Faster Time Response by the Use of Wire Electrodes in Capacitive Salinity Gradient Energy Systems

Odne S. Burheim,*,[†,‡,||] Fei Liu,[†,§,||] Bruno B. Sales,[†,§] Olivier Schaetzle,[†] Cees J. N. Buisman,[†,§] and Hubertus V. M. Hamelers[†]

[†]Centre of Excellence for Sustainable Water Technology, Wetsus, Agora 1, 8900 CC Leuuwarden, The Netherlands
[‡]Department of Chemistry, NTNU, N-7491 Trondheim, Norway
[§]Sub-department of Environmental Technology, Wageningen University, 6708 PB Wageningen, The Netherlands

ABSTRACT: Capacitive energy extraction based on Donnan potential (CDP) and capacitive energy extraction based on double layer expansion (CDLE) are novel electroctrochemical processes to convert the potential free energy of mixing sea and river water into electric work. This is done by the use of supercapacitor electrodes with and without ion exchange membranes. Currently, these techniques rely on improved mass transport in order to become more efficient and give higher power output. In this paper we evaluate the transport phenomena by diffusion and the electrode geometry when switching between sea and river water at open circuit potential (OCP). By changing the electrode geometry from a flat plate to a cylindrical one, experiments and analytical models in combination show that mass transport by diffusion is increased. This is demonstrated without any changes in the hydrodynamic conditions. Improving mass transport without changing the hydrodynamic conditions breaks with what has been the convention in the scientific community of salinity gradient power. Moreover, in sea water the transport phenomena appear to be controlled by diffusion, and the response time for building open circuit potential in CDP and CDLE under this condition is reduced by a factor of 2 when using wire electrodes instead of flat plate electrodes. In river water, the trend is similar though the response time is generally larger.
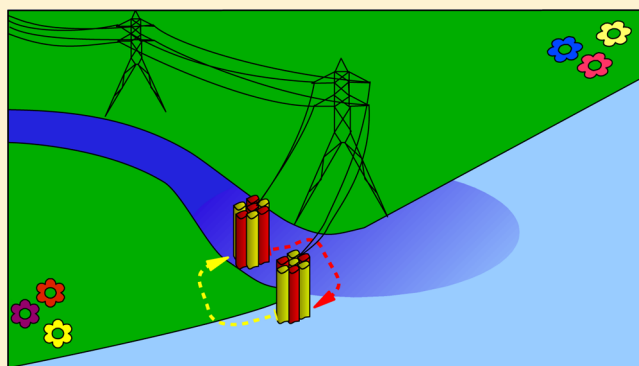
INTRODUCTION

The free energy of mixing sea and river water has a worldwide potential as a power source equal to more than 2 TW.[1,2] Considering the worldwide electricity consumption (2.3 TW in 2009[3]), one realize how beneficial this renewable electric power source potentially is to the human society. However, this requires river water mixed with infinite amounts of sea water. When mixing equal volumes of sea and river water, the worldwide potential is reduced to 1.7 TW,[2] which is still quite substantial. Comparing salinity gradient power to other ocean power sources, such as wind, ocean currents, wave, tidal streams, and thermal gradients, it is supreme partly in that it has the second largest power potential, but foremost because it is focused at river deltas (rather than being distributed over the ocean areas across the world).[4]

The history of salinity gradient energy conversion started when Pattle first reported the hydroelectric pile in 1954, where 47 pairs of ion exchange membranes were put together to convert free energy of mixing (sea/river water) into electric work.[5] Later this technology has been much more investigated, and today it goes under the name of reverse electrodialysis (RED).[6−13] Reverse electrodialysis is an electrochemical concentration cell where ion exchange membranes are used to allow aqueous solutions of different concentrations to drive

an electrochemical reaction at the end of a pile of these membranes. Another alternative for salinity gradient energy extraction is a technique known as pressure retarded osmosis (PRO).[14−18] This conversion process combines semipermeable membranes and a turbine. Thus, it converts the free energy of mixing into electric energy via an extra step of mechanical energy.

A third branch of technologies are those discussed in this paper. One is salinity gradient energy extraction by the means of supercapacitors and membranes and is called capacitive energy extraction based on the Donnan potential (CDP). It consists of alternating electrodes between sea and river water. Simultaneously, the free energy of mixing is converted into electric work.[19] Another technology that does not use membranes is the capacitive energy extraction based on double layer expansion (CDLE).[20−22] In this technology, the system is left at open circuit when replacing the water solutions. The electrodes are charged in sea water and return more work when discharged in river water. These two technologies are described in greater detail elsewhere,[23] though it is during the OCP steps

that diffusion limitation improvements are best displayed by the proposed wire design. Externally charging the CDP is a novel operation mode that can be seen as a cross-breed of the CDP and the CDLE.[24] This allows for increased energy conversion without increased amount of material. It is operated in a similar manner as the CDLE in the sense that there is a charging step followed by open circuit water switching, a discharging step, and a final open circuit water switching step, described in more detail in the Theory section. The technology is still CDP, though the novel operation mode allows for much more energy to be converted from the electrolytes. As we in this paper study factors affecting the time required for achieving open circuit potential when switching electrodes between two solutions, the present results are in particularly important for CDLE and externally charged CDP.

