# Nomination David Vermaas

# for EFCE Excellence Award in Membrane Engineering

## Extended abstract PhD thesis: 'Energy generation from mixing salt water and fresh water'

### Principle

The salinity difference between salt and fresh water streams can be used to generate renewable energy. This energy source utilizes the increase in entropy when fresh and salt water mix into a brackish solution; for example at locations where river water flows into the sea. The global runoff of river water into the sea has a potential to generate approximately 2.4 TW [1] of salinity gradient power, which is close to the current global electricity demand (2.3 TW) [2]. Additionally, salinity gradient power can be harvested mixing water from hypersaline lakes with seawater or using salinity gradients that are regenerated by waste heat (chapter 1 of corresponding PhD thesis).

This salinity gradient power can be captured using ion exchange membranes in reverse electrodialysis (RED). The salinity difference between seawater and river water induces a potential difference when separated by an ion exchange membrane, selective for cations (cation exchange membrane, CEM) or anions (anion exchange membrane, AEM). In a RED stack of alternating CEMs and AEMs, with seawater and river water in compartments between these membranes, the voltage over each membrane accumulates. This voltage can be used as a power source, using e.g. electrodes and a (reversible) redox reaction that convert the ionic current into an electrical current. Fig. 1 illustrates the RED process.

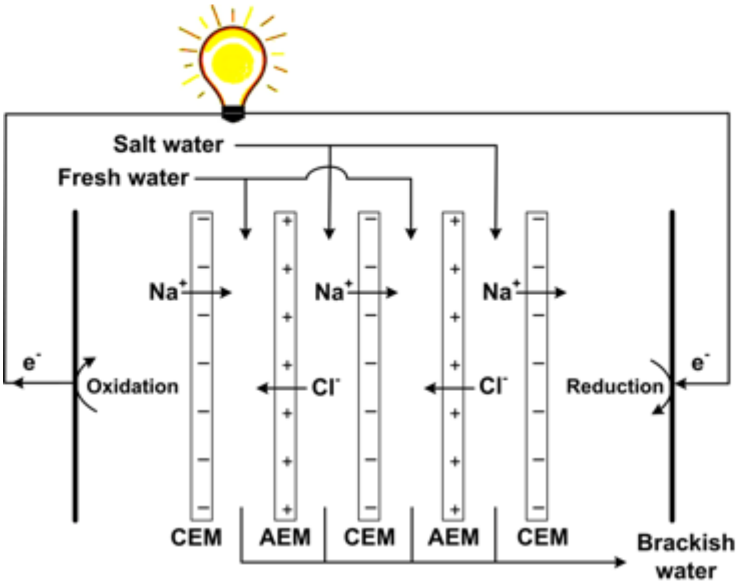

*Figure 1: Principle of reverse electrodialysis (RED). The salt water and fresh water flow alternately along cation exchange membranes (CEM) and anion exchange membranes (AEM). A (reversible) redox reaction (in an electrolyte that can be circulated) converts the ionic current into an electrical current.*

### Problem definition

Although the RED process has been reported already in 1954 [3], large scale application was never performed at the start of this PhD study. A relatively low power per membrane area and energy efficiency, and hence the high cost per produced kWh, hindered the commercial application of RED so far. Moreover, the use of natural feed waters requires fouling prevention strategies, to ensure a long lifetime of the RED membrane device. As a third challenge, the conversion of ionic current into electrical current at the electrodes should be facilitated with low overpotential and free of any toxic substances to ensure environmental friendly energy generation. This PhD thesis addresses these three issues, presents advances in the state of the art performance and indicates current challenges and limitations for further improving the RED technology.

**State of the art, scientific and technological advances, and results**

The highest experimentally obtained power density (i.e., the power per membrane area) of RED prior to this PhD study was 1.2 W/m$^2$, at an energy efficiency of 4% [4]. Higher energy efficiencies, up to 70%, are reported by recycling the feed water [5] but sacrifices power density. Previous research to the state of the art in reverse electrodialysis addressed the influence of e.g. membrane permselectivity [6, 7], stack resistance [8, 9] and temperature [10] on the performance. This prior research indicated that in particular the stack resistance provides room for improvement. The electrical resistance of a RED stack is composed of membrane resistances [11], its diffusive boundary layers, electrode overpotentials [12], ohmic feed water resistance and the spacer shadow of the non-conductive spacers in between the membranes [13].

