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Water desalination with Wires

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Abstract

We show the significant potential of water desalination using a novel capacitive wire-based technology in which anode/cathode wire pairs are constructed from coating a thin (order of 10 μm thick) porous carbon electrode layer on top of electrically conducting rods (or wires). Upon dipping an array of such anode/cathode pairs in water to be desalinated and applying a cell voltage between the anode and cathode side, salt is quickly adsorbed into the micropores in the electrodes. In the second half of the cycle, the wires are removed from the water and submersed into another water stream. Upon reducing the voltage (short-circuiting the cell pairs), salt is released in this increasingly saline water stream and a new cycle can start where the wires are contacted again with freshwater. We show experimentally how in six subsequent cycles we can reduce the salinity of 20 mM feed (brackish) water by a factor of three, while application of a cation exchange membrane on the cathode wires makes the desalination factor increase to four. Theoretical equilibrium modeling rationalizes the experimental findings, and predicts that system performance can be significantly enhanced when the membrane permselectivity can be improved, when both electrodes are coated with membranes and/or when the fraction of water adhering to the rods can be reduced. To treat large volumes of water quickly, multiple stacks of wire pairs can be used simultaneously in a “merry-go-round” operational mode, adsorbing salt from the increasingly freshwater, and releasing the salt into the brine stream.

Increasing global water demand for fresh water because of rising population, increasing standard of living, and expanding agriculture and industrialization is driving the development of new and energy-efficient water desalination technologies.¹⁻³ For the treatment of brackish water, which generally contains relatively few ions, there is significant potential to achieve high energy efficiency by technologies that specifically remove ions to desalinate the water, instead of the reverse approach where excess water molecules are removed from the salt solution as in the state-of-the-art technologies distillation and reverse osmosis. Such techniques include capacitive deionization,⁴⁻¹⁰ membrane capacitive deionization,¹¹⁻¹⁶ and desalination using microchannels,¹⁷ batteries,¹⁸ and microbial desalination cells.¹⁹ Several of these techniques are related to ongoing work on supercapacitor batteries,²⁰⁻²² and on the energy harvesting from controlled mixing of river water and seawater in capacitive porous electrode devices.²³⁻²⁶ Existing capacitive techniques (using pairs of

electrodes) operate in a sequential mode, where the water to be treated flows through a microchannel in between the two electrodes, and salt is adsorbed and freshwater is temporarily produced, followed by an ion release-step (by reducing or even switching the voltage) where adsorbed salt is released again and a concentrate, or “brine”-stream, is produced. The disadvantage of this mode of operation is the required repeated switching from adsorption to desorption, which during a brief period after switching leads to the mixing of just-produced fresh water with untreated water and with brine. The switching of the effluent stream requires operation by an electronically controlled valve, responding to the conductivity measured by an on-line conductivity meter. These auxiliary devices add to installment and maintenance costs.

