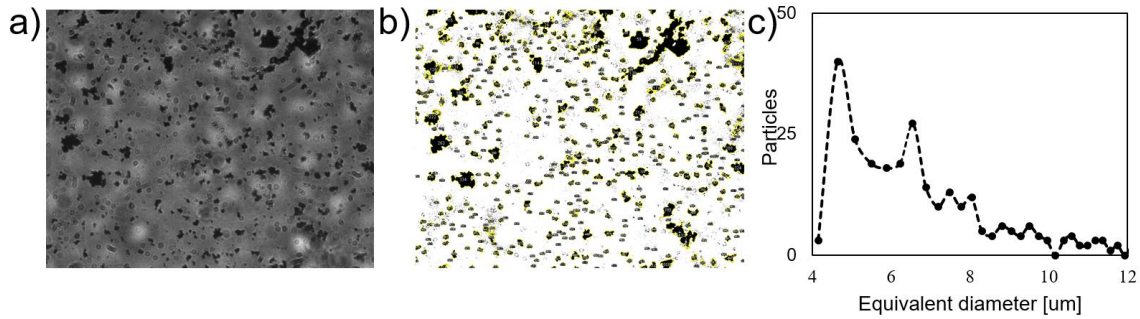
**Figure 7** a) Image of the Kuraray activated carbon particles taken with an inverted microscope b) ImageJ post-processing image c) particle distribution as a function of equivalent diameter of the particle.

### 2.4.3 Loading, Calibration, and Deposition

The AC slurry custom ink was loaded into empty *V-One* syringes by simply pouring out from the glass container. Next, the fit piston (either white, low precision, or red, high precision) was placed and pushed down until a small amount of slurry exited the syringe tip. Finally, the nozzle was screwed on and this entire assembly placed inside the *V-One*. This is shown in figure three.

## 3 CDI Cell Design

The cell consists of: a bottom substrate, activated carbon electrodes, gasket, and "roof" top substrate with microfluidic connectors. To visualize ion transport mechanisms in CDI, it is necessary for the bottom substrate to be clear. This section describes (in a complete, but concise form) the fabrication of all those components besides the AC electrodes. The figure below shows the critical components:
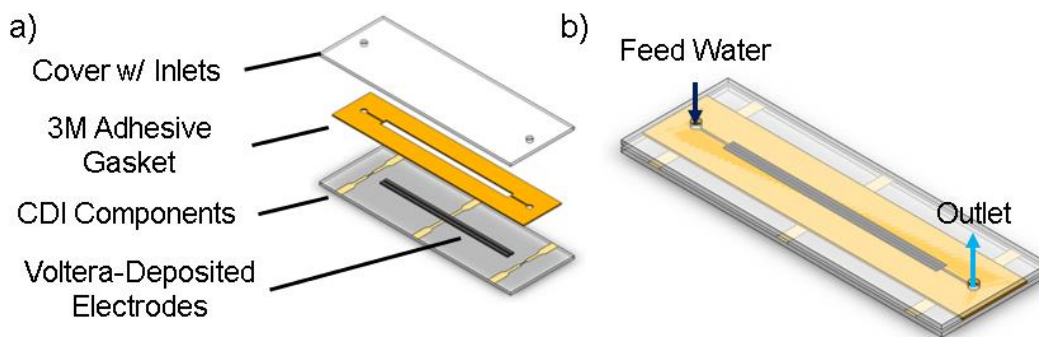


**Figure 8** Schematic of the critical components of a CDI cell a) Blow-up schematic of the component b) Schematic of the assembly of the fabricated desalination cell.

