DOI: 10.1002/celc.201300236



Electrochemical Desalination for a Sustainable Water Future

Kyle N. Knust,^[a] Dzmitry Hlushkou,^[b] Ulrich Tallarek,^{*[b]} and Richard M. Crooks^{*[a]}

We present an introduction to the broad field of desalination by providing a brief review of modern thermal, membrane, and electrochemical technologies. However, the main focus of this article is to introduce a fundamentally new and potentially powerful electrochemical approach to desalination: electrochemically mediated desalination (EMD). EMD is a membraneless desalination method that uses a simple power supply to oxidize a small fraction of the chloride ions present in seawater. This results in the generation of a local electric field gradient, which consequently separates ions to produce partially desalted water.

1. Global Water Challenges

Fresh water is required to sustain life. However, the world is facing a global challenge to reliably supply its population with safe water due to shortages stemming from population growth,^[1] climate change,^[2] contamination of available fresh water supplies,^[3] and public policy.^[4] Presently, the United Nations estimates that one third of the world's population (≈ 2.4 billion people) is living in water-stressed regions,^[5] meaning the annual water supply is < 1700 m³ per person.^[6] Even more alarming, this number is expected to approach two thirds of the world's population by 2025. Water shortages are not just limited to those living in arid or developing regions; the effects are now being acutely felt by those living in fresh water-rich environments.^[4b]

Increasing the availability of fresh water is a complex problem that does not have one simple solution. Consequently, technological developments providing a synergy of solutions will likely be required to address the world's water challenges. The first step toward ensuring water for all is the efficient use and conservation of currently available fresh water supplies. Encouragingly, there are examples in the developed world of per-capita water use decreasing due to more efficient agricultural, industrial, and personal practices.^[7] Nevertheless, similar to petroleum reserves, continued economic development of populous countries such as China and India will exert new stresses on world-wide water resources.^[8]

The available amount of water on Earth is relatively constant due to the hydrological cycle.^[9] However, supplies vary with time and location, therefore making localized water shortages

D. D. Hushkor, Prof. O. Tallarek Department of Chemistry, Philipps-Universität Marburg Hans-Meerwein-Strasse, 35032 Marburg (Germany) E-mail: tallarek@staff.uni-marburg.de

Table 1. Global water distribution. Adapted from Ref. [10].		
Source	Volume [×10 ¹⁵ m ³]	Percentage
oceans	1338.0	96.5
glaciers/permanent snow	24.1	1.74
saline groundwater	12.9	0.94
fresh groundwater	10.5	0.76
ground ice/permafrost	0.3	0.022
freshwater lakes	0.091	0.007
saline lakes	0.085	0.006
rivers/swamps/other	0.015	0.001
atmosphere	0.013	0.001

commonplace. Table 1 shows that only about 2.5% of water available on Earth is fresh water (<0.05% salts by weight).^[10] Of this amount, more than half is locked in glaciers and permanent ice, while remaining supplies are increasingly becoming contaminated with difficult-to-remove impurities.^[11] Importantly, about 97.5% of the world's water supply is contained in easily accessible saline reservoirs, with around 1.0% being brackish groundwater (0.05–3.0% salts) and the remaining 96.5% being seawater (3.0–5.0% salts). This suggests that the vast amounts of saline water could provide a nearly unlimited fresh water supply if coupled to an energy-efficient desalination technology.

Here, we present many of the underlying concepts guiding the development of desalination technologies, while highlighting a new electrochemical approach, electrochemically mediated desalination (EMD), that our groups are currently developing. Although not comprehensive, this article aims to provide an introduction to the broad field of desalination, including modern thermal, membrane, and electrochemical technologies. We are particularly enthusiastic about the opportunities available to electrochemists and hope that this article will inspire new electrochemical desalination technologies. Discussions of the environmental impacts of desalination,^[12] along with many of the other novel desalination strategies being developed, in-

[[]a] K. N. Knust, Prof. R. M. Crooks Department of Chemistry and the Center for Nano and Molecular Science and Technology, The University of Texas at Austin 105 E. 24th St., Stop A5300, Austin, TX 78712 (USA) E-mail: crooks@cm.utexas.edu
[b] Dr. D. Hlushkou, Prof. U. Tallarek

cluding forward osmosis,^[13] membrane distillation,^[14] microbial desalination,^[15] and freeze desalination,^[16] are not addressed in this article, but are discussed in the aforecited publications.

2. Desalination and Energy

Beyond sustaining life, water pervades many other facets of human life: agriculture, industry, and personal wellness; however, no sector is more interdependent with water than energy.^[17] With the exception of some renewable forms of energy, including solar and wind, most energy sources require water for production. For example, hydraulic fracturing,^[18] often known as fracking, a relatively new technology for extracting hydrocarbons, not only requires vast amounts of desalted water, but at the same time, reports suggest waste effluents contaminate existing drinking water reservoirs.^[19] Likewise, the production of clean, fresh water, whether by desalination or by other means, is an energy-intensive process. For example, each of the five main components of desalination, intake, pre-treatment, separation, post-treatment, and concentrate discharge, has an associated energy requirement. Furthermore, the transport and distribution of desalted water requires energy.