Spacer thickness and flow orientation

The present research shows that the power density of a RED stack fed by seawater and river water is mainly limited by the electrical resistance of the river water compartment (chapter 2). This is demonstrated in Fig. 2, which shows the calculated contributions to the ohmic resistance.

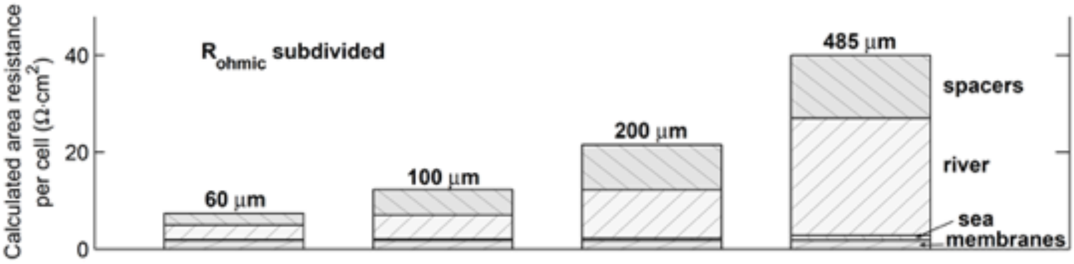

*Figure 2: The ohmic resistance ($R_{ohmic}$) subdivided in a contribution originating from the spacers, river water, sea water and membranes, based on membrane specifications and measured conductivities.*

The highest gross power density is obtained using compartments as thin as 100 µm. This power density (2.2 W/m$^2$) is, to the best of my knowledge, the highest experimentally obtained power for RED at this scale using seawater and river water. The corresponding energy efficiency is approximately 8%. However, a trade-off between energy efficiency and power density exists, as the energy efficiency is generally highest at low feedwater flow rates, while the power density benefits from higher feedwater flows (chapter 11). Even thinner compartments improve both the power density and energy efficiency (see Fig. 3), but at the expense of a higher power consumption for pumping (chapter 2).

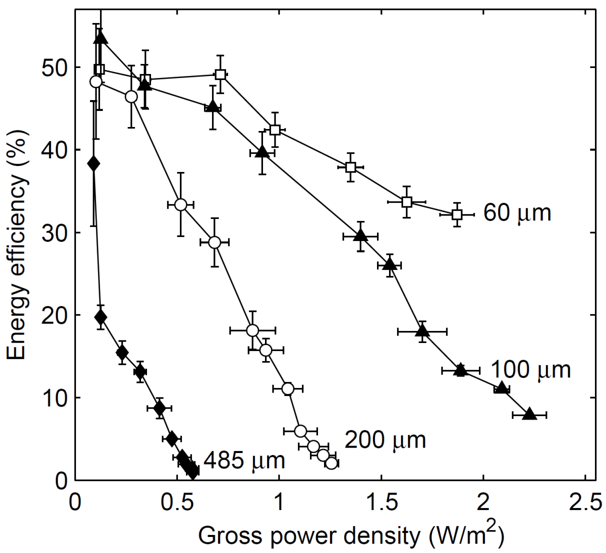

*Figure 3: The ohmic resistance ($R_{ohmic}$) subdivided in a contribution originating from the spacers, river water, sea water and membranes, based on membrane specifications and measured conductivities.*

Experimental power densities and energy efficiencies are measured usually in cross-flow orientation, while alternative flow directions are possible as well. The theoretical energy efficiency for RED using a single electrode pair is 40 - 95%, depending on the fraction of seawater with respect to river water and the flow orientation (chapter 5). This dependency is due to the interaction between the ion transport from the seawater compartments to the river water compartments and the corresponding electromotive force and electrical resistance. The energy efficiency in counter-flow orientation is highest, closely followed by a cross-flow design, while co-flow orientation predicts significant lower energy efficiencies. A strategy to obtain higher energy efficiencies for all cases, without sacrificing power density, is to capture energy in multiple stages e.g. using segmented electrodes (chapter 5).

