Capacitive deionization on-chip as a method for microfluidic sample preparation

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by,

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Introduction

- Sample preparation on-chip is essential to increase throughput, reproducibility and improve the detection limit of lab-on-chip analysis methods. Lab-on-chip technology is the ability to analyze small sample volumes in the nano- and picoliter range.

- Capacitive deionization (CDI) is an electrostatic desalination technique, which employs two porous electrodes facing each other, with the salt solution flowing in between them. Upon the application of a potential of approximately 1.2 V between the electrodes, ions with a high electrophoretic mobility in the solution migrate to the electrodes and are stored in the electrical double layer.

- Larger molecules with a lower mobility, such as proteins, will take more time to migrate to the electrodes. This difference in mobility between the salt ions and the proteins can be utilized to separate them.

- In this paper, they have demonstrated the application of CDI on chip as a microfluidic sample preparation method, through desalination of a sample where FITC-dextran is used as model compound for further analysis by MS. Additionally, a novel method is introduced to monitor the salt concentration between the desalination electrodes in a real time manner, based on impedance spectroscopy.

- This method is combined with fluorescent imaging to demonstrate the desalination of the model compound.

Introduction

Cell constant K [m−1] for a typical CDI setup consisting of two electrodes facing each other

$$K = d/a,$$

d - width of the channel
a - area of the electrodes

$$\text{Impedance } (Z) = \rho \cdot K$$

ρ - resistivity

The salt concentration as a function of time is monitored through impedance measurements at a single frequency using the same set of electrodes that is used to desalinate. The measurements give an average number of the concentration of NaCl between the electrodes.

This hypothesis calculates the concentration C [mol m−3] as a function of time t [s] at the exit of the desalination electrodes as well as the average concentration measured between the electrodes.

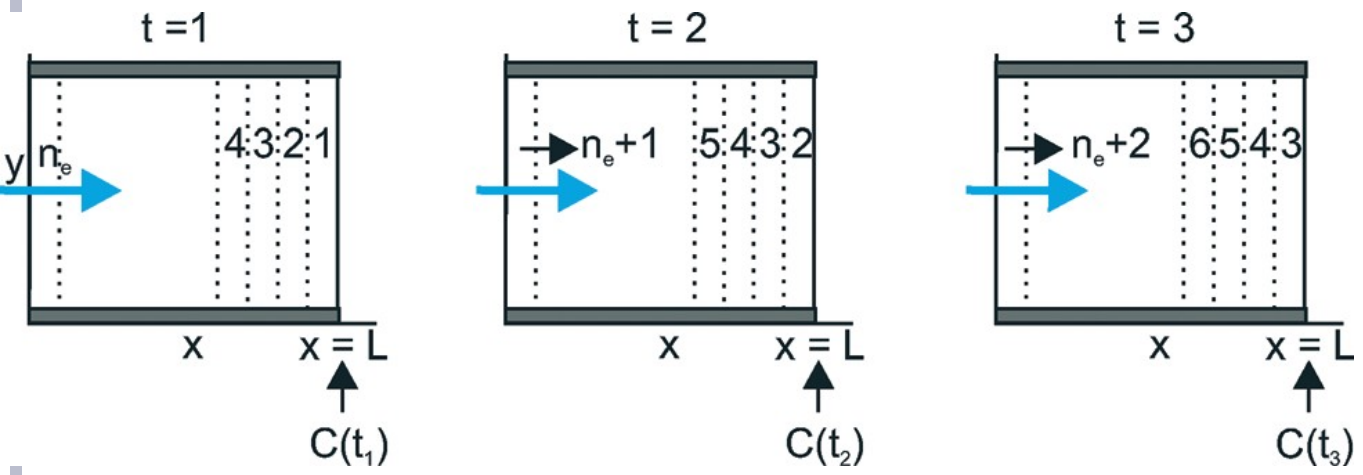
Theoretical Model of CDI

- The capacitor, with length L, is divided in ne elements.
- Initially each element is filled with the start concentration of 10 mM NaCl.
- During their residence time between the electrodes the elements are desalinated.