The minimum energy required to drive the separation of salt and water during the desalination process is dictated by the second law of thermodynamics.^[20] Importantly, this minimum energy requirement is independent of the process or pathway employed for desalination. The theoretical minimum energy is dependent upon the feed water salinity, amount of salt rejection, percent recovery of desalted water, and temperature. Percent recovery is defined as the percentage of desalted water produced relative to the quantity of feed water.

Figure 1 is a plot of the theoretical minimum energy required to fully desalinate water (containing the indicated percentages of NaCl) versus the percentage of fresh water recovered.^[20] The average seawater on Earth contains 3.5% (35 g L⁻¹) salts.^[21] The theoretical minimum energy required to produce



Figure 1. Theoretical minimum energy required to fully desalinate water (100% salt rejection) versus percent recovery for three concentrations of NaCl.

completely desalted water from a 3.5% NaCl feed at 50% recovery is about 1 kWh m⁻³ (Figure 1). Several important trends are represented in Figure 1. First, more complete salt removal increases the energy demand. Therefore, feed waters with higher salt concentrations will have higher energy requirements for a given percent recovery. Secondly, increasing the percent recovery, and hence the total salt rejection, raises the energy requirements. As 100% recovery is approached, the minimum energy required for separation increases exponentially. Consequently, most desalination techniques operate near 50% recovery. Lastly, if less than 100% salt rejection is required, the theoretical energy for desalination is lower than the values plotted in Figure 1.

Due to differences in infrastructure, feed water, and the required extent of desalination, it is difficult to directly compare desalination techniques. However, the separation process of all desalination strategies can be compared by dividing the actual operating energy efficiency by the theoretical minimum energy needed for the given separation process. Even with this figure of merit, however, there may still be considerable differences in intake, pre-treatment, post-treatment, and concentrate discharge requirements that are excluded from the fundamental efficiency calculation.

3. Thermal Desalination

The first widely used desalination technique was thermal distillation, which involves heating water until it vaporizes, thus separating the water vapor from salts left behind in the liquid phase. The vapor is then condensed and collected.^[22] This basic concept, which became commercially available in the 1950s, is now employed in modern-day multiple-effect distillation, multistage flash distillation, and mechanical vapor compression facilities.^[23] The minimum energy required to drive thermal desalination is directly related to the heat of vaporization of water, which is substantially higher than that of other desalination techniques. Consequently, large-scale thermal desalination is limited to geographical regions, such as the Middle East, rich in the energy resources required to drive the process and poor in natural fresh water sources. Although the energy costs are high, approximately 13 kWh m⁻³ for seawater desalination at 45% recovery,^[24] thermal desalination accounts for roughly 40% of desalinated water production,^[25] largely because of its reliability and minimal pre-treatment requirements.^[26] For these reasons, thermal desalination has a role to play in addressing the world's water needs, but improvements in energy efficiency are required if the method is to remain competitive. For example, solar^[24,27] and waste thermal energy from industrial processes^[28] are being implemented to lower desalination costs.

4. Membrane Desalination

Especially in the developed world, there is a preference for desalination methods that are less energy-intensive than thermal desalination, leading to increased use of membrane-based approaches.^[29] Reverse osmosis (RO),^[30] first introduced at scale in

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

CHEMELECTROCHEM CONCEPTS

the 1960s, has become the dominant water purification technique in recent decades and now accounts for roughly 51% of desalinated water production.^[25] RO is induced if a pressure differential greater than the osmotic pressure of the feed water is applied across a semi-permeable membrane. The minimum energy required for RO is therefore directly related to the salt concentration of the feed water. Currently, most RO facilities employ about 100 nm-thick polyamide membranes on a polysulfone/fabric support. Hydrated ions are unable to penetrate through the polyamide matrix, while water molecules pass via a solution-diffusion mechanism.^[31] This means water molecules first partition into the polyamide membrane, and then diffuse through due to the concentration gradient resulting from the pressure differential across the membrane.

With advances in membrane technology^[32] and energy recovery devices,^[33] RO can operate at roughly 2.0 kWh m⁻³ for seawater desalination at 50% recovery, which is about twice the theoretical minimum efficiency for 100% desalination. This is the best value for any commercialized method.^[20b] However, RO is now considered a mature technology, with future membrane materials resulting in only incrementally improved energy efficiencies. This is because of a trade-off between membrane permeability and salt rejection, meaning further increases in permeability will likely result in less salt rejection.^[34] Consequently, enhancements in energy efficiency are unlikely to be achieved through the development of more permeable membranes, such as those based on carbon nanotubes^[35] and aquaporins.^[36] Even so, RO is the benchmark for comparison of all other desalination technologies.