Profiled membranes

Further improvement is established by introducing profiled membranes, i.e., membranes with ion conductive ridges that create flow channels for feedwater. These membranes have been produced by hot pressing membranes in a tailor made aluminum mold and are illustrated in Fig. 4. Profiled membranes make the use of spacers obsolete and reduce the pumping power by a factor 4 - 8 (chapter 3 and 4). This allows smaller intermembrane distances, leading to high (gross and net) power densities and opens the possibilities for micro-designs (chapter 11). The ion conductive ridges of the profiled membranes further reduce the ohmic resistance, compared to RED stacks with spacers. However, the non-ohmic resistance, due to concentration changes in the boundary layer and along the feedwater channels, is higher.

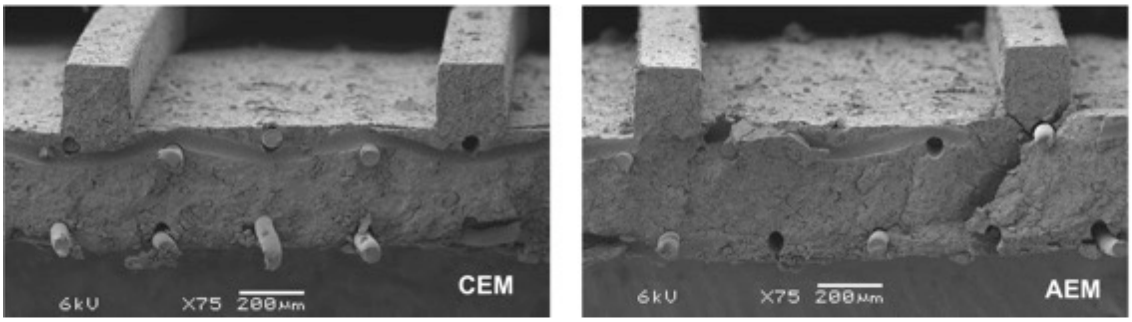

*Figure 4: Representative SEM-image of cross-section of the profiled CEM (CMH) left and AEM (AMH) right. The protruding fibers and black holes are remnants of the reinforcement (PES) in the membrane. The small crack in the AEM is due to cutting of the membrane.*

The diffusive boundary layer and the associated non-ohmic resistance can be decreased significantly when the feedwater is uniformly distributed over its compartments. Additional mixing promoters, such as twisted spacer structures or profiled membranes with 50 µm sub-corrugations, did not further decrease the boundary layer resistance at typical Reynolds numbers for RED (Re < 100) (chapter 4). This is supported from the absence of vortices in particle tracking measurements, as shown in Fig. 5.

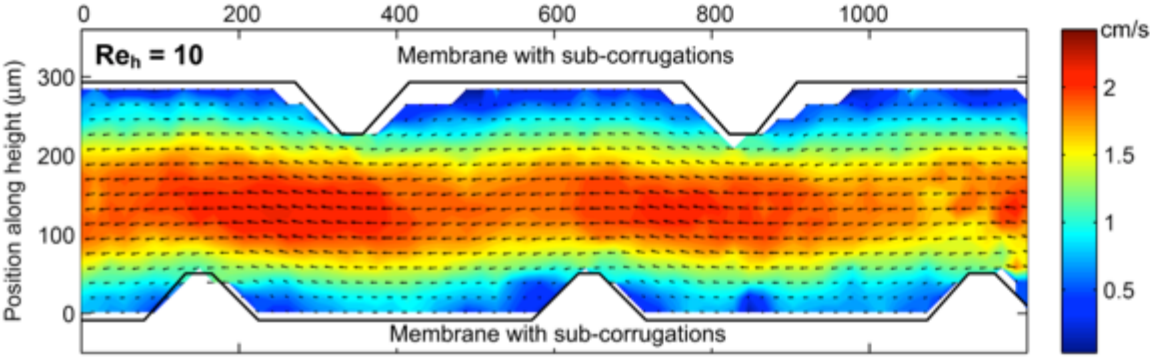

*Figure 5: Experimentally obtained velocity field between sub-corrugated membranes for Re$_h$ = 10. The colors indicate the velocity magnitude in cm/s, while the vectors indicate the flow direction and magnitude.*

### Membrane fouling

The necessity for uniform feedwater distribution emphasizes the importance of preventing colloidal fouling, which can make part of the feedwater compartments inaccessible, i.e., create preferential channeling (chapter 9 and 10). Such preferential channeling causes a serious decrease in performance, e.g., a 20% decrease in net power density when only 10% of the feedwater channels is inaccessible. The most sensitive indicator for preferential channeling is the response time of the voltage in chronopotentiometric measurements, as ion transport in feedwater channels that are inaccessible for flow is mainly dependent on diffusive transport (chapter 9).

Fouling of RED stacks using natural seawater and river water for a long period is mostly inorganic colloidal fouling (clay minerals, diatom shells), as shown in Fig. 6 and chapter 7 of the PhD thesis. Additional SEM-images show, in lesser degree, also scaling and biofouling. Stacks with spacers are much more sensitive to this colloidal fouling than stacks with profiled membranes. AEMs attract more colloidal fouling than CEMs, while non-conductive plastic sheets show no significant fouling at all.

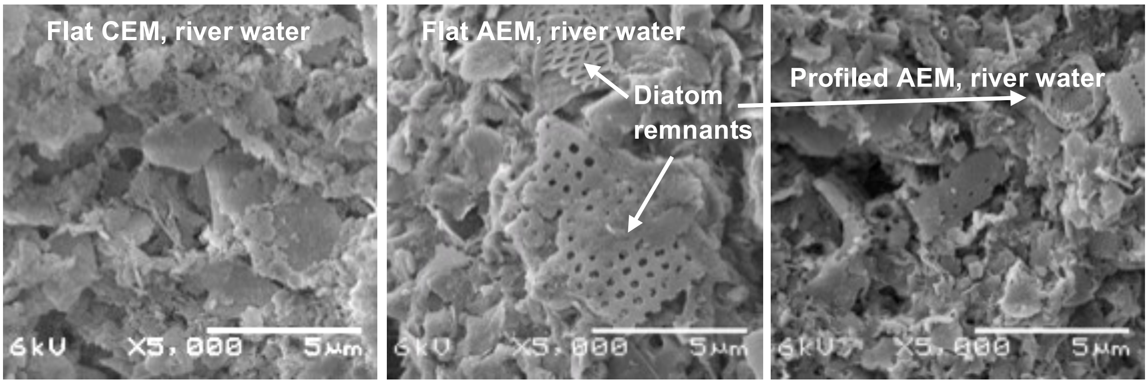

*Figure 6: SEM images of cation and anion exchange membranes (CEMs and AEMs). The shown samples were in contact with river water, obtained from flat membranes (left 2 images) and from profiled membranes (outer right image). Remnants of diatoms are indicated by arrows.*

In order to overcome the detrimental effects of fouling in RED, several environmental friendly anti fouling strategy are tested under natural conditions. The use of periodical air sparging effectively removes the majority of the colloidal fouling, which finally results in a significantly higher power density and lower pressure drop (chapter 10), which is demonstrated in Fig. 7.

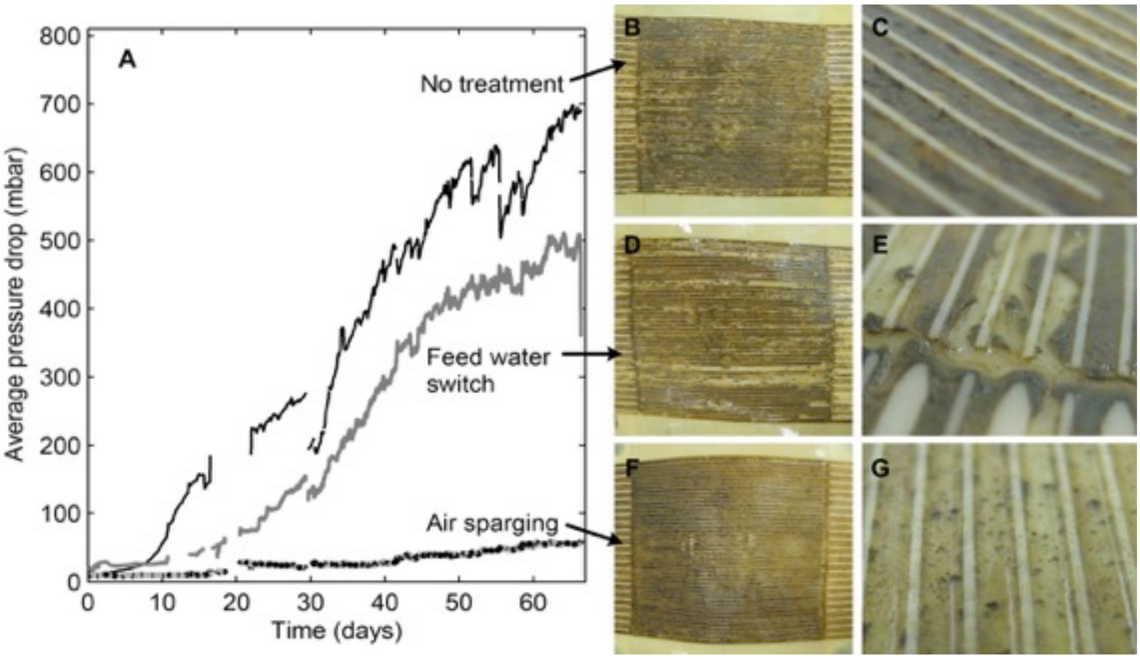

*Figure 7: Average pressure drop as function of the time (A) and photos of profiled cation exchange membranes from the fouled stacks at the end of the experiment (B-G). Photos B, D and F show the full area of 10x10 cm$^2$, while the right photos (C, E and G) show images of approximately 1x1 cm$^2$, zoomed close to the inflow of the feedwater compartments. The original membrane color is beige.*

Multivalent ion transport

Multivalent ions (e.g., $Mg^{2+}$ and $SO_4^{2-}$) that are present in natural feed waters cause a dramatic decrease in obtainable power density (chapter 8). The underlying mechanism is transport of multivalent ions against the concentration gradient in exchange for monovalent ions, due to the difference in ion valence and the associated difference in membrane potential. In addition, the apparent membrane permselectivity decreases when mixtures of monovalent and multivalent ions are present. The voltage response after a change in feedwater composition is in the order of hours (chapter 8), which is in agreement with observations using natural feed waters (chapter 10). Reversal of the electrical current direction, as imposed by switching the feed waters, results in higher power densities in the short term, and hence this approach can be applied as anti fouling strategy. However, dealing with fouling and multivalent ions in long term is an ongoing challenge for RED. Although the current anti fouling strategies already temper the effects of fouling, they cannot prevent that the power density is roughly halved when using natural feedwater instead of artificial NaCl solutions.

Membrane system with capacitive electrodes

For practical RED operation, capacitive electrodes are introduced, which make redox reactions obsolete and hence ensure safe and environmental friendly operation. Driven by the voltage over the ion exchange membranes, cations or anions are temporarily stored in capacitive electrodes, counterbalanced by electrons to obey electro-neutrality. A periodical switch of feed water is required to revert the ionic and electrical current direction. This ion and electron transport enables the conversion of the ionic current into an electrical current without redox reactions. Such novel capacitive reverse electrodialysis (CRED) system demonstrates an average power density only slightly lower than that of RED with conventional redox reactions of $Fe(CN)_6^{3-/4-}$, but much higher compared to capacitive mixing technologies (CAPMIX) or RED using NaCl as electrode rinse solution (Fig. 8). As an additional benefit, CRED can operate without the circulation of electrode rinse solution as no redox reactions are required, which simplifies the system and saves pumping costs.

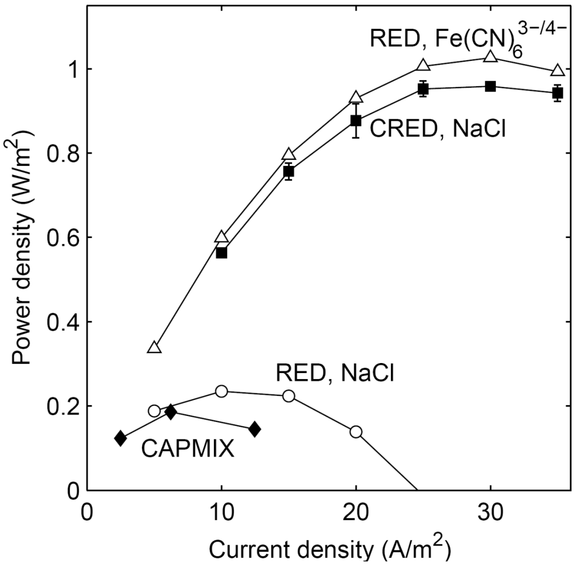

*Figure 8: Average (gross) power density obtained with capacitive reverse electrodialysis (CRED) and RED stacks with conventional electrode systems, both with 30 membrane cells, and the average power density obtained from capacitive mixing reported in previous research (CAPMIX) [14]. For CRED stacks, the feedwater was switched when 15 kC/m$^2$ was transferred. The feedwater was not switched in the conventional electrode systems. Standard deviations are available for the CRED measurements only (some are smaller than the marker).*

## Application and implementation

Commercial application of reverse electrodialysis requires a high power density, low pumping costs and insensitivity to membrane fouling. The (gross and net) power densities have been roughly doubled in this research, using microscopic thin fresh water compartments and introducing profiled membranes to integrate the spacer functionality. The use of air sparging and feed water switching as anti fouling strategies indicate that a RED stack with profiled membranes and air sparging can operate continuously with acceptable pumping losses using natural feed water for more than 2 months. Moreover, the use of capacitive electrodes and new membrane stack designs, filed in two patent applications [15, 16], provide designs for practical application of this technology.

This knowledge and corresponding improvements have been valorized in the world's first pilot plant for energy production from mixing seawater and river water, located at the Afsluitdijk in The Netherlands (Fig. 9). The operator of this pilot plant, REDstack B.V., has been closely participated in the performed PhD research and enabled to facilitate realistic experiment conditions. In a broader context, the development of profiled membranes and the present anti fouling strategies have interest in adjacent ion exchange membrane technologies, which are aiming as well for reduced ohmic resistance, increased active membrane area and minimized pumping costs. Research in e.g. microbial RED [17] and electrodialysis (ED) [18] have been referring to these advances already.

*Figure 9: Pilot plant facility for reverse electrodialysis at Afsluitdijk, The Netherlands. Salt water supplied from the left side of this dam (Wadden sea), while fresh water is obtained from the right side of the dam (IJsselmeer).*

Finally, the economical perspective for this technology has been estimated based on the state of the art. The economical perspective strongly depends on the practically obtained (net) power density and costs for fouling control (chapter 11). The financial feasibility can be estimated from the current RED stack performance, assuming the use of monovalent ions, optimization of the current design (resulting in a net power density of 2.7 $W/m^2$) and estimated costs for fouling control (1850 €/kW plus operational costs for pre-filtration with mesh sizes of tens of µm). Assuming these parameters can be met for large scale operation, RED can be competitive with other renewable energy sources at a membrane price of approximately 4 € per $m^2$ of membrane area. Although the current prices for commercial ion exchange membranes are an order of magnitude higher, this criterion is considered feasible, as the knowledge on ion exchange membranes specifically for RED has just been developed [19] and the RED-market has a huge potential to grow.

## References

[1] J.N. Weinstein, F.B. Leitz, Electric Power from Differences in Salinity: The Dialytic Battery, Science, 191 (1976) 557-559.

[2] EIA, International energy outlook 2010, U.S. Department of Energy, Washington D.C., 2010.

[3] R.E. Pattle, Production of Electric Power by mixing Fresh and Salt Water in the Hydroelectric Pile, Nature, 174 (1954) 660-660.

[4] J. Veerman, R.M.D. Jong, M. Saakes, S.J. Metz, G.J. Harmsen, Reverse electrodialysis: Comparison of six commercial membrane pairs on the thermodynamic efficiency and power density, Journal of Membrane Science, 343 (2009) 7-15.

[5] J.W. Post, H.V.M. Hamelers, C.J.N. Buisman, Energy Recovery from Controlled Mixing Salt and Fresh Water with a Reverse Electrodialysis System, Environmental Science & Technology, 42 (2008) 5785-5790.

[6] P.E. Długołęcki, K. Nijmeijer, S.J. Metz, M. Wessling, Current status of ion exchange membranes for power generation from salinity gradients, Journal of Membrane Science, 319 (2008) 214-222.

[7] R.E. Lacey, A.C. Tanquary, Energy by Reverse Electrodialysis, in, Southern Research Institute, Birmingham, Alabama, 1978, pp. 89.

[8] R.E. Lacey, Energy by Reverse Electrodialysis, Ocean Engineering, 7 (1980) 1-47.

[9] J. Veerman, J.W. Post, M. Saakes, S.J. Metz, G.J. Harmsen, Reducing power losses caused by ionic shortcut currents in reverse electrodialysis stacks by a validated model, Journal of Membrane Science, 310 (2008) 418-430.

[10] P.E. Długołęcki, A. Gambier, K. Nijmeijer, M. Wessling, Practical Potential of Reverse Electrodialysis As Process for Sustainable Energy Generation, Environmental Science & Technology, 43 (2009) 6888-6894.

[11] P.E. Długołęcki, B. Anet, S.J. Metz, K. Nijmeijer, M. Wessling, Transport limitations in ion exchange membranes at low salt concentrations, Journal of Membrane Science, 346 (2010) 163-171.

[12] O.S. Burheim, F. Seland, J.G. Pharoah, S. Kjelstrup, Improved electrode systems for reverse electro-dialysis and electro-dialysis, Desalination, 285 (2012) 147–152.

[13] P.E. Długołęcki, J. Dąbrowska, K. Nijmeijer, M. Wessling, Ion conductive spacers for increased power generation in reverse electrodialysis Journal of Membrane Science, 347 (2010) 101-107.

[14] F. Liu, O. Schaetzle, B.B. Sales, M. Saakes, C. Buisman, H.V.M. Hamelers, Effect of additional charging and current density on the performance of Capacitive energy extraction based on Donnan Potential, Energy & Environmental Science, 5 (2012) 8642-8650.

[15] D.A. Vermaas, J. Veerman, M. Saakes, Reverse electrodialysis energy generating system using capacitive electrodes and method there for, patent application WO2013147593 A1, 2012.

[16] D.A. Vermaas, I. Hitsov, O. Schaetzle, O. Galama, M. Saakes, Device and method for performing an ion-exchange process, patent application NL 2011331, 2013.

[17] J. Liu, G.M. Geise, X. Luo, H. Hou, F. Zhang, Y. Feng, M.A. Hickner, B.E. Logan, Patterned ion exchange membranes for improved power production in microbial reverse-electrodialysis cells, Journal of Power Sources, 271 (2014) 437-443.

[18] V.V. Nikonenko, A.V. Kovalenko, M.K. Urtenov, N.D. Pismenskaya, J. Han, P. Sistat, G. Pourcelly, Desalination at overlimiting currents: State-of-the-art and perspectives, Desalination, 342 (2014) 85-106.

[19] E. Guler, Y. Zhang, M. Saakes, K. Nijmeijer, Tailor-Made Anion-Exchange Membranes for Salinity Gradient Power Generation Using Reverse Electrodialysis, ChemSusChem, 5 (2012) 2262-2270.