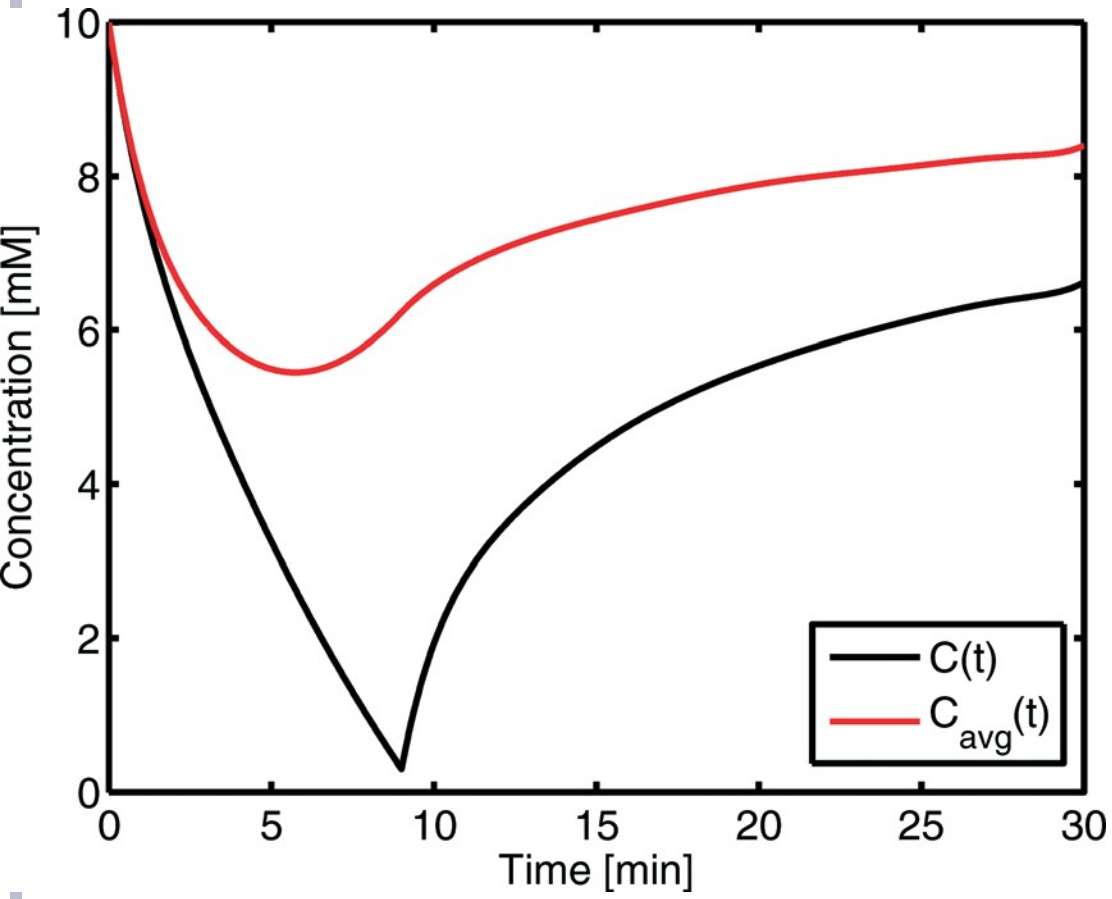
The salt concentration as a function of time at x = L can be described by:

$$C(t) = C_0 - \frac{\Gamma}{FV}\int_{t_0}^{t_n} I_n dt, \text{for } 0 < t < t_t \qquad C(t) = C_0 - \frac{\Gamma}{FV}\int_{t_n - t_t}^{t_n} I_n dt, \text{ for } t_t < t < t_e,$$

where F - Faraday constant [C mol−1], V - volume of a single element [m3], C0 [mol m−3] is the starting concentration of 10 mM NaCl, tn [s] – time, tt [s] – residence time of a single element in the capacitor, In [A] – current obtained from the measurements