Importantly, RO requires intensive pre-treatment of the feed seawater due to membrane fragility. These energy requirements are generally excluded from comparison with theoretical minimums. For example, costly chlorination is required to kill microorganisms that cause biofilm growth and membrane fouling, which results in decreased permeability and thus higher driving pressures.^[29] Unfortunately, the chlorine added for disinfection degrades the polyamide membrane, so a dechlorination step is also required prior to separation. If the product water is intended for consumption, the desalted water must be chlorinated again after desalination to ensure disinfection. Moreover, many of the pre-treatment steps required for thermal desalination, such as filtration and the addition of antiscaling chemicals, are also required for RO to prevent membrane fouling. Accordingly, future cost decreases for RO will largely result from reductions in pre-treatment, post-treatment, and infrastructure, rather than from increased efficiency in the actual separation of salt from water. One way of achieving these goals is through the development of chlorine-resistant membranes.^[37]

Another membrane-based technique that relies on electrochemistry is electrodialysis (ED).^[38] Scheme 1 shows that ED utilizes a series of perm-selective membranes (typically hundreds) placed between an electrode pair. When a potential bias is applied, cations and anions in the feed stream migrate through a cation- or anion-selective membrane, respectively, thus leaving behind desalted water. ED is most often employed for the desalination of brackish and other lower salinity waters, be-



Scheme 1.

cause the electrical current required for ED is proportional to the amount of salt removed. Consequently, the energy requirements for ED scale directly with salt rejection. Although not practical for seawater desalination, ED is competitive and often advantageous for brackish water desalination when compared to RO. Currently, ED accounts for approximately 4% of desalinated water production.^[25] ED requires only a moderate amount of pre-treatment and employs chlorine-resistant membranes. Moreover, membrane fouling can be prevented by reversing the electrode polarities in a process called electrodialysis reversal (EDR). As a result of these benefits, ED/EDR has an important role to play in brackish water desalination.

5. Membraneless Electrochemical Desalination

The most developed, yet still largely considered as an emerging electrochemical desalination strategy, capacitive deionization (CDI), sometimes referred to as capacitive desalination, was first introduced in the 1960s.^[39] The technique separates ions from water by using two highly porous electrodes, such as carbon aerogels, to capacitively adsorb ions into the electrical double layer, thereby removing them from solution (Scheme 2). Once the ionic capacity of the electrodes becomes saturated, the polarity is reversed to release the ions, and the cycle is repeated.^[40] Because CDI is intrinsically a batch process, relying on polarity reversal, it has proven difficult to implement in a continuous process.^[41] Similar to ED, the electrical current flowing during CDI is dependent on the amount of salt removal. Therefore, CDI is also more suitable for desalination of brackish water than seawater. However, because CDI is capacitive, the sequestered ions represent a source of energy. If this



Scheme 2.

energy could be effectively recovered, reports suggest more concentrated salt solutions, including seawater, could be competitively desalted.^[41] However, engineering a truly continuous and energy efficient CDI separation for seawater remains a challenge.

Continuous separations are possible using another electrochemical desalination technique based on a phenomenon called ion concentration polarization (ICP).^[42] ICP generates an ion depletion zone (region of high solution resistivity) when a potential bias applied across two fluidic channels causes a large proportion of ionic current to be carried by either anions or cations through a perm-selective material (e.g. Nafion) or a nanochannel that exhibits electrical double layer overlap. The resulting ion depletion zone creates a local conductivity gradient and electric field where ions can be redirected by a combination of migration and convection. This approach was adapted to seawater desalination for a small-scale system,^[43] but it was later found that the energy efficiency of the system was significantly lower than originally reported.^[44] Even so, efforts are being made by groups to increase the scale of this technology.[45]

Recently, our groups have shown that faradaic reactions can be employed to generate ion depletion zones and electric field gradients for the enrichment,^[46] separation,^[47] depletion,^[48] and controlled delivery^[49] of ions. Each of these applications is based on the principles of electrokinetic equilibrium and the difference between electromigration and convective counterflows.^[50] The key to these techniques is the generation of a localized electric field gradient. Recently, we discovered these same principles can be used to desalt seawater by a technique called electrochemically mediated desalination (EMD).^[51] For seawater desalination, this approach is more energy efficient than CDI because only a small fraction of the total number of ions present draw current.

The basic design of our current EMD apparatus is illustrated schematically in Figure 2a. It consists of a Y-shaped poly(dimethylsiloxane) (PDMS)/glass hybrid channel network outfitted with a 100 μ m-wide Pt electrode near the Y-intersection that extends 50 μ m toward the channel center. The channel height is 22 μ m, with widths of 100 and 50 μ m for the inlet and outlets, respectively. An optical micrograph of the region near the electrode is shown in Figure 2b, and a photograph of the entire chip is provided in Figure 2c.