### 3.1 Substrate with Current Collectors

A 4" glass wafer with 500 um thickness was chosen for the bottom substrate was chosen to take advantage of the tools svgdev and svgcoat. A straightforward lift-off process was used to deposit the current collectors. The current collectors were designed in Solidworks and exported as a DXF file which was later tweaked and prepped for use with the Heidelberg using L-edit. Firstly, the surface roughness of the glass wafers was increased using a 2% HF bath for 10 seconds and

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subsequently rinsed with water. Next, a 1 μm thickness LOL2000 layer was deposited followed by baking in a hot plate for 5 mins at 200 °C. The wafers were then run through svgcoat where a 7 um thickness layer of Shipley 3612 was deposited. Subsequently, the wafers were exposed in the Heidelberg MLA 150 using 120 mJ/cm$^2$ dose, -2 defocus. Next, svgdev was used to develop the job. After Innotec sputtering of a Cr (10 nm) and Au (200 nm) layers, the wafers were placed in an acetone bath for 4 hours. Substrate with the desired design were produced. The general process is also shown in the figure below:
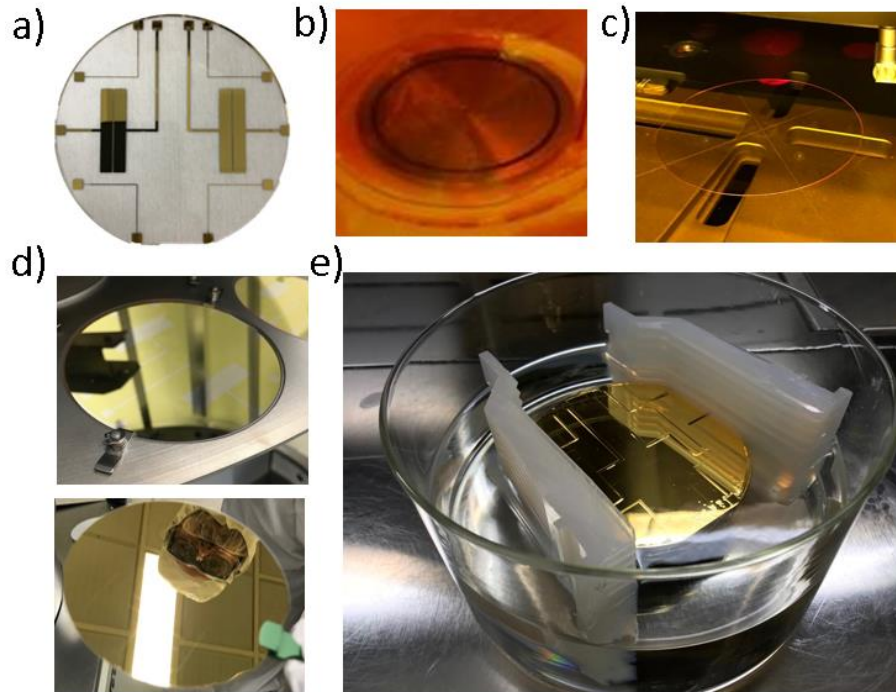