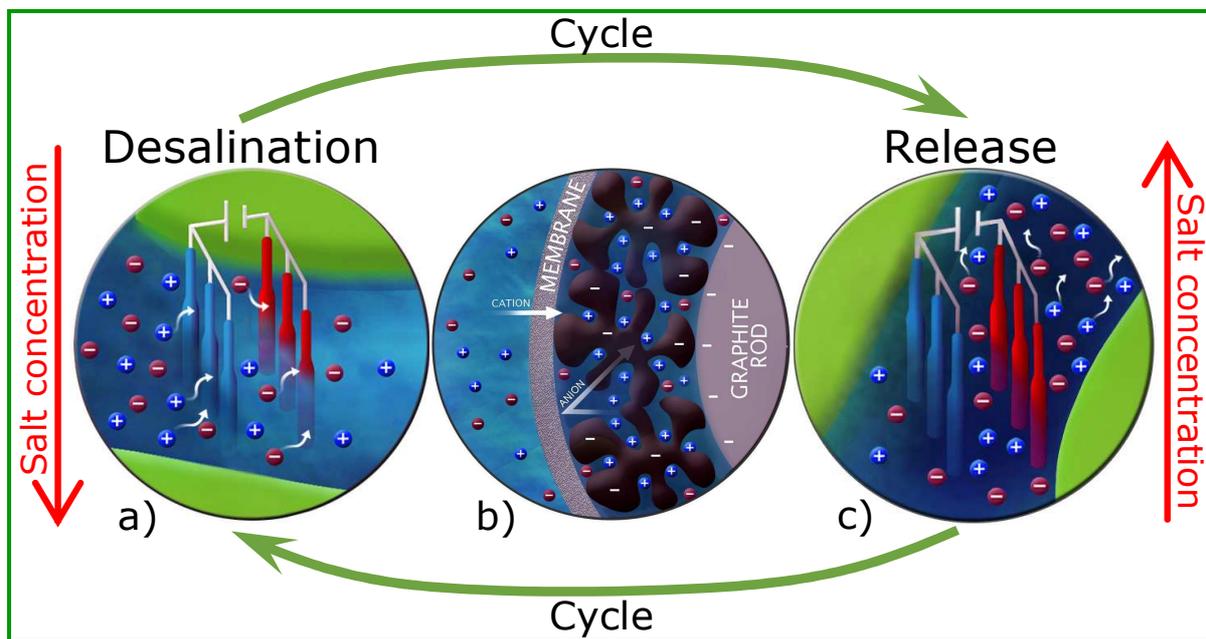


Figure 1: Schematic view of desalination with wires. a). Adsorption of salt by multiple pairs of (membrane-coated) porous electrode rods (anode-cathode combination) upon applying a cell voltage. b). Detailed view of cation transport through cation-exchange membrane into porous electrode upon applying a voltage. Co-ions are locked into the electrode structure. c). Release of salt in brine compartment after short-circuiting the cells, after which the wires are transferred back to the desalination compartment.

It would be more elegant and more efficient if we could simply split the feed water (not the effluent) into two continuous streams before any desalination takes place, and devise a method to take out the salt from one water stream, and release it into the other, in order to create a continuous stream of freshwater and of brine. By making the device work harder or slower (e.g. using the cell voltage as control parameter, as in the technique proposed below), or by having more of these devices operate simultaneously, we can robustly tune the degree of desalination to any setpoint. By adjusting the split ratio in upstream water flow rate between freshwater and brine, we can tune the water recovery, which is the fraction of the inlet water converted into freshwater.