As shown in Figure 2a, a voltage is applied between the microfabricated Pt anode and wires present in the grounded reservoirs at the microchannel terminals. This voltage is adjusted to a value that results in the oxidation of Cl^- [Eq. (1)] present in seawater:

$$2 \operatorname{CI}^{-} - 2 \operatorname{e}^{-} \leftrightarrow \operatorname{CI}_{2} \tag{1}$$

This reaction reduces the number of ionic charge carriers (Cl⁻) present in the vicinity of the anode, thus giving rise to the depletion zone shown in red (Figure 2a). Once the depletion zone forms, a disproportionate percentage of the applied voltage is dropped in this region and results in a locally elevat-



Figure 2. a) Schematic representation of the two-electrode desalination device. The dashed black line represents the extension of the anode into the channel. b) Optical micrograph of a two-electrode PDMS/glass desalination device with an embedded Pt electrode (100 µm wide) extending 50 µm towards the channel center. c) Photograph of a two-electrode PDMS/glass desalination device with an embedded Pt electrode. d) Schematic representation of ionic redirection near the Y-intersection of a desalination device, owing to a local depletion zone and electric field strength.

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

ed electric field. Note that in our first report of EMD,^[51] a bipolar electrode^[52] was used to generate this field, but here we focus on the more general and simplified two-electrode configuration illustrated in Figure 2a.

The net velocity vector of ions present within the channel is determined by a summation of convection and electromigration (Figure 2 d). There is no net electroosmotic flow because it would be directed toward both the inlet and outlets from the channel center, but the absence of a fluid reservoir at the channel center precludes fluid flow (Figure 2 c). Convection, in the form of pressure-driven flow (PDF), is created by using a solution height differential between the inlet and outlet reservoirs (Figure 2 c). This results in a parabolic laminar flow profile that is uniform along the length of the channel. The local fluid velocity due to laminar flow is designated as $u_{\rm i}$, and this value varies across the width and height of the channel. The electrophoretic velocity ($u_{\rm ep}$) of ions is governed by Equation (2):

$$u_{\rm ep} = \mu_{\rm ep} V_{\rm I} \tag{2}$$

where μ_{ep} is the electrophoretic mobility and V_1 is the local electric field strength. Because the electric field strength is highest in the depletion region, u_{ep} will be greatest near the Y-intersection.

In all regions of the channel in Figure 2d, except near the depletion zone, ionic transport is dominated by PDF. Accordingly, the net movement of ions is toward the outlets. However, as ions approach the depletion zone and elevated V_{ν} they experience an increasing $u_{\rm ep}$. When the condition $-u_{\rm ep} > u_{\rm l}$ is satisfied along the elevated $V_{\rm h}$ the coupled transport between migration and convection causes cations to migrate away from the depletion zone and toward the brine stream, consequently producing desalted water. This situation is illustrated schematically by the vectors shown in Figure 2d. To maintain electroneutrality within the microchannel, anions are also redirected into the brine stream. An approximation of the necessary $V_{\rm l}$ for desalination to occur can be calculated if the $u_{\rm l}$ and $\mu_{\rm ep}$ for a given ion are known.

Figure 3 presents fluorescence micrographs that confirm ionic redirection at the Y-intersection with a total PDF of approximately 0.1 μ Lmin⁻¹. For the experiment shown in Figure 3 a, the voltage between the anode and reservoirs was set to 1.4 V, and $[Ru(bpy)_3]^{2+}$ (bpy=2,2'-bipyridine) was added to seawater collected from Port Aransas, Texas (USA). Sand and debris were removed from the seawater sample by sedimentation. $[Ru(bpy)_3]^{2+}$ is used as a traceable proxy for ions present in seawater. The key point is that the fluorescence intensity due to the presence of $[Ru(bpy)_3]^{2+}$, is greatly diminished in the desalted stream compared to both the brine and feed streams. Indeed, we have previously shown that roughly 25% salt rejection can be achieved using EMD conditions similar to those presented here.^[51] Importantly, if the voltage between the anode and reservoirs is set to zero, the fluorescence intensity is identical in all regions of the channel network (Figure 3 b). Likewise, to demonstrate the importance of Cl⁻ for EMD, if the seawater solution is replaced with a Na₂SO₄ (no Cl⁻) solution of the same salt concentration, results identical to



Figure 3. Fluorescence micrographs showing the location of 20.0 μ M $[Ru(bpy)_3]^{2+}$ tracer, representative of the ions present in seawater. a) The tracer is redirected into the brine stream with a 1.4 V potential bias. b) Same as (a) except with no potential bias, which results in the tracer flowing equally into both outlets. In all cases, the two-electrode scheme depicted in Figure 2 was used with a total PDF of approximately 0.1 μ Lmin⁻¹. The channel walls are highlighted in red.

those shown in Figure 3b are obtained, even in the presence of an applied voltage sufficient to desalinate a Cl⁻-containing solution.