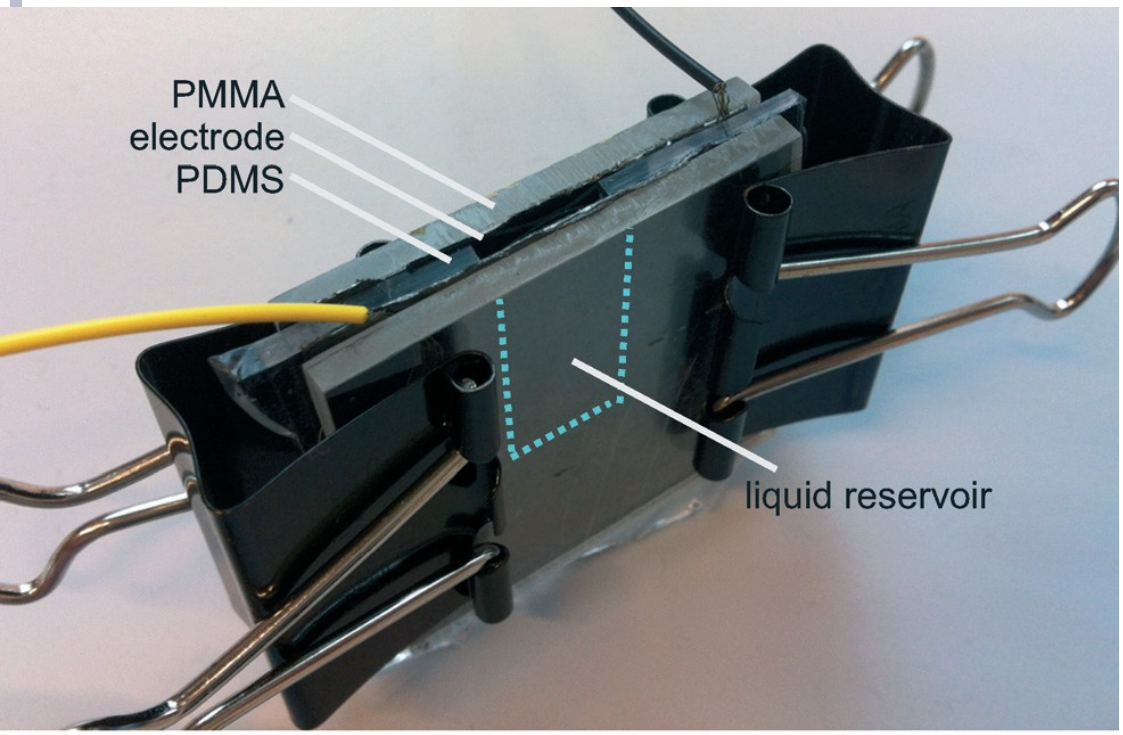
- Schematic of the desalination electrodes for the first three time intervals.
- The flow direction is indicated with the blue arrow.
- The concentration C is determined at the exit of the electrodes at x = L for n elements.
- The number of elements that fit in the capacitor is ne.



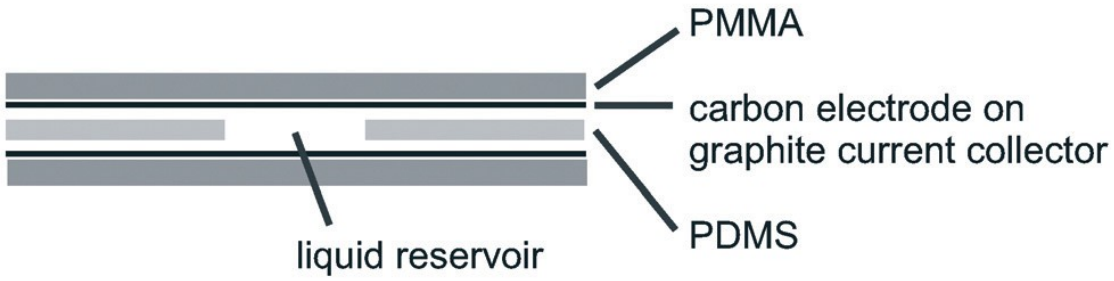
•Results from the element model calculations. C(t) represents the concentration directly at the exit of the CDI cell for CDI on chip.

•The flow rate is 1 μL min−1. Cavg(t) represents the concentration as it is determined with the desalination electrodes. Cavg(t) gives a maximum desalination percentage of 45% while the locally achieved desalination percentage is calculated at 97%.

Experimental



a)



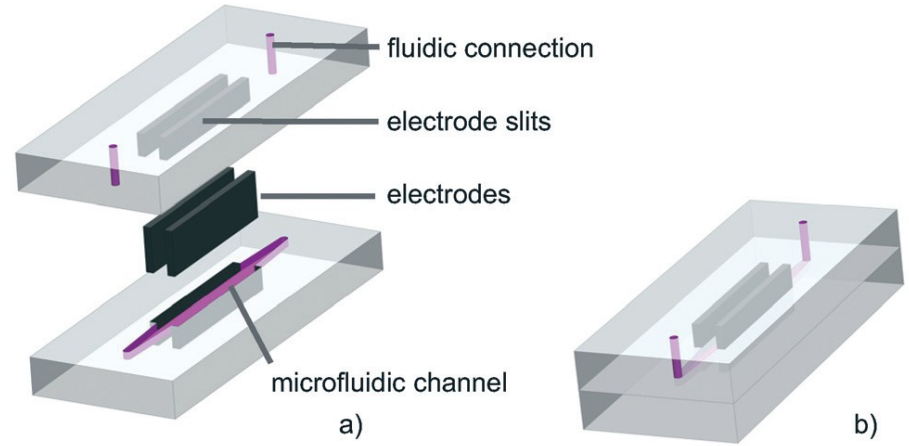
b)

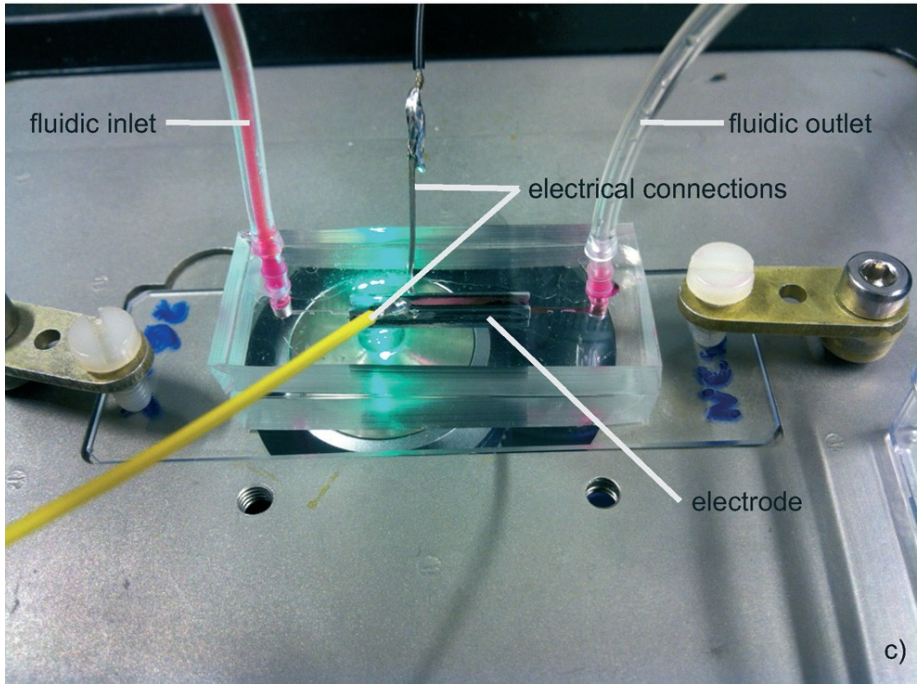
Photo of the macrofluidic cell (a) and schematic cross-section of the cell as seen from the top (b). The cell consists of two polymethyl methacrylate (PMMA) sheets separated by a u-shaped spacer of thickness 2.25 mm.

The liquid volume of the liquid reservoir formed by the spacer is 0.45 ml.

On each side of the spacer carbon electrode material is placed.

Experimental



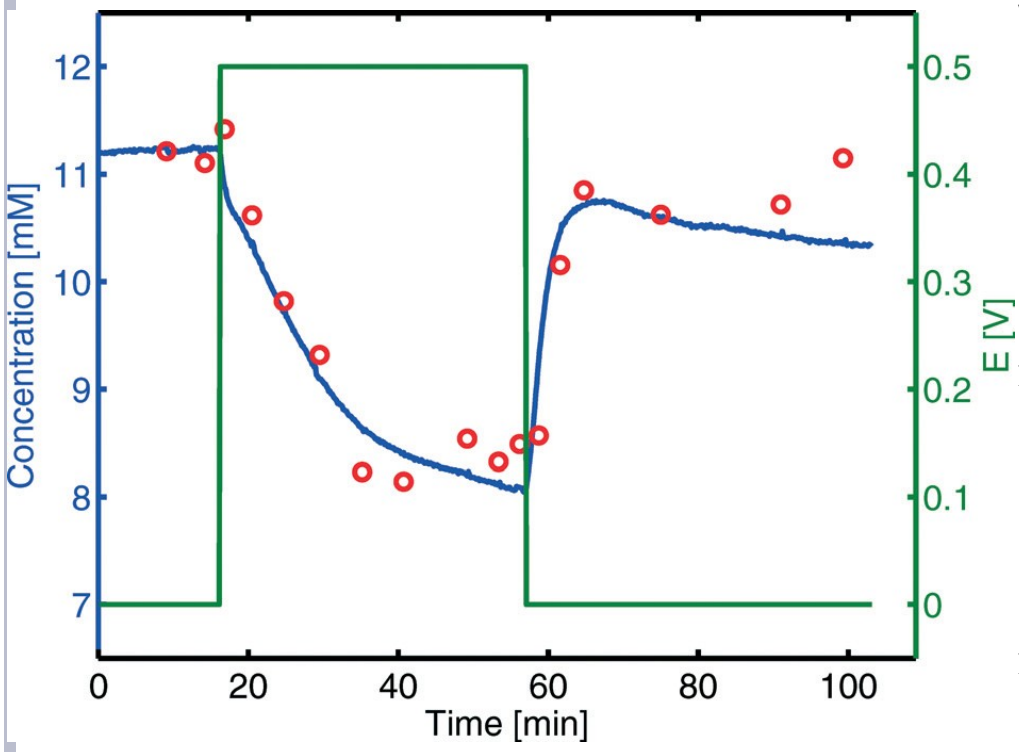


a) Exploded view of the chip. The fluidic channels are colored in violet. The carbon electrodes are colored black.
b) Assembled chip.
c) Photograph of the microfluidic chip on a stage from an inverted microscope. The chip is connected to a syringe pump through tygon tubing. Stainless steel wires connect the carbon electrodes to the potentiostat.

The distance between the electrodes **-1.5 mm**.
The height and length of the channel are **0.4 and 12 mm** respectively

These electrodes are proprietary material from Voltea and consist of a sheet of graphite, forming the current collectors, coated with porous carbon.

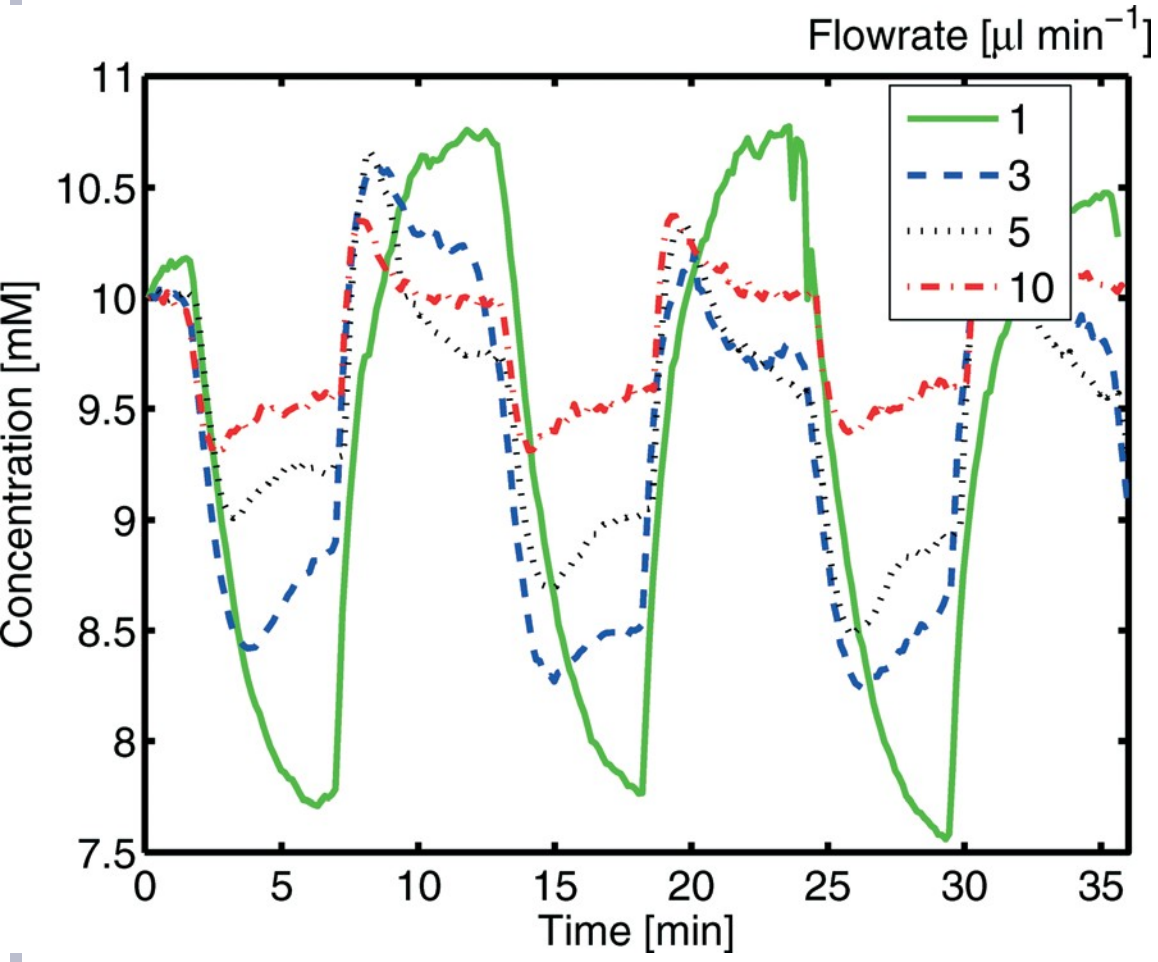
Results



Verification of online monitoring of the salt concentration in the macro cell

- Measured salt concentration as a function of time during a desalination cycle of the macro cell containing 10 mM NaCl.
- The green line shows the applied desalination potential.
- The blue line represents the concentration obtained from impedance spectroscopy measurements with the desalination electrodes at frequency 11.7 kHz.
- These results agree well with the reference measurements, obtained from extracted samples (red circles).

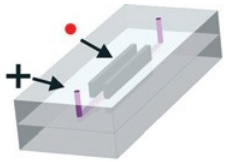
Results

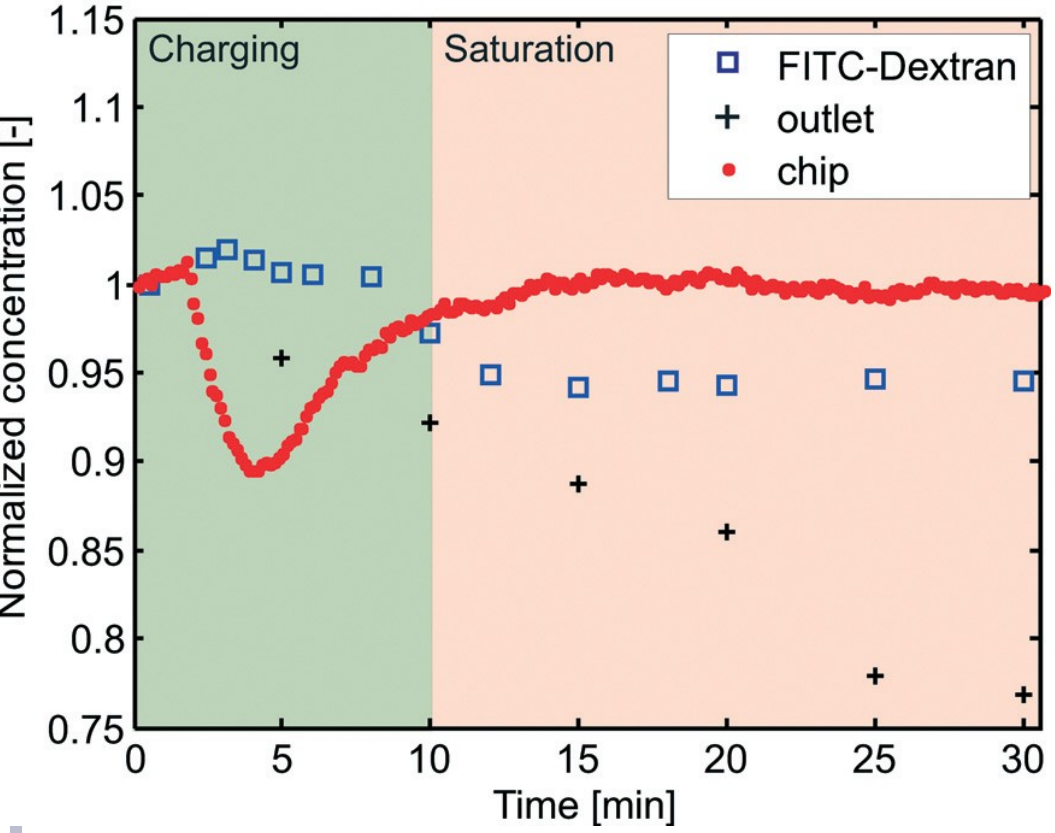


Desalination and online monitoring of CDI on chip

- Measured impedance over time at a frequency of 11.7 kHz.
- The applied desalination potential is 0.5 V, each cycle of charging and discharging takes 10 min.
- The flow rate varies from 1 to 10 µL min−1.

Results





•This figure shows the desalination of FITC-dextran upon the application of a potential of 0.5 V starting at t = 2 min. and continuing for 30 minutes.

•The fluorescence intensity of FITC-dextran is plot in blue squares.

•The buffer concentration measured at the outlet is plot in black (+). The red dots represent the buffer concentration measured with the desalination electrodes. All values are normalized and experiments are performed with a flow rate of 1 μL min−1.

•The observed drop in buffer concentration at the outlet of the chip is 23% after 30 min.

•The drop in fluorescence intensity of FITC-dextran is only 6% and most likely due to pH variations.

Results

Model and experimental agreement

- The desalination percentage between the electrodes of 11% is lower than earlier observed for desalination of 10 mM NaCl at a flow rate of 1 μL min−1.

- This is attributed to blockage of electrode pores by FITC-dextran which results in a decrease of the effective surface area and amount of ions absorbed.

- The CDI model predicts an underestimation of the local desalination percentage at the exit of the electrodes of a factor of 2.

- Hence, the locally achieved desalination percentage is expected to reach 22%.

- It was concluded that the concentration of FITC-dextran remains constant over time, while the buffer concentration at the outlet is decreased by 23%.

Conclusions

- They have demonstrated that CDI can be used as an on-chip sample preparation method through desalination of a sample where FITC-dextran is used as a model compound.
- The concentration of FITC-dextran remains constant over a time-span of 30 min, while the buffer concentration measured at the outlet of the chip is reduced by 23%.
- At the same time they have shown a novel method to measure the average online salt concentration on chip, using impedance spectroscopy with the desalination electrodes.
- The application of this method was demonstrated on-chip, through a variation in flow rate of the solution as well as a variation in the applied desalination potential.
- From these measurements they have confirmed the hypothesis that the relative amount of salt removed from the liquid decreases as the flow rate increases.


Thank
you...
Don't Fear Moving Slowly Forward,
Fear Standing Still.....