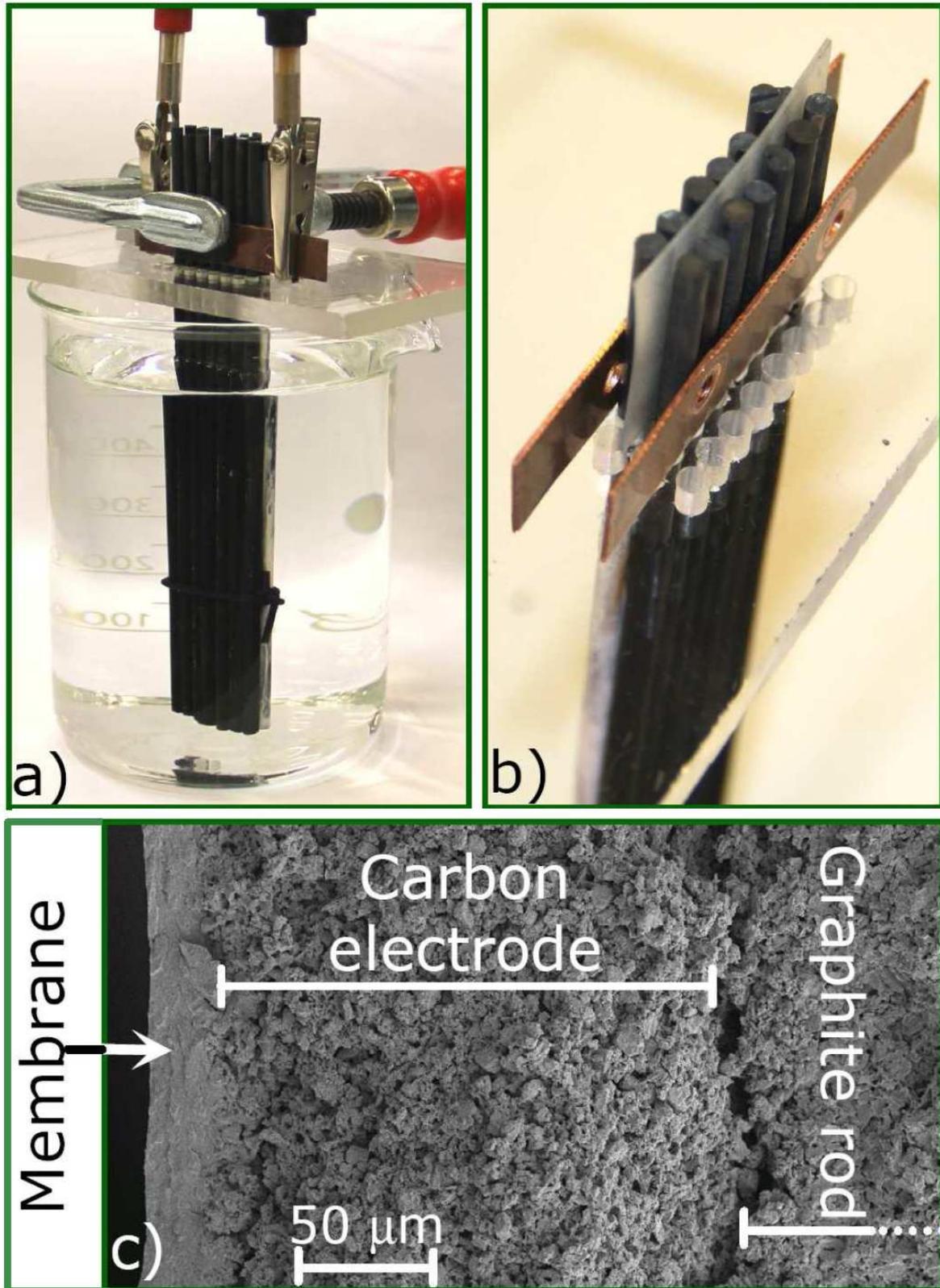


Figure 2: Experimental setup for desalination with wires. a) View of the 7 pairs of graphite rods positioned ~ 0.5 mm apart, dipped into water. b) An electrical voltage difference can be applied between the anode and cathode rods via copper strips. c) SEM-picture of membrane-electrode assembly.

In the present work, we propose such a method which we call “water desalination with wires.” The wires here are rigid rods having a length about 40x their thickness. Experiments with these rods show that the approach is valid. Ultimately, thin and flexible wires may be preferred. On the cylindrical outer surface of the wires we coat a porous carbon electrode layer. Two of those wires together form a “wire pair” and are dipped into the stream of water that is to become freshwater, see Fig. 1a. Upon applying a cell voltage difference between the two wires, the one of negative polarity acts as the cathode and adsorbs cations (such as Na^+), with the other serving as the anode, adsorbing anions (like Cl^-). This is a capacitive process and ions are temporarily stored in the electrical double layers (EDLs) formed within the micropores inside the carbon particles that constitute the electrode, see Fig. 1b. Ions do not adsorb (electro-)chemically and do not react away. Faradaic chemical reactions, as essential in batteries, or pseudo-capacitance effects, are not the driving force for ion adsorption in this capacitive process.

After some contact time in the freshwater the wire pair is lifted from the solution and brought in contact with (what will become) the brine stream. The electric field is reduced or removed (for instance, the electrical connection between the wires is short-circuited) and the stored ions are released into solution, making the salinity go up, see Fig. 1c. Our goal in the present work is to investigate if this method of desalination is feasible and what desalination degrees can be reached. We will compare the “bare” system as described above (system W-0), with a modification in which a cation-exchange membrane is coated on top of the cathode, which we call system W-1, where “W” stands for wire, and the number 1 stands for the use of one membrane. The reason that a membrane might be advantageous is that without them during the desalination step in which ions of one charge sign are attracted into an electrode (the counterions), that in this period, ions of the opposite charge sign (co-ions, having the same charge as the electronic charge in the carbon matrix) are released from the electrode, thereby degrading the desalination efficiency. The use of a membrane selective only to counterions effectively blocks the co-ions from escaping from the electrode, which increases desalination efficiency, see Fig. 1b.^{12,15}