**Figure 9** a) 4" glass wafer (500 um thick). HF 8 seconds → SRD → YES oven. , b) Spincoat LOL-2000 250 nm (*Headway*, 1800 RPM, 1 min) → Hotplate @ 200 °C, 5 mins → Spincoat Shipley 3612 1 um (*Svgcoat*, recipe # 7). c) (2) *Heidelberg* expose @ 120 mJ/cm^2 dose, -2 defocus → PEB (*Svgdev*: station #1, recipe #9 then station #2, recipe #1) → DEV (*Svgdev*: station #1, recipe #3 then station #2, recipe #1). d) (3) *Innotec* E-beam evaporation Cr (2% power, 10 nm) and Au (14% power, 200 nm) e) Acetone bath overnight → DEV for LOL removal (*Svgdev*: station #1, recipe #3 then station #2, recipe #1).
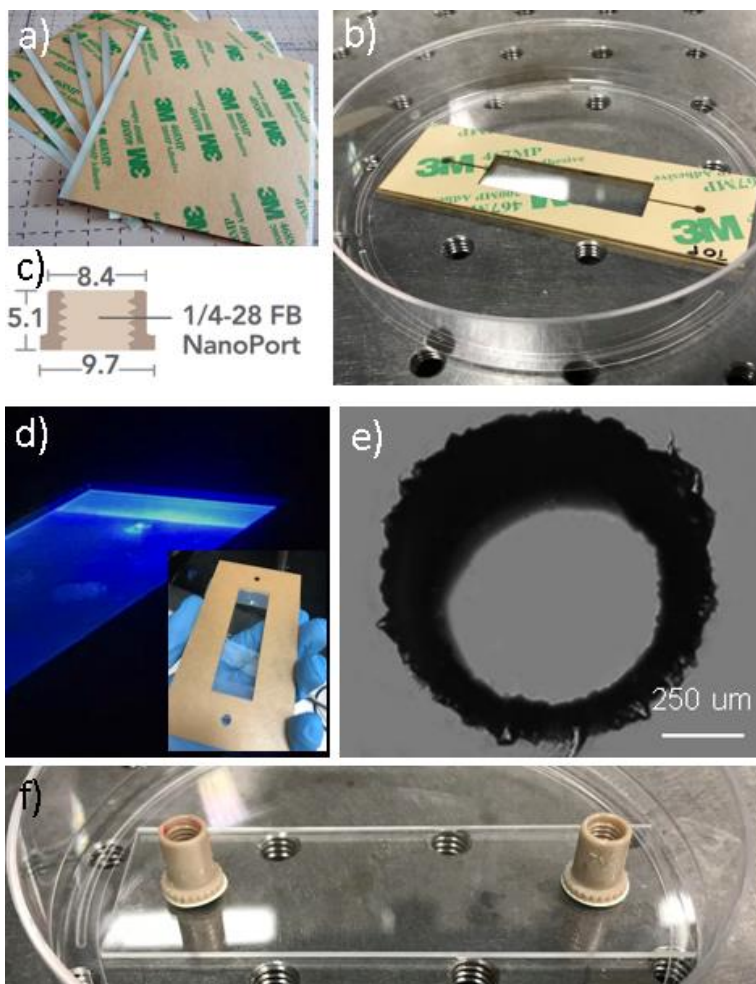
## 3.2  Adhesive Gasket

The adhesive gasket was chosen to provide a gap between the bottom substrate and the top substrate. It is important that the gasket have uniform wall thickness above the thickness of the activated carbon electrodes. For this reason, a commercially available double-sided adhesive was used: 3M 200MP double-sided adhesive.

## 3.3  Top Substrate with Microfluidic Connectors

We leveraged a developed process for laser ablation of glass to cut holes on a microscope slide and adhesive-bond microfluidic connections. Two 1.5 mm diameter holes were cut into a regular 1mm thick microscope slide using a UV laser. The raster was done using 0.040 mm gaps

between crosshatched perpendicular lines. Since the focal range of the laser used was ~ 300 um, three Z movements were needed to cut through the glass by ablating the surface ~300 um, moving the slide that same distance down, ablating the next 300 µm, etc.

The microscope slides were then sealed using IDEX pre-formed epoxy rings ("epoxy fritz") and IDEX 14-28 FB Nanoports. These connect with readily available IDEX 10-32 fittings. The result is a strong, removable connection.



**Figure 10** a) 3M adhesive layer before laser cutter. b) 3M adhesive layer after laser cutter used as gasket to avoid water leakage. c) Nanoport used for microfluidics connections. d) Laser ablation on glass slide to make a roof for the desalination cell. e) Close up image of the ablated hole. f) Bonding of Nanoports on top of glass slide with holes.