Another novel technique, to which an electrode wire design will be highly beneficial, is the "battery electrode" proposed by LaMantia et al.[25] In this technology, accumulative mixing takes place as electrodes sensitive to salt concentration is switched between sea- and river water-like solutions.

Moreover, all salinity gradient power systems stems somehow from a desalination process. The opposite techniques of the CDP and the CDLE are capacitive deionization by the use of supercapacitors with or without membranes.[26,27] In this sense, the results of this paper will also benefit the development of these techniques.

Whereas RED and PRO apply steady streams of water in their processes, the novel technologies alternate the water solutions. Alternating the sea and river water solutions may at first appear less intuitive—simply because a process design going at steady conditions with the same solutions in the same compartments is simpler to design and operate. However, when exposing salinity gradient power system to nature, which is inevitable, microbial fouling, algae-induced fouling, and scaling are reduced by alternating the sea and river water solutions.[28−31] This is an argument for alternating the water solutions, however not further discussed in this paper.

Recently, Sales et al. revealed that the use of wire electrodes instead of flat plate electrodes in CDP salinity difference power systems can strongly improve the power output because of lower ohmic resistance without introducing large pumping pressure energy costs.[32] For long, the understanding in the scientific community has been that there is a trade-off between lowering the ohmic resistance and increasing the pumping pressure.[33] With this present study and the former,[32] we introduce a technical improvement that, because it contradicts the way we have been thinking about electrochemical salinity gradient energy up to this point, presents a paradigm shift. Capacitive salinity gradient energy extraction technologies are unique in that they are the only salinity gradient energy extraction technologies that can advantage of wire electrodes.

In this paper we demonstrate that mass transport by diffusion is favored when cylindrical rather than flat plate electrodes are used. Improved mass transport by diffusion allows for faster time response, resulting in a higher power output. This is relevant for all the three capacitive salinity gradient power systems. We demonstrate in which manners changing the geometry is beneficial not only with respect to ohmic resistance but also to mass transfer by diffusion. We also studied the asymmetric behavior of response time in concentrated saline solution and dilute saline solution that is reported for our branch of technologies. We discuss these subjects using measurements and analytical descriptions of the problem.

■ THEORY

In this research paper we focus on the open circuit potential (OCP) of the CDP electrodes when alternated between two solutions.

There are several good reasons for performing OCP studies in relation to the CDP and the CDLE techniques. As we shall see, the OCP of the CDP is dictated by the membrane permselectivity and the Gibbs free energy of mixing. The latter is an intensive thermodynamic property; i.e., it is independent of the size of the system. Hence, the OCP is independent of the electrode size, system ohmic resistivity, and any other geometrically related property of our experiments. However, the time it takes to reach the stationary OCP when going from one concentration to another does rely on the geometry of our experiments. Lowering this time will allow for more energy to be converted per unit time. In other words, studying the CDP by the means of OCP will allow us to understand how to reach higher power output in capacitive salinity gradient power systems.

System Description. The CDP system consists of two electrodes. These electrodes consists of activated carbon on in inert conductive material, such as carbon or platinum. One of the electrodes is covered by a cation exchange membrane (CEM) and the other by an anion exchange membrane (AEM). In operation all parts are exposed to saline water of some concentration. This pair of electrode membrane assembly (MEA) is in an alternating manner exposed to water solutions of two different concentrations, e.g., sea and river water.

The water−carbon interface and the membrane−water interface are of a capacitive nature, described by the double layer given by the Guy−Chapman−Stern theory.[34] The rest of the system has ohmic resistance as characteristics. Hence the system can, as a first-order approximation, be described by RC models such as the one given in Figure Figure 1.[23,35]
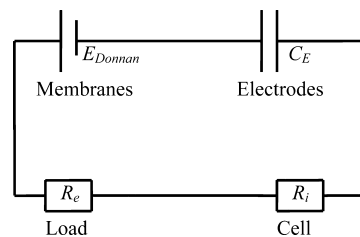

Figure 1. Closed circuit analogy of a CDP system.