We performed numerical simulations to better understand and optimize the EMD process (Figure 4). In this case, we used a 0.55 \pm NaCl solution (identical to the average total concentration of Cl⁻ in seawater) with the assumption of Cl⁻ oxidation at a 100×50 μ m embedded electrode. The three-dimensional geometry of the simulated device was exactly the same as that used for the experiments. The numerical model is based on equations describing the coupled three-dimensional hydrodynamic, mass/charge transport, and electrostatic problems. The local flow velocity field (\mathbf{u}) can be described by the Navier– Stokes equation [Eq. (3)]:

$$\rho\left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u}\nabla\mathbf{u}\right) + \nabla p - \eta\nabla^2 \mathbf{u} = 0$$
(3)

Here, $\rho = 1.023 \times 10^3 \text{ kg m}^{-3}$ and $\eta = 0.966 \text{ mPas}$ are the mass density and dynamic viscosity of the solution, and p is hydrostatic pressure. Spatiotemporal variations in the concentrations of Na⁺ and Cl⁻, n^+ and n^- , respectively, are governed by balance equations [Eq. (4)]:

$$\frac{\partial \boldsymbol{n}^{\pm}}{\partial t} = -\nabla \boldsymbol{j}^{\pm} = \boldsymbol{D}^{\pm} \nabla^2 \boldsymbol{n}^{\pm} \mp \frac{F \boldsymbol{D}^{\pm}}{RT} \nabla (\boldsymbol{n}^{\pm} \nabla \phi) - \nabla (\boldsymbol{n}^{\pm} \mathbf{u})$$
(4)

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 4. a) Distribution of the axial electric field in the central plane ($z = 11 \mu$ m) of the device shown in Figure 2, simulated for a 0.55 M NaCl solution with a total PDF rate of 0.1 μ L min⁻¹, a current through the electrode of 50 nA, and an electrode potential of 0.9 V. b) Corresponding simulated salinity distribution normalized to the inlet value (0.55 m) showing a 20% decrease in salt concentration in the desalted stream. The channel height is 22 μ m, with widths of 100 and 50 μ m for the inlet and outlets, respectively.

where j^+ and j^- are the fluxes of Na⁺ and Cl⁻, respectively, D^+ = 1.334×10⁻⁹ m²s⁻¹ and D^- =2.033×10⁻⁹ m²s⁻¹ are the corresponding diffusion coefficients, ϕ is the local electric potential, and *F*, *R*, and *T*=293.16 K represent the Faraday constant, molar gas constant, and temperature, respectively. The local concentrations of the ionic species and the local electric potential are related by the Poisson equation [Eq. (5)]:

$$\varepsilon \nabla^2 \phi = -q_{\rm e} (n^+ - n^-) \tag{5}$$

where q_e is the elementary charge and $\varepsilon = 6.9 \times 10^{-10} \,\mathrm{Fm^{-1}}$ is the solution permittivity. A reduction in Cl⁻ concentration due to the faradaic reaction at the electrode [Eq. (1)] was realized by the imposition of a boundary condition [Eq. (6)] for Equation (4) at the electrode surface:

$$j^{-} = \frac{l}{Sq_{\rm e}} \tag{6}$$

where j^- is the flux of Cl⁻ normal to the electrode surface, *I* is the current through the electrode, and $S = 50 \times 100 \,\mu\text{m}$ is the area of the electrode surface immersed in the solution (Figure 2 b). As the region close to the electrode surface is characterized by steep gradients of the electric field strength and ionic species concentrations, a non-uniform cubic grid with adaptable grid step was employed to resolve Equations (4) and (5) by finite-difference schemes.

The flow velocity field was simulated by using a lattice– Boltzmann method; a kinetic approach based on the solution of the Boltzmann equation discretized in the phase space. Details regarding the numerical methods can be found in a previous publication.^[51] The simulation of a 10 s operation time of the device required roughly 24 h at 1024 processor cores of an IBM BlueGene/Q supercomputer (Jülich Supercomputering Centre, Jülich, Germany).

In Figure 4a, the simulated steady-state distribution of the local electric field strength in the central plane of the device

Although Cl⁻ oxidation is known to be the dominant anodic process occurring in seawater under the conditions used in our experiments, water oxidation also occurs according to Equation (7).^[53]

$$2 \operatorname{H}_2 \operatorname{O} - 4 \operatorname{e}^- \leftrightarrow \operatorname{O}_2 + 4 \operatorname{H}^+ \tag{7}$$

In principle, electrogenerated H⁺ arising from water oxidation may be neutralized by buffer species, such as bicarbonate and borate, present in seawater thus further contributing to ion depletion and the elevated value of $V_{\rm I}$. However, measurements of the axial electric field strength in solutions of NaCl and seawater indicate the contribution of these buffering species is insignificant compared to Cl⁻ oxidation.^[51] Therefore, fortuitously, the naturally abundant Cl⁻ concentration (0.55 m) in seawater is critical to forming the depletion zone for EMD.^[21]