### 3.4 Assembly

After deposition of current collectors, on the glass wafer substrate (as well as the *Voltera*-deposited AC electrodes), the adhesive gasket was placed on the substrate via manual alignment along with the connectors slide.
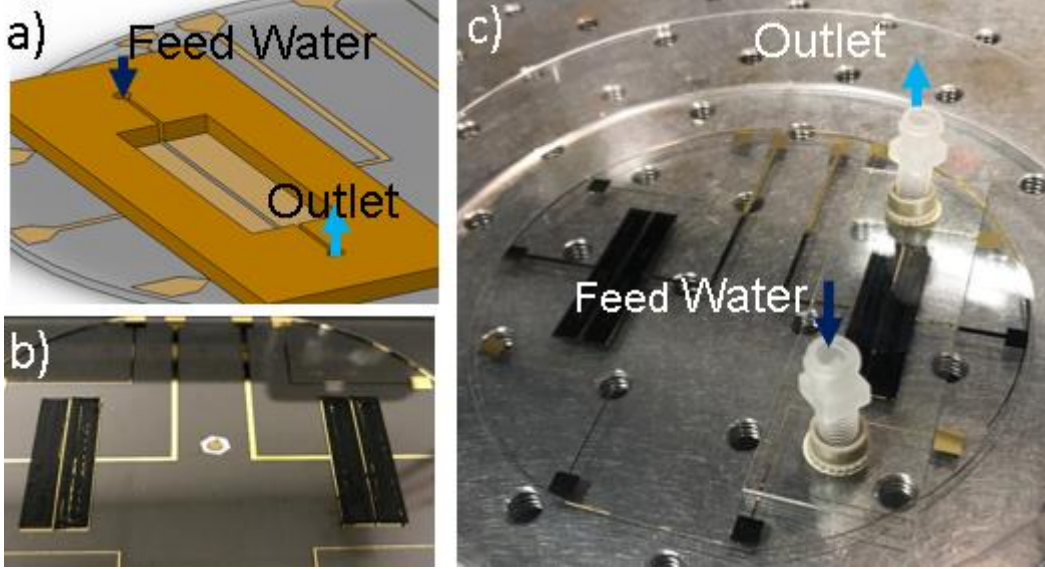
**Figure 11** a) CAD file of the current collector with the adhesive layer. b) AC slurry deposited on top the current collector. c) Final assembly of the microfabricated CDI cell.

## 4 Preliminary results and future studies for desalination

In this section we present the common methods used to evaluate CDI performance.

### 4.1 CDI metrics

The first metric is average salt adsorption rate (ASAR) in units of moles of salt per total electrode area per time and can be defined as

$$ASAR = \frac{\Gamma_{ads}}{NAt_{cycle}} = \frac{Q}{NAt_{cycle}} \int_0^{t_{charge}} (c_0 - c)dt$$

where $\Gamma_{ads}$ is amount of salt adsorbed during charging (in units of moles), $N$ is number for electrode pairs, $A$ is single electrode area, $t_{cycle}$ is cycle time, $t_{charge}$ is charging time, $Q$ is flow rate, and $c$ and $c_0$ are effluent and influent salt concentrations, respectively. This metric quantifies the throughput of the desalination process.

The second metric is energy normalized adsorbed salt (*ENAS*) in units of moles of salt per Joules of energy lost and is defined as

$$ENAS = \frac{Q \int_0^{t_{charge}} (c_0 - c)dt}{E_{in} - E_{out}}$$

where *Ein is* the energy input to the cell during charging (J) and *Eout* corresponds to Energy recovered during discharging (J)

### 4.2 Cyclic voltammetry

Cyclic Voltammetry (CV) is an electrochemical technique which measures the current that develops in an electrochemical cell. This method is used to determine the capacitance, $C_D$, of a CDI cell. To obtain a proper CV reading Faradaic reactions must be avoided. This can be achieved

by controlling the applied voltage window. During CV the recorded current, $i_c$ has capacitive nature and is directly proportional to scan rate $v$: $i_c = C_D v$. CV experiments can be performed under a potential such that a region at several scan rates and then plot $i_c$ vs v to determine $C_D$. This measurement will be performed to our microfabricated desalination system.

## 4.3 EIS - Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is technique to characterize electrochemical systems and to determine the contribution of the involved resistances on the electrode or electrolytic processes. The fundamental aspect of EIS is the frequency dependent measurement. This is used to generate a Nyquist plot, which can be correlated with equivalent circuits. For example, a classical system is a resistance in series with a capacitor and a resistance. This electrical circuit is similar to basic CDI cycles. The underlying idea of this is to fit the experimental EIS measurements with a previously known equivalent circuit to extract relevant information, such as, ohmic resistance or Faradaic resistance.
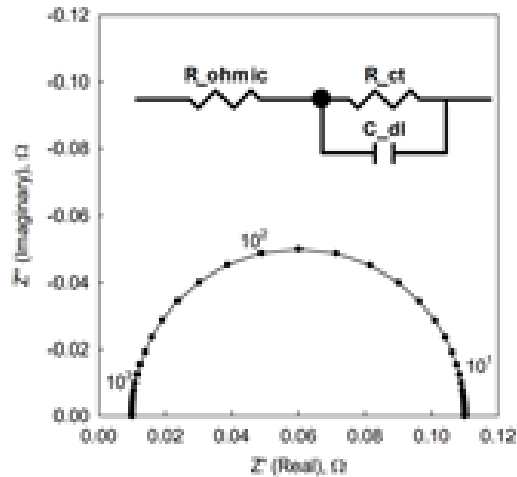


**Figure 12** Schematic and impedance for an EIS model consisting of a parallel RC circuit in series with an ohmic resistance.