To fabricate the electrodes, a carbon slurry was prepared by adding 85 wt% of porous carbon material (YP50-F, Kuraray Chemical, Osaka, Japan), 5 wt% of carbon black (Vulcan XC72R, Cabot Corp., Boston, USA) and 10 wt% of polyvinylidene fluoride (PVDF) (Kynar HSV 900, Arkema Inc., Philadelphia, USA) to N-methyl-2-pyrrolidone with a 30:1 NMP:PVDF weight ratio. After intensive mixing, the slurry was de-aired and stored at 50 °C for 24 h to obtain a homogeneous mixture. Wires were prepared by painting graphite “mini-rods” (Poco EDM-3, total length ~15 cm, coated length 11 cm), diameter ~3 mm, Saturn Industries, Inc., USA) with the carbon slurry, and drying in air. The average coating thickness after three applications of slurry was approximately 200 μm . Per single rod the mass of porous electrode material is on average 0.167 g, and thus the electrode mass density is $\rho_e=0.38$ g/mL. For part of the experiments (system W-1), cationic ionomer solution (Fumion FLNMP-15, Fumatech, St. Ingbert, Germany) was subsequently coated on the outside of the wires that would serve at cathode. After drying, a thin (approximate thickness ~15 μm) ion-exchange membrane layer is thus formed, preferentially allowing cations (such as Na^+) access to the electrode, and blocking transport of anions (Cl^-). Application of an anion-exchange material on the anodes did not have a

measurable influence on desalination performance compared to system W-0, suggesting that the membrane was not properly formed, and that leaks may have been present. Thus, we do not present experimental results of the system with two ion-exchange membranes (W-2). In the experiments, a set of $N=7$ pairs of rods (“wires”) were placed close together, by clamping their ends into a plastic holder. The closest-approach distance between cathode and anode rods was kept the same along the length of the rods by inserting thin strips of flexible silicon material of about 450 μm thickness at 10 cm intervals between the anodes and cathodes. At the top of the holder, the cathode wires were squeezed against a copper strip, and likewise, but separately, were the anode wires squeezed against another copper strip. Electrical wires running from those copper strips were connected to a potentiostat that served as an external power source (Autolab PGSTAT 30, Metrohm Autolab B.V., Utrecht, The Netherlands). At the start of the experiment, the whole system consisting of the N wire pairs was placed inside the freshwater compartment of a total volume of $V=50$ mL. Upon applying a cell voltage, V_{cell} , desalination starts, and so the freshwater concentration decreases. After some time, wires were lifted from this compartment and inserted into the brine compartment, of the same total volume. There, the adsorbed salt is now released upon short-circuiting the cell ($V_{\text{cell}}=0$ V). The wire pairs are lifted from the brine compartment and re-inserted in the freshwater and a new cycle starts. The freshwater conductivity change is measured after the wire pairs are removed, and is recalculated back to concentration. Experiments based on this procedure leading to ongoing desalination are shown in Fig. 4. In the experiments presented in Fig. 3, however, the water (both containers) is replaced each time by fresh (20 mM salt) solutions, to evaluate reproducibility of the desalination performance of the wire pairs.

To describe performance of this system, a simple equilibrium model is set up based on theory of the formation of electrostatic double layers (EDLs) formed inside the pores of the porous carbon electrode. This model can be extended in a later stage to describe time-dependent salt transport and storage in porous electrodes.^{22,27-29} Here we limit ourselves to describing equilibrium salt adsorption in a pair of anode/cathode wires for the case that both wires are coated with ion exchange membranes (system W-2). This model can be modified to describe systems W-0 and W-1. Note that the same set of equations is valid for both the freshwater and brine compartments.