Given the preceding discussion, the minimum energy required to drive EMD is only dependent on the energy required to drive a sufficient amount of Cl⁻ oxidation to yield an ion depletion zone and local electric field gradient. Importantly, oxi-

 $⁽z=11 \ \mu m)$ is shown. For clarity, only the region of interest close to the junction of the branched microchannel is presented. The simulation was performed for a total flow rate of 0.10 μ Lmin⁻¹, with 50 nA of current flowing through the anode, and an electrode potential of 0.90 V relative to the grounded inlet and outlet reservoirs. The simulation results confirm that Cl⁻ oxidation [Eq. (1)] at the anode leads to the formation of an ion depletion zone and corresponding increase in the local electric field strength. Following the coupled local electromigration-convection transport balance and electroneutrality, ions are preferentially diverted into the brine stream. The resulting steady-state redistribution of the local salinity, normalized by its value at the inlet (0.55 M), is shown in Figure 4b. The average reduction of salinity in the desalted stream simulated by using the above conditions is 20%, which is close to the experimental findings $[(25 \pm 5)\%]$, operating under similar conditions.^[51]

dation of only a small fraction ($\approx 0.01\%$) of the total Cl⁻ concentration is necessary to power EMD; most of the Cl⁻ is redirected into the brine stream.^[51] While only a small percentage of the Cl⁻ in seawater is oxidized, further investigations are required to determine the minimum Cl⁻ concentration necessary to drive EMD. It might, for example, be possible to use EMD for the desalination of brackish water.

EMD does require PDF, but the power required for this gravity driven flow, at least in the currently employed small-scale systems, is negligible compared to that required to drive Cl⁻ oxidation. Accordingly, the energy efficiency of EMD can be calculated from the total current flowing through the anode. EMD devices operating at steady-state currents of 20 nA across a potential bias of E=3.0 V yield a power consumption (P=IE) of 60 nW.^[51] The average volumetric flow rate of desalted water ($F_{v,desalted}$) in these devices is approximately 0.04 µL min⁻¹; this results in an energy efficiency (efficiency = $P/F_{v,desalted}$) of 0.025 kWh m⁻³ for 25% salt rejection at 50% recovery. This value is near the theoretical minimum energy calculated by using the same parameters (≈ 0.017 kWh m⁻³).^[54]

Importantly, the only pre-treatment currently required to perform EMD is sedimentation of sand and debris present in the seawater to prevent obstruction of the channel. Because pre-treatment is minimal for this membraneless approach, considerable cost savings could be provided compared to the intensive pre-treatment requirements of RO. Also notable is that Cl⁻ oxidation [Eq. (1)] results in Cl₂ generation, which subsequently undergoes hydrolysis to produce hypochlorous acid, HOCl, a common water disinfectant.^[29] This means EMD could serve as a single-step disinfection and desalination approach, thus reducing the required post-treatment for water intended for human consumption.

6. Conclusions and Future Outlook

There is a clear need for a reliable and sustainable fresh water supply beyond those that are currently available. Although proper water management practices are crucial, these solutions alone cannot meet rising demand. With conventional water treatment costs continually rising, while desalination costs have been steadily decreasing, desalination is becoming an increasingly viable solution for meeting global water challenges.^[25] In fact, desalination is already becoming a component of many nations' water supply portfolios. Since 1960, there has been an exponential growth in desalination, which is expected to continue in the coming decades.^[23,25]

It is increasingly likely that a variety of desalination technologies will be required to supplement natural fresh water reserves. A number of novel desalination technologies are being developed to lower the overall cost of desalination by overcoming the limitations of currently available strategies. For example, RO has plateaued in terms of energy efficiency for the separation process, but reducing the intensive pre-treatment expenditures required for RO would lower the cost of desalination, thereby increasing its viability. EMD, which operates at energy efficiencies comparable to RO, but requires less pretreatment and does not require a membrane, could potentially achieve this goal.

Although EMD provides a number of benefits relative to existing desalination technologies, it faces several key challenges. Primary in this regard is the feasibility of scaling the technology to a commercially viable level. In addition, higher salt rejection rates are required for producing potable water. However, not all uses of desalinated water require the production of potable water. For example, water used in industrial cooling towers may contain substantially higher salt concentrations than that required for drinking water.^[55] EMD could also be used as a first stage for a hybrid desalination strategy incorporating RO.

Lastly, many governments, including our own (USA and Germany), do not currently have a targeted basic research program directed towards the development of new technologies for increasing fresh water supplies. A more carefully reasoned public policy in this regard could prevent disastrous consequences in the not-too-distant future. Indeed, even now, the economic and human impact of insufficient water, in terms of famine, illness, death, and war, far exceeds the cost of a modest research investment for this essential resource.^[56]

Acknowledgements

R.M.C. and K.N.K. gratefully acknowledge the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (contract no. DE-FG02-06ER15758) for supporting the basic research that led to the development of this technology. Okeanos Technologies, LLC, provided support for certain aspects of the technological implementation. The Robert A. Welch Foundation provides sustained support for our research (Grant F-0032). U.T. and D.H. thank the Deutsche Forschungsgemeinschaft (Bonn, Germany) for support of this work under grant TA 268/5-1. Finally, we thank Prof. Don Paul (UT-Austin) for enlightening discussions about desalination.