OCP of the CDP. The open circuit potential of the CDP is defined by the potential difference that can be measured when a pair of CDP electrodes are equilibrated in a solution of concentration A, C_A, and subsequently at stationary state in a solution of concentration B, C_B. Assuming ideal solutions at temperature T, the corresponding potential at stationary state is thus given by the Donnan potential equation[7]

$$E_{\text{Donnan}} = -\bar{\alpha}\frac{\Delta G_{\text{mix}}}{F} = \bar{\alpha}\frac{2RT}{F}\ln\left[\frac{C_A}{C_B}\right] \quad (1)$$

where $\bar{\alpha}$, R, and F are the mean permselectivity of the two membranes, the ideal gas constant, and the Faraday constant, respectively. ΔG_{mix} is Gibbs free energy of mixing. In order to reach this potential, the concentration at the surface of the membranes must reach the second concentration level, C_B. Thus, the OCP depends only on the concentration in the new

solution. If now, alternating the pair of electrodes at open circuit between two solutions A and B of concentrations C_A and C_B, after first completely discharging the electrodes in solution A, will result in the potential alternating between 0 and the one defined by eq 1. This procedure describes the experiments that we perform with different electrode geometries in this paper.

Power Source Processes. The CDP and the CDLE processes are most often reported when converting energy.[19,24,32,35,36] These are cyclic processes and can be divided into several subsections or phases. The externally charged CDP has four characteristic phases, as exemplified in Figure 2. First,
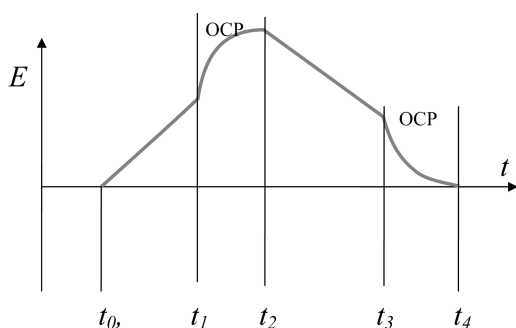

Figure 2. Sketch of the cell potential as a function of time for the externally charged CDP.

when in sea water, the capacitor electrodes are charged from an external source. This first phase, t_{0-1}, is the charging period when the electrodes are in sea water. Next, the electrolyte solution is changed from sea water to river water, t_{1-2}, and the cell potential increases equivalent to the Donnan OCP reported in this paper. Within this phase, the concentration at the surface outside the electrodes is rising, and the Donnan potential reaches its other stationary state.[24] After this, in the time frame of t_{2-3}, the cell is discharged and the electrodes return more electric energy than they received during the charging. After the electrodes are discharged and electric work is delivered, the solutions are replaced at open circuit, t_{3-4}. Thus, the present experiments are representative for the second, t_{1-2}, and fourth, t_{3-4}, phases gaps of Figure 2.

As can be seen from Figure 2, it is really only time steps t_{1-2} and t_{3-4} that can be subject to mass transport limitations only by diffusion. In the other time frames there are other mass transport phenomena in addition to diffusion. Because the phenomenon that we are interested in takes place within these two time frames, we chose to study the open circuit potential of a pair of CDP electrodes alternatingly immersed in sea and river water.

Mass Transport by Diffusion. The OCP of any of the three processes is dictated by the salt concentration at the surface of the membrane, C_s, as long as we consider the permselectivity, α, and the electrode compartment is kept constant. Because only the concentration outside the membrane is changed during open circuit phase, these are reasonable assumptions.

When CDP flat sheet electrodes are taken from a solution with low salt concentration, e.g. river water, and immersed into saline water, such as sea water, a thin film of water will remain on the surface. In the absence of convection, salt will diffuse through this film and into the membrane surface. This is illustrated in Figure 3. From the left is the porous supercapacitor carbon, the membrane, the residual river water film
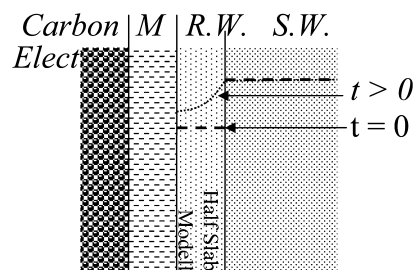

Figure 3. Sketch of the a membrane electrode assembly with a residual river water film immediately after immersion into sea water.

and finally the sea water solution. Also, sketches of the concentration profiles at zero time and time greater than zero are indicated. The equation governing the process of changing the concentration in the dilute residual film layer on a plate (that is infinitely wide and high) is given by

$$\frac{\partial C}{\partial t} = D_{s,w} \frac{\partial^2 C}{\partial y^2} \tag{2}$$

C is the concentration given by time, t, and position, y, inside the river water film remaining on the membrane surface when immersed into sea water, and $D_{s,w}$ is the diffusion coefficient of salt, NaCl, in water. In cylindrical coordinates the governing equation is

$$\frac{\partial C}{\partial t} = D_{s,w} \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \tag{3}$$

For exemplification here, we consider the geometry of a slab of thickness 2δ and a cylinder with diameter $2R$ for the flat plate and the cylinder (wire). Both these are classical examples within transport phenomena and are probably recognized by many readers. The is a secondary argument for choosing the examples, nevertheless relevant.