## 4.4 Water Desalination

Our experimental set-up includes a flow-through conductivity meter sensor and an on-chip two probe measurement. Further studies of the microfabricated desalination cell will lead to quantification of the desalination performance.

## 4.5 pH Visualization

For the preliminary pH visualization experiments the fluorescent dye fluorescein was used to visualize the ion transport and pH variations inside the desalination cell. The microfabricated CDI cell was placed on top the epifluorescence microscope. Fluorescein contained in a syringe was put in a syringe pump to supply the flow to the cell. Platinum electrodes were used to connect the current collector to the source meter. An oscillating voltage between 1V to -1V was applied with the system to visualize ion transport, as shown in figure 13.

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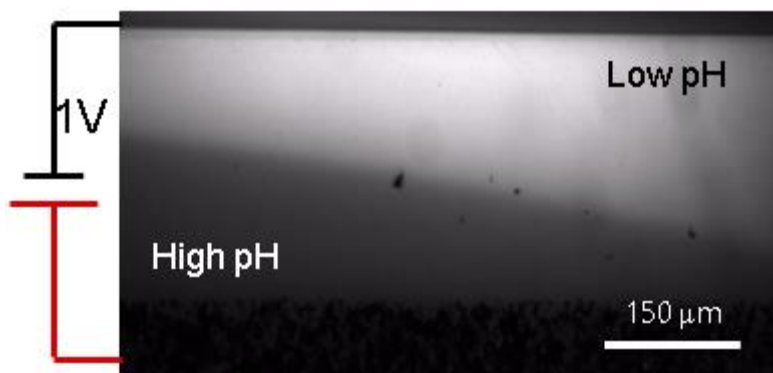
**Figure 13** Preliminary results for pH visualization. 1 V was applied to the CDI cell.

## 5    Conclusion

Four billion people experience water scarcity per year. RO is the most commonly used technology for seawater desalination. However, 80% of the desalination market in the USA is brackish water. CDI has the potential to perform 5x better than RO for brackish water. To accomplish this, current limitation of CDI should be addressed. These limitations include decrease of contact resistance, tailored geometry to decrease diffusion time, and fundamental understanding due to the lack of visualization experiments. We proposed a microfabricated technique to address these limitation, using the Voltera V-One to deposit AC on top of a gold deposited current collector. We successfully accomplished the fabrication of a microfabricated CDI cell and first pH visualization experiments. Future work includes the characterization of contact resistance, capacitance, and energy consumption. Also, a detailed theory for pH visualization was presented.

## 6    Appendix
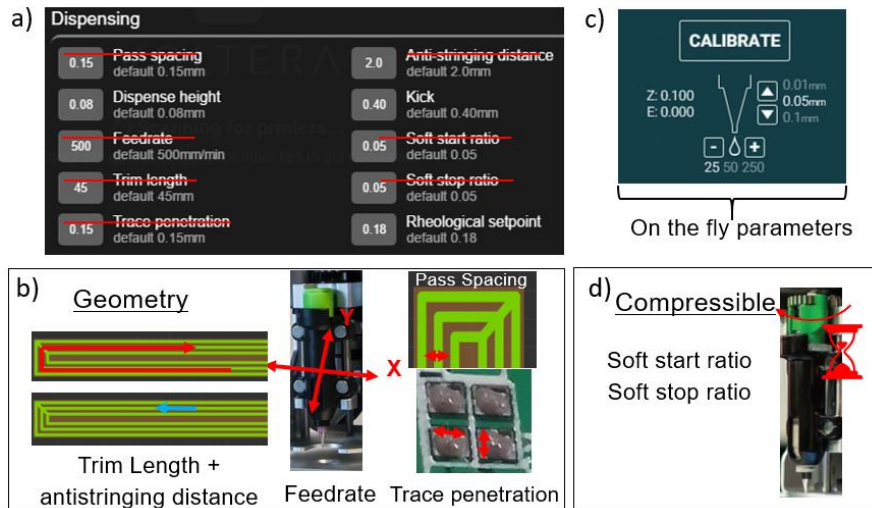### 6.1    Recommended *Voltera* Ink Parameters for new ink deposition
There are three categories of parameters sorted by functionality: Geometry parameters for complex geometries, includes trim length, antistringing distance, feed rate, pass spacing, and trace penetration; Compressible parameters for compressible fluids, includes soft start ratio and soft stop ratio; New ink parameters to control the homogeneity and consistency of deposition with new inks, includes kick, dispense height, and rheological set point. Hence, users with new inks should focus