Keywords: desalination · electrochemistry · electrophoresis · numerical simulation · water

- [1] C. J. Vörösmarty, P. Green, J. Salisbury, R. B. Lammers, *Science* 2000, 289, 284–288.
- [2] V. Ramanathan, P. J. Crutzen, J. T. Kiehl, D. Rosenfeld, Science 2001, 294, 2119–2124.
- [3] R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. von Gunten, B. Wehrli, *Science* 2006, 313, 1072–1077.
- [4] a) S. L. Postel, G. C. Daily, P. R. Ehrlich, Science 1996, 271, 785-788;
 b) The World's Water: The Biennial Report on Freshwater Resources, Vol. 7 (Ed.: P. H. Gleick), Island Press, 2012.
- [5] United Nations, World Water Development Report 2, 2006.
- [6] M. Falkenmark, J. Lundqvist, C. Widstrand, Nat. Resour. Forum 1989, 13, 258–267.
- [7] J. F. Kenny, N. L. Barber, S. S. Hutson, K. S. Linsey, J. K. Lovelace, M. A. Maupin, *Estimated Use of Water in the United States in 2005*, U.S. Geological Survey, 2005.
- [8] International Energy Agency, World Energy Outlook 2013.
- [9] T. Oki, S. Kanae, Science 2006, 313, 1068–1072.
- [10] P. H. Gleick, Water in Crisis: A Guide to the World's Fresh Water Resources, University Press, Oxford, 1993.

CHEMELECTROCHEM CONCEPTS

- [11] a) J. O. Nriagu, J. M. Pacyna, *Nature* **1988**, 333, 134–139; b) J. Fick, H. Söderström, R. H. Lindberg, C. Phan, M. Tysklind, D. G. J. Larsson, *Environ. Toxicol. Chem.* **2009**, *28*, 2522–2527.
- [12] N. X. Tsiourtis, Desalination 2001, 141, 223-236.
- [13] J. R. McCutcheon, R. L. McGinnis, M. Elimelech, *Desalination* 2005, 174, 1-11.
- [14] M. Khayet, Adv. Colloid Interface Sci. 2011, 164, 56-88.
- [15] X. Cao, X. Huang, P. Liang, K. Xiao, Y. Zhou, X. Zhang, B. E. Logan, *Environ. Sci. Technol.* 2009, 43, 7148–7152.
- [16] R. Fujioka, L. P. Wang, G. Dodbiba, T. Fujita, *Desalination* 2013, 319, 33– 37.
- [17] a) C. W. King, A. S. Holman, M. E. Webber, *Nat. Geosci.* 2008, *1*, 283–286;
 b) M. Hightower, S. A. Pierce, *Nature* 2008, *452*, 285–286; c) R. Semiat, *Environ. Sci. Technol.* 2008, *42*, 8193–8201.
- [18] a) C. T. Montgomery, M. B. Smith, J. Pet. Tech. 2010, 62, 26–32; b) D. J. Miller, X. Huang, H. Li, S. Kasemset, A. Lee, D. Agnihotri, T. Hayes, D. R. Paul, B. D. Freeman, J. Membr. Sci. 2013, 437, 265–275.
- [19] S. G. Osborn, A. Vengosh, N. R. Warner, R. B. Jackson, Proc. Natl. Acad. Sci. USA 2011, 108, 8172-8176.
- [20] a) K. S. Spiegler, Y. M. El-Sayed, *Desalination* 2001, *134*, 109–128; b) M. Elimelech, W. A. Phillip, *Science* 2011, *333*, 712–717.
- [21] W. M. Haynes, CRC Handbook of Chemistry and Physics, 93rd ed., CRC Press, Boca Raton, FL, 2012.
- [22] M. Al-Sahali, H. Ettouney, Desalination 2007, 214, 227-240.
- [23] National Academy of Sciences, *Desalination: A National Perspective*, The National Academies Press, Washington, DC, 2008.
- [24] A. Cipollina, G. Micale, L. Rizzuti, Seawater Desalination: Conventional and Renewable Energy Processes, Springer, Berlin, 2009.
- [25] Sustainability Science and Engineering Vol. 2: Sustainable Water for the Future: Water Recycling versus Desalination (Ed.: I. C. Escobar, A. I. Schäfer), Elsevier, Amsterdam, 2010.
- [26] I. C. Karagiannis, P. G. Soldatos, Desalination 2008, 223, 448-456.
- [27] J. Koschikowski, M. Wieghaus, M. Rommel, Desalination 2003, 156, 295 304.
- [28] R. Schwantes, A. Cipollina, F. Gross, J. Koschikowski, D. Pfeifle, M. Rolletschek, V. Subiela, *Desalination* 2013, 323, 93–106.
- [29] G. M. Geise, H.-S. Lee, D. J. Miller, B. D. Freeman, J. E. McGrath, D. R. Paul, J. Polym. Sci. Part B 2010, 48, 1685 – 1718.
- [30] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, Desalination 2007, 216, 1–76.
- [31] a) H. K. Lonsdale, U. Merten, R. L. Riley, J. Appl. Polym. Sci. 1965, 9, 1341–1362; b) D. R. Paul, J. Membr. Sci. 2004, 241, 371–386.
- [32] K. P. Lee, T. C. Arnot, D. Mattia, J. Membr. Sci. 2011, 370, 1-22.
- [33] M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas, A. M. Mayes, *Nature* **2008**, 452, 301–310.
- [34] G. M. Geise, H. B. Park, A. C. Sagle, B. D. Freeman, J. E. McGrath, J. Membr. Sci. 2011, 369, 130–138.