In the theory we assume that the EDLs inside the micropores of the carbon particles that form the electrode are strongly overlapping, which allows us to use a Donnan model in which we only have to consider the Donnan potential, $\Delta\phi_d$, counted from the macropores to the micropores. This classical Donnan approach is extended in two ways. Firstly, we consider an atomically thin dielectric layer (Stern layer) located in between the carbon material itself and the ions present in the electrolyte in the micropores.^{7,15,30,31} Secondly, we include a chemical attraction energy μ_{att} accompanying ion entry into the micropores, in agreement with the fact that also uncharged carbon materials adsorb some salt.³² In the Donnan approach for microporous carbons,^{15,31,33-35} the micropore ion concentration is related to that in the macropores according to

$$c_{j,\text{mi}} = c_{j,\text{mA}} \cdot \exp\left(-z_j \cdot \Delta\phi_d + \mu_{\text{att}}\right) \quad (1)$$

where $z_j=+1$ for the cation, and $z_j=-1$ for the anion.

The difference between $c_{\text{cation,mi}}$ and $c_{\text{anion,mi}}$ is the volumetric charge concentration $c_{\text{charge,mi}}=c_{\text{cation,mi}}-c_{\text{anion,mi}}$ in the micropores. The charge concentration relates to the Stern layer potential drop according to

$$c_{\text{charge,mi}} \cdot F = -V_T \cdot \Delta\phi_{\text{St}} \cdot C_{\text{St,vol}} \quad (2)$$

where F is Faraday's constant, and $C_{\text{St,vol}}$ a volumetric Stern layer capacity. As described in refs. [33,35], for the Stern layer capacity the empirical expression $C_{\text{St,vol}}=C_{\text{St,vol,0}}+\alpha \cdot c_{\text{charge,mi}}^2$ is used, to reflect that at high charge the capacity goes up, e.g. due to electrostatic compression,^{30,36,37} resulting in the ions approaching the carbon surface more closely. In the macropores the anions and cations have the same concentration, i.e., the macropores are charge neutral.

These macropores are in direct contact with the membrane in front of the electrode. In the model we assume that the membranes are perfectly selective for the counterions, i.e., the ions that possess a sign opposite to that of the membrane charge and opposite to the electronic charge in the electrode, these ions are allowed complete passage, while the membrane is completely blocking transport for the ions of equal charge sign, the co-ions. This effectively means that co-ions are locked in behind the membrane inside the electrode compartment. This leads to a simple co-ion balance in the electrode, namely the effective co-ion concentration, $c_{\text{co-ions,eff}}=v_{\text{mA}}c_{\text{mA}}+v_{\text{mi}}c_{\text{mi,co-ion}}$, is constant throughout the process, where v_{mA} and v_{mi} are macro- and micropore volumes of the electrode.

On the system level, we assume that the two electrodes are symmetric, which implies that the applied cell voltage between the anode and cathode wire, V_{cell} , is equally distributed over each electrode.³³ The cell voltage for the whole CDI stack is therefore given by

$$V_{\text{cell}}/(2V_T) = (\Delta\phi_{\text{d}} + \Delta\phi_{\text{St}} + \Delta\phi_{\text{mem}})_{\text{single electrode}} \quad (3)$$

where V_T is the thermal voltage, $RT/F \sim 25.7$ mV, and where $\Delta\phi_{\text{mem}}$ is the equilibrium membrane potential, which develops across the membrane because of the salt concentration difference, which for perfectly permselective membranes is given by

$$\Delta\phi_{\text{mem}} = \ln(c_{\text{out}} / c_{\text{mA}}) \quad (4)$$

where c_{out} is the salt concentration in the water outside the wires.

To calculate the salt concentration in the container at the end of each dipping step, we must analyze how many ions are present in 1. the micropores (micropore volume $v_{\text{mi}}= 0.045$ mL per rod, times $c_{\text{cation,mi}}+c_{\text{anion,mi}}$), 2. in the macropores ($v_{\text{mA}}=0.15$ mL per rod, times $2 \cdot c_{\text{mA}}$), 3. in the "transfer volume," and 4. in the container. The transfer volume, v_{tra} , estimated at 0.25 mL per single electrode rod, is solution adhering to the outside of the wires. This volume is inadvertently transferred every time the wires are moved from the freshwater to the brine, and back. This transfer volume is a limiting factor for wire-based desalination, since it determines how many salt molecules are transferred back from brine to freshwater, which there mix again with the freshwater. One can imagine that hardly any desalination takes place if the salt adsorption capacity of the wires is smaller than, or equal to, the amount of salt in this transfer volume. Parameter settings in the theory are: $\mu_{\text{att}}=2.0$ kT, $C_{\text{St,vol,0}}=105$ MF/m³ and $\alpha=19.2$ F·m³/mol².

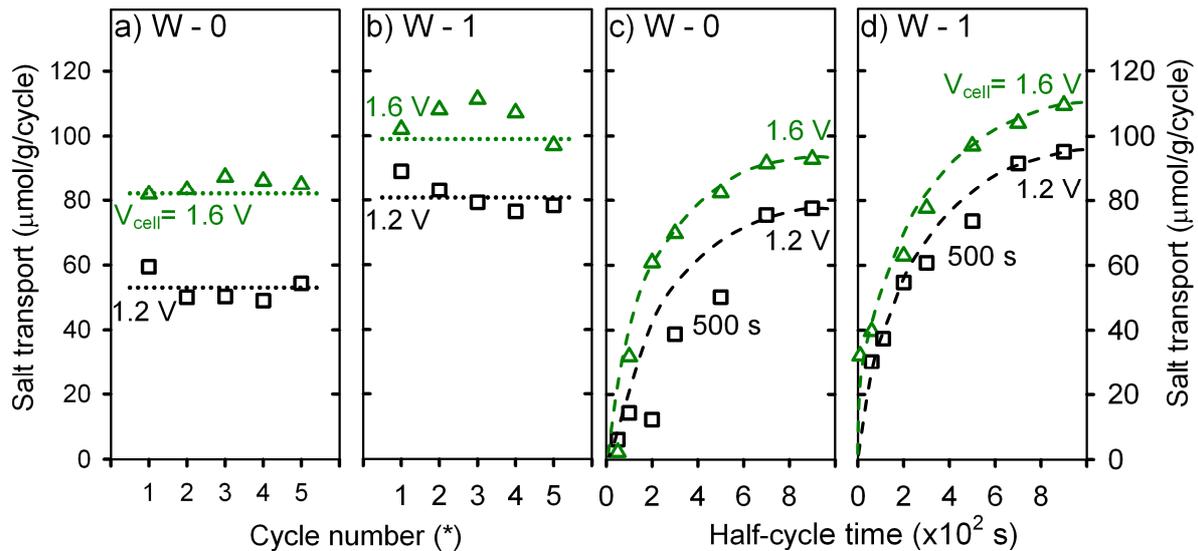


Figure 3: Repeatability of initial cycle salt transport capacity for 20 mM NaCl solutions, for two values of the cell voltage and for systems *W-1* and *W-0*, i.e., either with (*W-1*) or without (*W-0*) cation exchange membranes coated on the cathode electrodes. Data are given for the transport of salt per cycle, per mass of both electrodes combined. a,b). Salt transfer for half-cycle-time HCT=500 s and five repeat experiments (symbols: data; dashed lines: theory). c,d). Average salt transfer per cycle as function of HCT (lines are guide to the eye).

Results of our experimental program are presented in Figs. 3 and 4, and are compared with theoretical equilibrium modeling in Figs. 3a,b and 4. Fig. 5 presents a theoretical forecast when functioning membranes can be coated on both the anodes and cathodes (system *W-2*) and when these membranes can be made perfectly selective for counterions only. Fig. 3a,b show results of experiments where we test robustness of the wire-concept, by transferring salt from one beaker at 20 mM to another at 20 mM, multiple times. Fig. 3a shows results of system *W-0* where the electrodes do not have a membrane coating, while Fig. 3b reports results for system *W-1* where on the cathodes a cation exchange membrane is coated. Results in Fig. 3a,b are based on a procedure where after each cycle the two beakers are brought back to the initial salt concentration. Fig. 3a,b clearly shows that over 5 cycles we find a basically unchanging adsorption capacity. As Fig. 3a shows, the higher the cell voltage, the higher the adsorption capacity, and the same for Fig. 3b. Comparison of these two figures shows that when a membrane is successfully coated on the electrode, the desalination capacity increases. Dashed lines in Fig. 3a,b show fitted calculation results for the salt transport capacity per gram of all electrodes combined.

Fig. 3c,d show similar results, again of “first desalination cycles” only, but now as function of the dipping time to adsorb and to release salt, again both for system *W-0* and *W-1*. As can be inferred, the longer the dipping time, the more salt is adsorbed and released, and again we find that system *W-1* performs better than system *W-0*. Note that the dashed lines are solely to guide the eye. As Fig. 3c,d show, the cycle time of 500 s used for the experiments of Fig. 3a,b and Fig. 4 is not yet enough to reach the maximum transport capacity per cycle, though to optimize the desalination rate on a per time-basis, a half-cycle time of 500 s is actually beyond the optimal point.

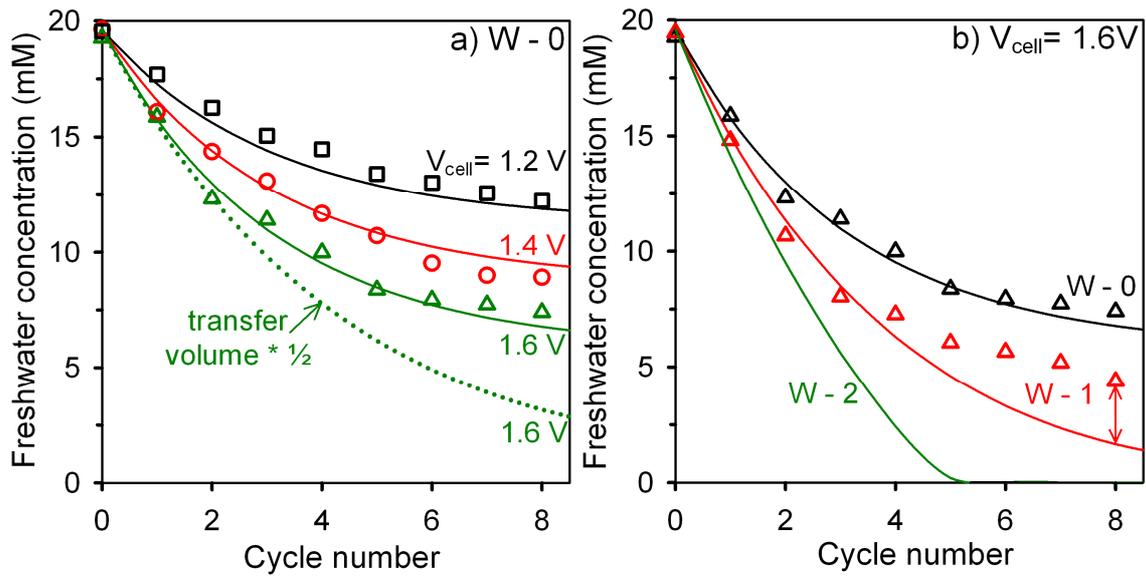


Figure 4: Ongoing desalination with wires. Symbols are data, lines are theory (HCT=500 s). Decrease of freshwater salinity (a). as function of cell voltage, for system W-0. Dashed line is prediction for optimized system with 50% reduced “transfer volume.” (b). Comparison of system W-0 and W-1 ($V_{cell}=1.6 V$). Shown (h) is discrepancy between model and data, suggesting the effect of membrane imperfections. Furthermore shown as dashed line is prediction for system performance in case both electrodes are coated with ideally selective membranes (system W-2).

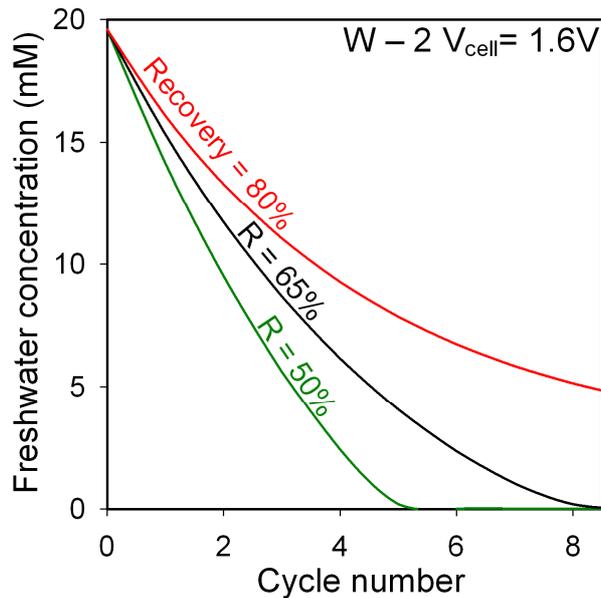


Figure 5: Theoretical prediction of achievable desalination degree for system W-2 (membranes on all electrode wires) as function of water recovery. For instance, a recovery of 80% implies that for each 100 litre of feedwater, 80 litre of freshwater is produced.

Fig. 4 shows results of desalination cycles where the freshwater becomes increasingly dilute, and the brine stream becomes increasingly concentrated. In Fig. 4 we plot the salt concentration in the freshwater container as function of the cycle number. Fig. 4a shows results for system W-0 (no membrane) at various voltages, and as expected we observe more desalination at a higher cell voltage. At $V_{cell}=1.6 V$ we find after 8 cycles that the initial concentration is reduced to about $1/3^{rd}$ its initial level, which implies that we have gone from brackish water (20 mM) to potable water (<10 mM).

As Fig. 4a shows, each data set slowly levels off with increasing cycle number, which we ascribe to the negative effect of the “transfer volume”, being water adhering on the outside of the electrode pairs, “travelling back and forth” between the containers. When water is transferred back from the brine to the freshwater container, some salt is transferred back, in the end limiting the desalination degree. A theoretical calculation in which this transfer volume is reduced by 50% to only 0.07 mL per electrode, predicts that after 8 cycles, the final salt concentration in the freshwater is about a factor of 2 lower (compare dashed green line with solid green line).

Fig. 4b shows experimental and theoretical results at $V_{\text{cell}}=1.6$ V for systems W-0, W-1 and W-2. As explained above, we were not yet able to coat a functioning anion-exchange membrane on the anode rods, and thus for system W-2 we only present a theoretical prediction. Fig. 4b shows that system W-1 functions better than system W-0, and we predict that system W-2 will do even better, leading to quite complete desalination after only 5 cycles. To have such performance, it is required that membranes can be made very selective to counterions only, blocking transport of coions completely. Our model making this assumption of ideal permselectivity deviates from the actual data after 4 cycles for system W-1 (see vertical arrow in Fig. 4b for deviation between model and data) which we ascribe to the non-perfect permselectivity of the membrane.

Finally, Fig. 5 shows calculation results for the most optimal system W-2, and shows the effect of water recovery on the freshwater concentration. Data and calculations in Fig. 4 were based on a recovery of 50%, implying that for each litre of freshwater produced one litre of brine is simultaneously produced as well. Higher values for the water recovery (the percentage of feed water converted into freshwater) are more advantageous. Calculation results show that using this system even at a very high water recovery of 80%, desalination by a factor of 4 is still possible after 8 cycles. Of course, instead of cycling one set of wire pairs multiple times, in practice we can also use many more wire pairs in parallel to accelerate the desalination process.

In conclusion, we have shown experimentally how electrode-coated wires, or rods, can desalinate brackish water in a cyclic, capacitive process using moderate cell voltages of for instance $V_{\text{cell}}=1.6$ V. Such small values of a DC voltage can be produced directly, e.g. using small solar panels. Ion-exchange membranes coated on the electrodes increase desalination performance. We predict that when membranes can be applied (both cationic and anionic membranes) which both have a high selectivity toward their respective counterion (thus perfectly blocking for the co-ion), then very high desalination degrees are possible, also for water recoveries above 50%. Water desalination with wires has advantages over traditional (membrane) capacitive deionization as freshwater is produced as a continuous stream instead of being produced intermittently, which may lead to inadvertent mixing of produced freshwater with untreated water. Wires can be placed close together without requiring a spacer layer filling the whole gap between the electrodes, thus reducing pressure drops and fouling risk.

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