on kick to control the thickness of the trace, rheological set point to control the homogeneity of the trace, and dispense height to make sure that the tip of the nozzle is not disturbing the deposited slurry.
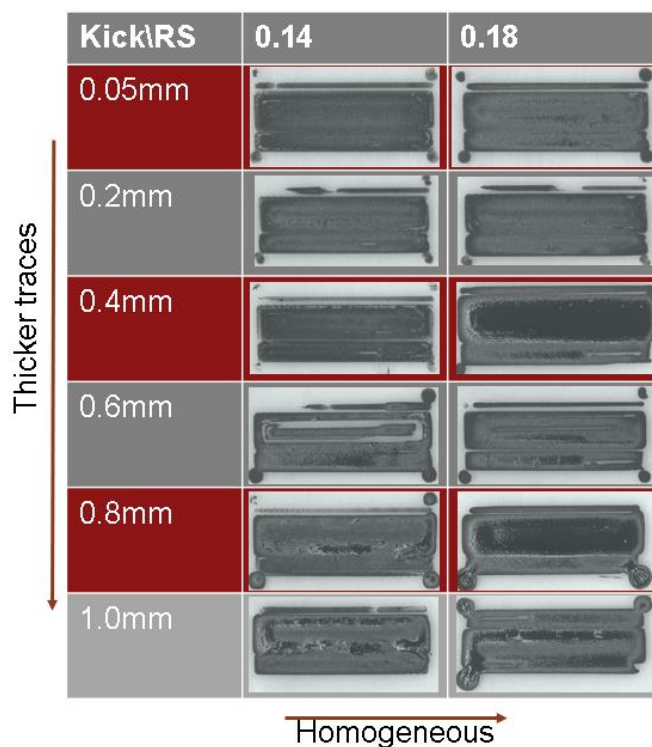


**Figure 14** Recommended parameters for new ink deposition with the Voltera V-One a) The list of all the available parameters, red dash line correspond to the geometry or compressible ink parameters. Non-dashed parameter are the suggested parameters for new ink deposition b) Parameters that will influence a complex geometry deposition c) On the fly parameters during the deposition of ink d) Parameters that should be change for compressible inks.

## 6.2 Suggestion of pattern for design of experiments for new inks

A simple pattern is recommended to test the deposition of new inks with the Voltera. Critical lengths of the design, such as gap the gap between traces, must be tested at this stage. The DOE should focus on kick and rheological set point. Kick is used to control the thickness of the trace and rheological set point is used to control the homogeneity of the trace.
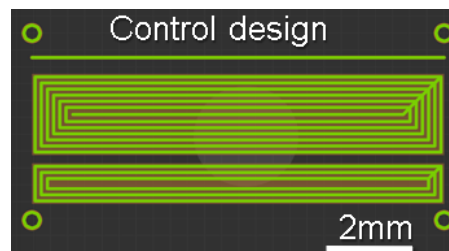


**Figure 15** Recommended design to test new inks. Spacer between lines should be correlated with the minimum feature size wanted.

**Figure 16** Recommended design of experiments for new inks. Initiate the process with default parameters, then adjust based on what is desired.

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