The slab geometry applied in combination with eq 2 acts a representative example for the flat plate, in the sense that the remaining liquid film on the flat plate is equivalent to half a slab of river water immersed into sea water. Obviously, water will never be a slab when in its liquid state. In fact, the most slab-like part of our experimental setup is the membrane electrolyte assembly (MEA) plate. Try however to think of the classic slab example when the slab is cut in two in the center plane and a planar MEA is put in between. The half slab-like water film is indicated in Figure 3. The cylinder geometry applied to eq 3 can be seen as the extreme example of a very thin wire, i.e., when the wire is thick the remaining water film surrounds it as a cylindrical shell and as the wire becomes thinner the water film approaches a true cylindrical geometry. These two geometries represents the extreme analytical solution of the problem defined in this paper. They are meant to aid explaining the difference in the OCP time response of the two geometries deployed in our experiments.

Introducing a dimensionless concentration, $\Gamma = (C - C_0)/(C_1 - C_0)$, where C_0 is the concentration of the remaining (river) water film and C_1 is the concentration of the new (sea) water solution, eqs 2 and 3 become

$$\Gamma_{FP} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left[-(2n+1)^2 \pi^2 \frac{D_{s,w}t}{4\delta^2}\right]$$
$$\cos\left[\frac{2n+1}{2} \frac{\pi y}{\delta}\right] \tag{4}$$

$$\Gamma_{Cyl} = 1 - 2 \sum_{n=1}^{\infty} \exp\left[-\beta_n^2 \frac{D_{s,w}t}{\delta^2}\right] \frac{J_0\left(\frac{r\beta_n}{R}\right)}{\beta_n J_1(\beta_n)} \tag{5}$$

where J_0 and J_1 are the Bessel functions of order zero and one and $\beta_n{}^a$ is given in refs 37 and 38. The Bessel function for the present case is defined as

$$J_j(x) = \sum_{k=0}^{\infty} \frac{(-1)^k}{2^{(2k+j)} k!(k+j)!} x^{(2k+j)} \tag{6}$$

Obviously, water does not act as solids and during immersion convection, and thereby mixing can take place. The mathematical terms behind eqs 4 and 5 are derived under the assumption that water is not subject to diffusion and that the water momentum is zero. As we proceed through the Results section, we shall see that the two analytical models do indeed serve as adequate models for explaining the mass transport by diffusion in the process of dipping CDP electrodes in two solutions with different salinity.

In the analytical model we apply a diffusion coefficient for salt (NaCl) in water, $D_{s,w}$, of 1.2×10^{-10} m^2 s^{-1}.

MATERIALS AND METHODS

Materials Preparation. The CDP electrodes were made by first brush painting the activated carbon slurry (ACS) onto inert wires and plates (circular like in shape with a length of 10 cm). The wires were either graphite foil strips or titanium coated with platinum (2 mm thick and 60 mm long, Magneto Special Anodes BV, The Netherlands). Both wires had the same behavior and are thus not further discussed in this paper. The plates were titanium coated with platinum. After the carbon coating, the electrode wires and plates were dried and coated with the ionomer,[b] anionic or cationic exchange type. The total thickness of these two layers was 120 μm.

The porous capacitive electrode slurry was made by mixing a nonaqueous binder (poly(vinylidene fluoride) (PVDF) (KYNAR HSV 900, Arkema Inc., Philadelphia, PA) in 1-methyl-2-pyrrolidone (NMP)) solution together with dried AC material (DLC Super 30, Norit, Amersfoort, The Netherlands) in a ball mill for 30 min at 450 rpm. The PVDF content of the dried materials was 10 wt %.

The ion exchange membrane (IEM) layers were obtained by brush-coating an ionomer solution over the carbon layer. Anionic selective ionomer (Fumion FAA, Fumatech, St. Ingbert, Germany) was used to make the anion exchange membrane coating on the electrode and cationic ionomer (Fumion FLNMP-915, Fumatech, St. Ingbert, Germany) was used to make the cationic exchange membrane coating on the other electrode. After this procedure the membrane electrode assemblies were dried overnight in an oven at 50 °C.

Setup and Measurement Procedure. Pairs of AEM- and CEM-coated electrodes were assembled in parallel in a holder. The holder was made such that the distance between the center of the wires and the plates were approximately 20 and 10 mm, respectively. The pair of plates and the pair of wires were

connected to an potentiometer (IviumStat, Ivium Technologies, The Netherlands) measuring the OCV.

The electrode pairs were then submerged in river water-like solution, 1 g NaCl dm^{-3}, until the cell potential reached steady state. Next the pair of electrodes were submerged into a sea water-like solution, 30 g NaCl dm^{-3}, until the cell potential reached steady state. This procedure was repeated several times keeping the electrodes as still as possible. An exception was made for the plates in river-like water. Because the potential took an extremely long time to reach steady state when held still, the holder holding the pair of electrodes was on a few occasions rapidly moved side ways (back and forth) as to create convection streams on the membrane surface. Sideways in this case means the direction perpendicular to the radial axis of the circularly shaped plates.

When transferring an electrode from one solution to another, a film of water from the first solution is brought along. At the end of the the Results and Discussion we consider this film in greater detail. When the electrodes were transferred between two solutions, we used dust-free tissues to remove these water films. Another crude experiment that was done in order to investigate the diffusion was to wave the electrode plates in the water reservoirs. The plates were held in a rig, 1 cm apart from each other, and moved back and forth, i.e., perpendicular to the surface of the plates.

RESULTS AND DISCUSSION

We first present measured OCP results of the CDP electrode pairs and then the results in the light of the analytical diffusion models.

Measured OCP Time Response. Figures 4 and 5 give the OCP versus time for the wire and flat plate CDP electrode pairs
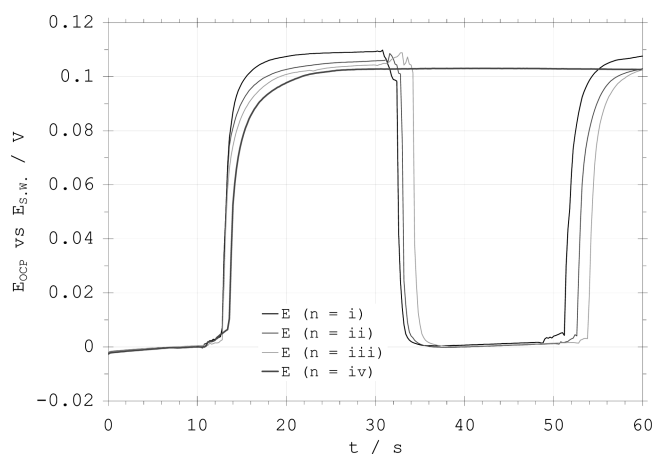

Figure 4. Measured open circuit potential for wire CDP electrodes immersed in sea (reaching 0 V) and river (reaching 0.11 V) water.

when alternatingly switched between sea and river water solutions. The OCP equal to zero corresponds to sea water. In principle, this is not a real zero potential, only an arbitrarily chosen reference potential.

If considering the wire results only (Figure 4), one can see that there are clearly two different OCP time responses; i.e., there is an asymmetry between the time response between the two solutions. This can also be seen from Table 1. The OCP time responses, Δt^{OCP}, are 13 ± 4 and 3.7 ± 1.5 s in river water and in sea water, respectively.
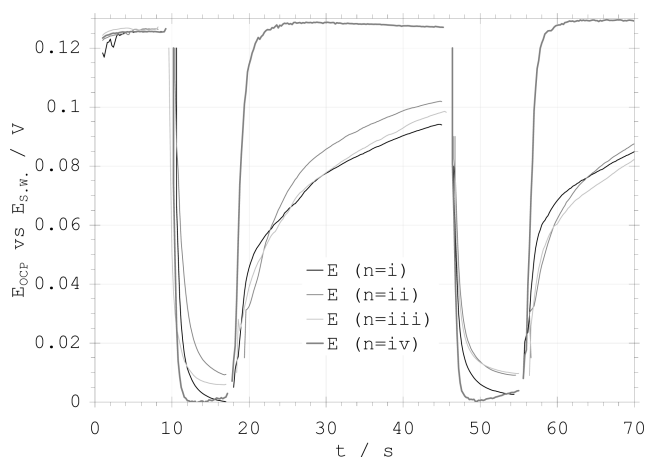
Figure 5. Measured open circuit potential for flat plate CDP electrodes immersed in sea (reaching 0 V) and river (reaching 0.13 V) water.

Table 1. OCP Time Response of CDP Electrode Pairs When Submerged into in Sea and River Water Solutions

solution	wire	par Pl	PP + stirring
Δt_{RW}^{OCP} /s	13 ± 4	30 ± 10	6.7 ± 0.8
Δt_{RW}^{OCP} /s	3.7 ± 1.5	8 ± 2	3.2 ± 0.1
$f_{\Delta t_{RW}/\Delta t_{SW}}$	3.5 ± 1.8	3.8 ± 1.6	2.1 ± 0.3

As discussed in the Theory section, the Donnan potential of the CDP refers to the concentration at the membrane surface at a given time, C_B, and the concentration of the solution the electrodes were transferred from; e.g., when a pair of CDP electrodes is equilibrated, by long-term cell short circuiting, in sea water and are next submerged into river water, the Donnan potential is at any time given by the membrane surface concentration, here C_B, and the sea water concentration, C_A. In this process and the given example, the membrane surface concentration will gradually change from sea water to river water. Thus, the potential depends on the concentration difference between the two solutions. In other words, the Donnan potential can only be obtained when the surface concentrations of the membranes have reached the one of the bulk solution. At open circuit and in the absence of convection this is described by diffusion. We discuss this more detailed at the end of this section.

Looking next at the CDP plate electrodes, the time dependency is somewhat similar to that of the wire electrodes with the exception of the OCP response time. Immersing the CDP plate electrodes into sea water results in a much shorter time response than that of immersing the electrode plates into river water. This is similar to that of the wires. The reasons for this could simply be related to the material properties of water with salinity. We discuss also this is in more detail later. In sea water the response time for the plate electrodes is about twice the time response of the wire electrodes in sea water, i.e., approximately 4 and 8 s. In river water, on the other hand, the CDP plate electrodes demonstrate an OCP time response 3−4 times that of the wire electrodes in the same solution.

The proposed rate-determining step the OCP time response of both the electrodes geometries is mass transport by diffusion. Hence, the plates were waved in the water solutions in the beaker when immersed. The plate interdistance remained unchanged during this stirring procedure, and moreover, the

plates were moved perpendicular to the length and width plane. Doing this lowered the time response severely for the CDP plate electrodes both in sea water and in river water. In fact, this stirring made the moving plate time response in sea water equal to the one of the wires in sea water. Also, the moving plate time response in river water was shorter than the time response of the wire in river water.

From these observations we argue that the OCP time response for CDP parallel plate and also the wire electrode pairs is almost entirely limited by diffusion. When arbitrary stirring is introduced by moving the plates, the OCP time response of the plates in sea water becomes equal to that of the wires in sea water (which were held still). This demonstrates that wires without stirring can be as effective as plates with stirring, and thus because stirring is associated with added work, the wire design holds potential for being more efficient than plates, not only with respect to ohmic resistance[32] but also to mass transport by diffusion. In the river water-like solution, the wire OCP time response is shorter than the one of plates when stirring is absent or negligible.

It is clear from the reported experiments that a wire design gives a much faster OCP time response when comparing to plates in the same solution and with similar stirring or convection conditions. It is also clear that mass transport by diffusion is impeding, if not limiting, the transport processes at open circuit for the CDP and the CDLE.

Analytical Expressions. Having seen that mass transport by diffusion is significantly different for plate design and wire design and learned that the Donnan potential relies on the surface potential of the membrane, we shall now discuss the transport of salt by diffusion only—both for a flat film (on a plate) and for a cylindrical layer.

Reproducing the experimental results of those in Figures 4 and 5 by a model is here performed by considering two extreme geometries. The first geometry is a thin layer of water on a flat plate, much like that leading to the results of Figure 5, and is described by eq 4. The second geometry considers a thin layer of water on a infinitely thin wire. This second analytical model is meant to illustrate the results of Figure 4 and is given by eq 5. Obviously, the most appropriate model would be a cylindrical shell versus a plate; however, we are interested in the potential effect when the wire diameter is reduced to a minimum. The thought behind the models is that a thin water film of a given concentration, C_0, is suddenly placed next to a concentration of a solution with a larger concentration, C_1. For this modeling we consider the sea water solution concentration at the edge of the electrode water film being constant at C_1. This process is meant to represent the process of a CDP or a CDLE electrode pair equilibrated in river water and then, at OCP, immersed into sea water solution. In the thin water layer on the electrode surface, C is the concentration of salt at any time and position and gives the dimensionless concentration term $\Gamma = (C - C_0)/(C_1 - C_0)$. The concentration profiles at different time can be expected to be similar to those of Figure 3.

Figure 6 gives the time response for the analytical expressions for the concentration profiles in the thin water layer of the flat plate, Γ_{FP}, and on the cylinder, Γ_{Cyl}, at various times after immersion into the sea new concentration. Equations 4 and 5 only have four variables: the thickness of the water film, δ/R, the diffusion coefficient of salt in water, D_{SW}, the time, t, and of course the position within the water film, y/r. The time, t, and the position, y/r, give the coordinates for the concentration and are not related to the system itself. The diffusion coefficient is
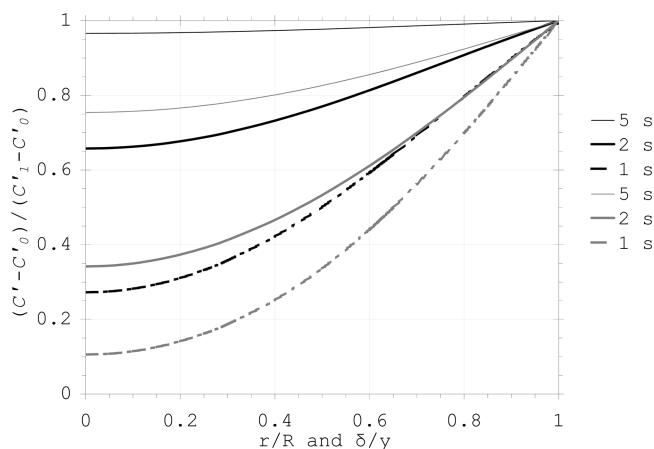
Figure 6. Dimensionless concentration profiles for a cylinder (black) and for a flat plate (gray) at various times (1, 2, and 5 s) after immersion into sea water.

an intrinsic property of the salt water system (and temperature). The only property that can be altered in the analytical model in order to fit the OCP time responses to the experimental results is thus the thin water film thickness. In the present case, when fitting the analytical models to the experimental response time of immersing both the electrode geometries into sea water, the film thickness, δ, was found to be in the order of 30 μm. 30 μm is a rather thin layer and of an order likely to remain attached to the CDP electrode surface when transferring the electrodes from one solution to another.

In Figure 7, the surface concentrations of the CDP electrodes at various times are used in order to demonstrate how the OCP
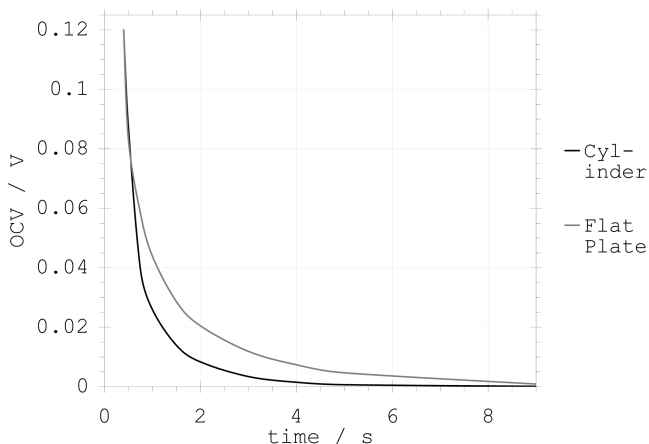

Figure 7. OCP as a function of time by the analytically modeled surface concentration.

potential will respond in time when pairs of CDP electrodes are taken from river water and immersed into sea water. The OCP response times for the wires and plates predicted by the model are around 4 and 8 s, respectively. Looking at Table 1, the experimentally measured times for the same processes are 3.7 ± 1.5 and 8 ± 2 s, respectively. This suggests that when CDP electrode pairs are immersed into sea-like water, the only phenomena limiting the OCP response time is mass transport by diffusion. Thus, using wire electrodes rather than flat plate electrodes has the potential to lower the CDP process in water by a factor of 2 without forcing convection. Moreover, the modeled and measured OCP time response for a wire pair of

electrodes are shown together in Figure 8, where one can see the excellent fit.
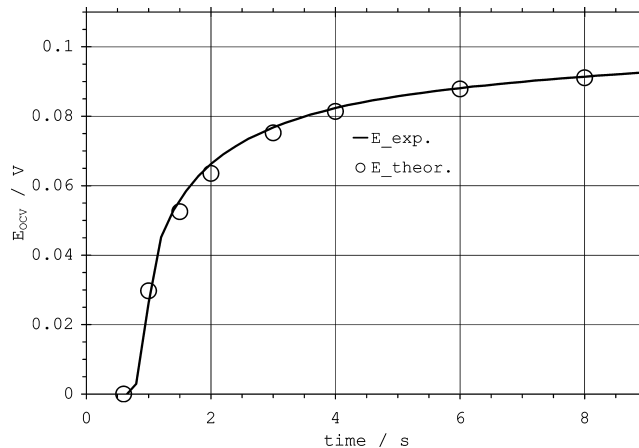

Figure 8. Modeled and measured OCP as a function of time when immersing wire electrodes into sea-like water.

When submerging the CDP electrode pairs into river water, however, the geometric effect is present, i.e., wire design lowering the OCP response time; it is however not numerically similar to what is modeled for the sea water immersion process. We shall return to this difference in the next paragraph. Nevertheless, there is no doubt that based on the experimental and analytical part of this paper, the wire design increases the diffusion rate near the CDP electrode surface by at least a factor of 2.

From the modeling point of view, decreasing the thickness of the transferred water film by one-third results in lowered OCP response time by a factor of 2. Such high sensitivity makes it interesting to postulate that the water film that is carried along with the membranes/electrodes is actually different when going from sea water and from river water. We observe that the OCP response time in river water is the longest. This would mean, in light of our analytical model, that the water film carried along from the sea water would be thicker than the water film carried over from the river water solution. One explanation for the water film carried from the sea water being thicker than the water film carried from the river water could be the difference in viscosity. Chen et al. measured the (kinematic) viscosity of sea water of different concentrations and temperature and reported an viscosity increase of 2%.[39] Table 2 gives some

Table 2. Donnan Potential Response Time and Relative Increase in Transferred Water Film Thickness

δ/R (μm)	rel increase (%)	$\Delta t_{Pl./wire}^{OCP}$ (s)
30	0	8/4
34	12	10/5
45	50	17/9
53	75	20/11
60	100	30/16

examples accordingly. From the first-order stationary momentum equation, one can extrapolate that the thickness of the layer transferred is proportional to the viscosity. An increase of 12% in viscosity only leads to an OCP time response difference of 25%, not 300% as observed in our experiments. In order to reach such a response time difference between the two

solutions, the film thickness transferred from the sea water must be around 75% thicker than the one transferred from the river water. This may be explained also from wetting properties of saline water and the membranes having an additional effect; i.e., the sea water wets the membrane much better than the river water, e.g., because of the salt content and the active groups on the membrane surface. The last parts of this discussion can be seen as highly speculative as no information on the wetting properties between different salinity levels and our specific membranes is available. However, in capacitive desalination using ion exchange membranes, it was recently reported that when using wires and exchanging them between two solutions, the transferred water film would at some point limit the desalination; i.e., the water film from the desalinated solution would transfer desalinated water into the brine and vice versa.[27] As a brief investigation of the transferred water film, we tried removing it by the use of dust-free tissues. We lifted the electrode plates out of the beaker, dried the membrane surface twice with tissues, and immersed the electrodes into the water for around 30 s, before waving them as described previously in Materials and Methods. This was also done without using tissues for drying. The results can be seen in Figure 9. The
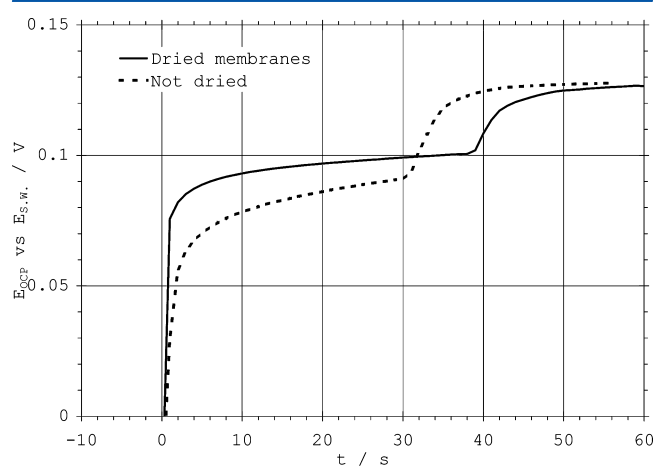

Figure 9. OCP time response for a pair of flat plate MEAs immersed into river water.

figure shows the OCP time response after immersing into river water. It can be seen that there is a significant improvement by the tissue drying procedure. Removing all the water from a hydrophilic membrane with a "rough" surface did not remove all the water (in light of these experiments). The point of this test was only to verify that there actually is a transferred water film that slow down the OCP time response.

Nevertheless, we have in this paper demonstrated that the most energy efficient manner to shorten the OCP time response for CDP is to go from a plate electrode design to a wire design. This is one of the main advantages of the CDP.

CONCLUSION

In this work, using an analytical model and experiments, it was demonstrated the time response for reaching open circuit potential (OCP) of CDP electrodes in sea and river water is controlled by diffusion. Because of the manner which CDLE is operated, the results are also relevant for this technology.

Using a wire electrode design instead of plates has the potential to decrease the time response of the OCP build up by at least a factor of 2.

Replacing plate electrodes with wire electrodes presents an improvement equal to that of adding forced convection on the plates. Hence, work related to pumping water can be mitigated.

AUTHOR INFORMATION

Corresponding Author
*E-mail: odne.burheim@wetsus.nl.

Author Contributions
∥Authors share equal contributions to the paper.

Notes
The authors declare no competing financial interest.

ADDITIONAL NOTES

[a]For the given problem the coefficients $\beta_1, \beta_2, ..., \beta_6$ are 2.4048, 5.5201, 8.6537, 11.7915, 14.9309, and 18.0711, respectively.[37]
[b]Ionomer in this context is an ionic exchange membrane dissolved in a suitable solvent.

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