- [35] H. Y. Yang, Z. J. Han, S. F. Yu, K. L. Pey, K. Ostrikov, R. Karnik, Nat. Commun. 2013, 4, 2220.
- [36] C. Y. Tang, Y. Zhao, R. Wang, C. Hélix-Nielsen, A. G. Fane, *Desalination* 2013, 308, 34–40.
- [37] a) J. Glater, S.-k. Hong, M. Elimelech, *Desalination* 1994, *95*, 325–45;
 b) H. B. Park, B. D. Freeman, Z.-B. Zhang, M. Sankir, J. E. McGrath, *Angew. Chem. Int. Ed.* 2008, *47*, 6019–6024; *Angew. Chem.* 2008, *120*, 6108–6113.
- [38] H. Strathmann, Desalination 2010, 264, 268-288.
- [39] Y. Oren, *Desalination* **2008**, *228*, 10–29.
- [40] S. Porada, R. Zhao, A. van der Wal, V. Presser, P. M. Biesheuvel, Prog. Mater. Sci. 2013, 58, 1388–1442.
- [41] M. A. Anderson, A. L. Cudero, J. Palma, Electrochim. Acta 2010, 55, 3845–3856.
- [42] T. A. Zangle, A. Mani, J. G. Santiago, Chem. Soc. Rev. 2010, 39, 1014– 1035.
- [43] S. J. Kim, S. H. Ko, K. H. Kang, J. Han, Nat. Nanotechnol. 2010, 5, 297– 301.
- [44] S. J. Kim, S. H. Ko, K. H. Kang, J. Han, Nat. Nanotechnol. 2013, 8, 609.
- [45] B. D. MacDonald, M. M. Gong, P. Zhang, D. Sinton, Lab Chip 2014, 14, 681–685.
- [46] R. Dhopeshwarkar, D. Hlushkou, M. Nguyen, U. Tallarek, R. M. Crooks, J. Am. Chem. Soc. 2008, 130, 10480-10481.
- [47] D. R. Laws, D. Hlushkou, R. K. Perdue, U. Tallarek, R. M. Crooks, Anal. Chem. 2009, 81, 8923 – 8929.
- [48] E. Sheridan, K. N. Knust, R. M. Crooks, Analyst 2011, 136, 4134-4137.
- [49] K. Scida, E. Sheridan, R. M. Crooks, Lab Chip 2013, 13, 2292-2299.
- [50] J. G. Shackman, D. Ross, Electrophoresis 2007, 28, 556-571.
- [51] K. N. Knust, D. Hlushkou, R. K. Anand, U. Tallarek, R. M. Crooks, Angew. Chem. Int. Ed. 2013, 52, 8107–8110; Angew. Chem. 2013, 125, 8265– 8268.
- [52] a) K. N. Knust, E. Sheridan, R. K. Anand, R. M. Crooks, *Lab Chip* **2012**, *12*, 4107–4114; b) S. E. Fosdick, K. N. Knust, K. Scida, R. M. Crooks, *Angew. Chem. Int. Ed.* **2013**, *52*, 10438–10456; *Angew. Chem.* **2013**, *125*, 10632–10651.
- [53] J. E. Bennett, Int. J. Hydrogen Energy 1980, 5, 401-408.
- [54] Y. Çerçi, Y. A. Çengel, B. Wood, Proc. ASME Adv. Energy Syst. Div. 1999, 39, 545-552.
- [55] D.-J. Choi, S.-J. You, J.-G. Kim, Mater. Sci. Eng. A 2002, 335, 228-235.
- [56] a) P. H. Gleick, Int. Security 1993, 18, 79–112; b) World Health Organization, Safer Water, Better Health: Costs, benefits and sustainability of interventions to protect and promote health, 2008.

Received: November 29, 2013 Published online on March 11, 2014

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim