Technoport RERC Research 2012

CAPMIX - Deploying Capacitors for Salt Gradient Power Extraction

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Abstract

The process of mixing sea and river water can be utilised as a power source. At present, three groups of technology are established for doing so; i) mechanical; Pressure Retarded Osmosis PRO, ii) electrochemical reactions; Reverse ElectroDialysis (RED) and Nano Battery Electrodes (NBE) and iii) ultra capacitors; Capacitive Double Layer Expansion (CDLE) and Capacitors charge by the Donnan Potentials (CDP). The chemical potential for salt gradient power systems is only limited by the feed solution concentrations and is the same for all types of salt power branches, but the electric work to the grid, however, relies on the route of conversion and means chosen therein. The CAPMIX project is a joint project to develop and explore ultra capacitors for doing so.

Ultra-capacitor materials can interact with sea and river water in order to be deployed as an electricity source. The author consortium is currently exploring two routes to extract the potential free energy from mixing sea and river water by such means. These two routes are the Capacitive Double Layer Expansion (CDLE) and Capacitors charge by the Donnan Potentials (CDP), which are both recently reported, since 2009. The denominator of the two processes is the porous carbon capacitors constituting the capacitors where the chemical energy is converted into electric energy (current). The CDP differs from the CDLE mainly because it includes the use of membranes in addition to the capacitor materials.

Keywords: Salt Gradient Power (SGP), Blue Energy, Capacitive Double Layer Expansion (CDLE), Capacitive Donnan Potential (CDP), Reverse ElectroDialysis (RED), Pressure Retarded Osmosis (PRO)

1. Introduction

Ever since Pattle reported electricity production from the hydroelectric pile containing 47 pairs of membranes [1], the interest for harvesting the potential free energy of mixing naturally occurring water bodies

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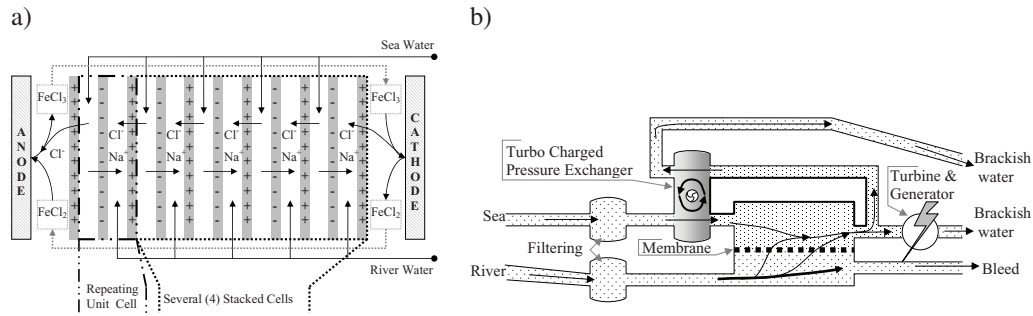
a)   b)

Fig. 1: a) gives a schematic over view of an RED plant [12, 13] and b) of a surface PRO plant [14, 15]. The figures are modified reproductions.

has remained. Pattle reported a process that today is known as Reverse ElectroDialysis (RED), however, many other technologies have emerged since then. All over, the family of salt gradient power technologies have been given the name "*Blue Energy*" [2, 3].

The interest for Blue Energy has been intensified over two time periods, in the seventies and during the last decade, both periods recently after a lowered oil feed supply security [4]. In the seventies and until quite recently, the two dominating technologies for Blue Energy where Reverse ElectroDialysis (RED) and Pressure Retarded Osmosis (PRO), respectively.

The world wide potential power for this benign and non-polluting electricity source is in the order of 2 TW [5, 6]. If converting a fifth of the world potential, Blue Energy holds potential to supply a good fraction of the present electricity consumption (2.3 TW in 2009 [7]). During the seventies, Lacey concluded that the membrane prices were too expensive for commercial RED [8]. Skilhagen et al. stated that with currently commercial available PRO/RO[1] membranes a power density of 5 W m^{-2} would be required in order to justify the investment. Commercial membranes only offer in the order 3 W m^{-2} with sea and river water solutions [9], while new non-commercial membranes offer potentially up to 10 W m^{-2} [10]. Cost estimates for the latter is yet to be seen, though perhaps the RED membrane cost estimation is more promising. Post et al. suggested that because the current RED/ED[2] membrane prices is characterised by niche markets and therefore relatively high, the enormous area requirements for Blue Energy applications (in the order km^2 per MW$_e$) will change the market situation and lower the membrane price. Moreover, the assumption that the price will reduce to a level low enough for RED commercialisation is based on the fact that the cost of the polymeric materials used in membrane manufacturing is half of the price required RED commercialisation. In other words, producing and supplying membranes for large scale RED holds room for significant profit margins within the price requirement for RED [11].

1.1. CAPMIX - a novel approach

With two technologies at pre-commercialisation, other novel technologies emerge as a natural consequence of the increased attention within the field of Blue Energy. The CAPMIX is a European consortium project aiming to explore two such technologies. The chosen technologies are still quite immature and the objective of this paper is to give an introductory review at an early stage in the technological development.

2. Traditional Blue Energy

2.1. Reverse Electrodialysis - RED

A process scheme for RED is depicted in Fig. 1a. The core of the technology is the repeated unit of sea water feed compartment, Cationic Selective Membrane (CSM), river water feed compartment and an Anion

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[1]RO - Reverse Osmosis

[2]Reverse ElectroDialysis/ElectroDialysis

Selective Membrane (ASM). [12, 13] In the repeated unit cell a majority of anions migrate towards the anode and cations towards the cathode. This spontaneous process of ionic current is converted to electronic current by a red-ox reaction, here exemplified with iron chloride [16], though many other possible red-ox systems exists [17]. For a pair of membranes, the potential, $\Delta\phi_{Donnan}$, between two solutions at constant temperature is given by Eq. 1 [18, 19], where $\bar{\alpha}$ is the mean perm selectivity of the two membranes, R is the universal gas constant, T is the temperature, F is the Faraday constant and a_i is the activity of salt in the two solutions, respectively.

$$\Delta\phi_{Donnan} = \bar{\alpha}\frac{RT}{F}\ln\left[\frac{a_c}{a_d}\right] \tag{1}$$

Currently the largest *membrane* area specific power density for RED is reported to be 2.2 W m^{-2} [20]. Due to inconvenient spacer and flow compartment design, a loss of 1 W m^{-2} must be accounted for [20]. Thus the reported net power density is 1.2 W m^{-2}. Cleaning and pretreatment for the feed waters is reported to be less than ten percent of the electric work generated in the stack. Scaling up the RED technology plant is currently planned to happen during the spring and the summer of 2012, when a 50 kW plant will be built in the north of the Netherlands. It has previously been stated that membrane prices required for RED should be less than 10 euro m^{-2} with a net power density of 1.2 W m^{-2}[11]. The price of the membrane will drop with technology development and increased volume (membrane total area) demands.

2.2. Pressure Retarded Osmosis - PRO

A possible process scheme for a surface PRO plant is sketched in Fig. 1b. Due to the difference in chemical potential of the water, the osmotic pressure builds up across a membrane mainly selective to water [21]. The dilute water (river water) will thus pressurise the concentrated solution (sea water) and permeate the membrane such that the excess water stream of the concentrated feed compartment can be used to drive a turbine. The osmotic pressure difference, $\Delta\pi$, can be expressed by the activity of the salt in in the two solutions by van't Hoff's equation, Eq. 2 [22].

$$\Delta\pi = RT\,(a_c - a_d) \tag{2}$$

The Norwegian company Statkraft has been working on PRO since 1997 and has built the first scale up power plant in the world located at Hurum - an hour's drive outside Oslo (capital of Norway) [23]. Accordingly, Statkraft reported to initially operate this as a 10 kW prototype power plant using 2000 m^2 of membrane.

3. Emerging Blue Energy

Deploying electrochemical ultra (or sometimes referred to as super) capacitors for salt gradient power is among the most significant recent advances within the research field of Blue Energy. The novelty and significance lies within the transient nature of the processes and also the non-red-ox and non-mechanical conversion of the energy. Currently two approaches are being exploited, Capacitive Double Layer Expansion (CDLE) and energy extraction by the means of Capacitors and the Donnan Potential.

In adition to the ultra capacitor techniques, one other approach for Blue Energy were also recently discovered and reported [24]. As a proof of principle, the Nano Battery Electrode approach (NBE) obtained in the order 10 - 15 μW m^{-2} [24]. Again, also for this technology the driving potential is given by the reversible potential difference (chemical potential divided by the Faraday constant) between sea and river water solutions.

Blue energy can in general be said to still be an emerging technology, taking into account that there is at least 200 publications in 2011 for Reverse Osmosis alone and about 15-20 for Blue Energy [25, 26]. Still, however, within the community of Blue Energy, CDLE, CDP and NBE are genuinely newcomers. This is clearly illustrated from Fig. 2 where one can see that not only are these three technologies novel - they are also fairly unexplored. The figure consider searches including hits for the wordings "Pressure Retarded Osmosis", "Reverse Electrodialysis", and the required equivalents within the time frame the last thirty five years. Superimposed in the upper right corner is an expansion of the journal dissemination that in addition fractionate the three novel technologies in the time frame of 2006 and up to this point.
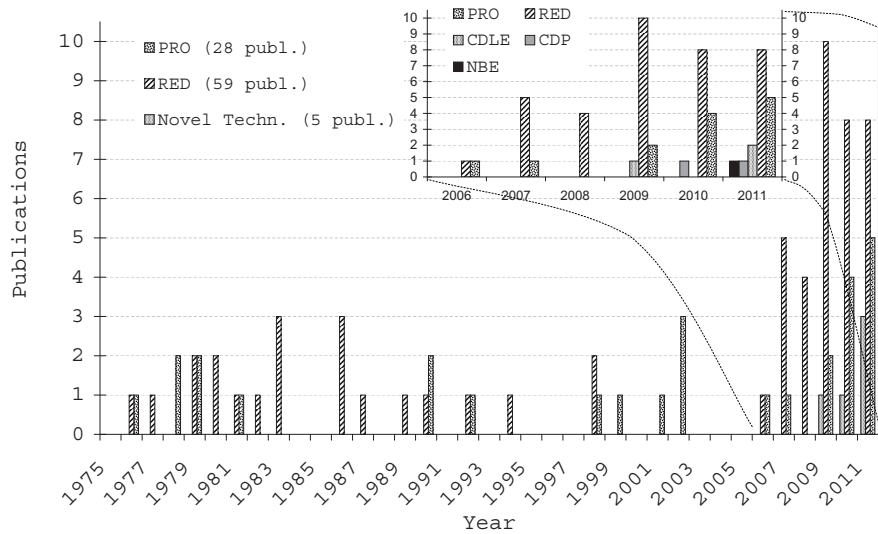
Fig. 2: Citation overview for the last 35 years for the Blue Energy technologies mentioned in this paper [25, 26].

3.1. Blue Energy by Capacitive Double Layer Expansion - CDLE

The first report on capacitors deployed for Blue Energy was by Brogioli [27]. The sketches to the left in Fig. 3 shows first the circuit analogy for the system, next the conceptual design and finally an example of a potential-charge cycle [28]. The CDLE technique is based on naturally occurring double layers inside the porous capacitors deployed. By the Guy-Chapman-Stern theory (GCS) the possible route to modify the potential and charge of these layers is given [31, 32]. These process potential and charge steps can be seen by the blue (upper, river water) and the red (lower, river water) lines in the lower left graph in Fig. 3. With the help of the corresponding circuit analogy, it can be understood that the external power source increases the potential and the charge of the capacitors while the circuit is closed and subject to sea water. Next, as indicated in the middle sketch, where an aqueous solution is flowing between two porous carbon coated electrodes, a river water solution can replace the sea water solution. Doing this at open circuit with an already charged pair of electrodes results in an additional increase in the potential. Next, closing the circuit, the potential is lowered while a current is being drawn with a behaviour much like what is described by Eq. 3, where $\Delta\phi_i$, C_{cell}, t and R_{cell} are the cell potential, the capacitance, time from the start of a cycle step and the ohmic resistance of the cell. At a convenient point (see the green frames in lower left of Fig. 3 the dilute (river) water stream is replaced by a concentrate (river) water stream. As it is explained that during the second and fourth step the double layer of the electrodes expands (and contracts respectively), the technology is abbreviated by CDLE for Capacitive Double Layer Expansion [28].

$$\Delta\phi_{CDLE}(t) = \Delta\phi_{initial}\exp\left(-\frac{t}{C_{cell}R_{cell}}\right) \tag{3}$$

In the first part of this four step cycle electric work is added, but the electric work received from the third step is larger so that the net electric energy balance is spontaneous. Thus it can be justified to deliver this first fraction of work by an external source. The power density for these first technology demonstration cells were in the order 7 mW m^{-2}, though improving the capacitance, C_{cell} and the resistance of the cell circuit, R_{cell}, holds great potential for improving the output power - a subject we to return to later.

3.2. Blue Energy by Capacitors and the use of the Donnan Potential - CDP

The second Blue Energy technology that reported to deploy capacitors was reported by Sales et al. shortly after the initial CDLE paper [29]. By covering one electrode with an ASM (Anionic Selective

Capacitive Double Layer Expansion - CDLE
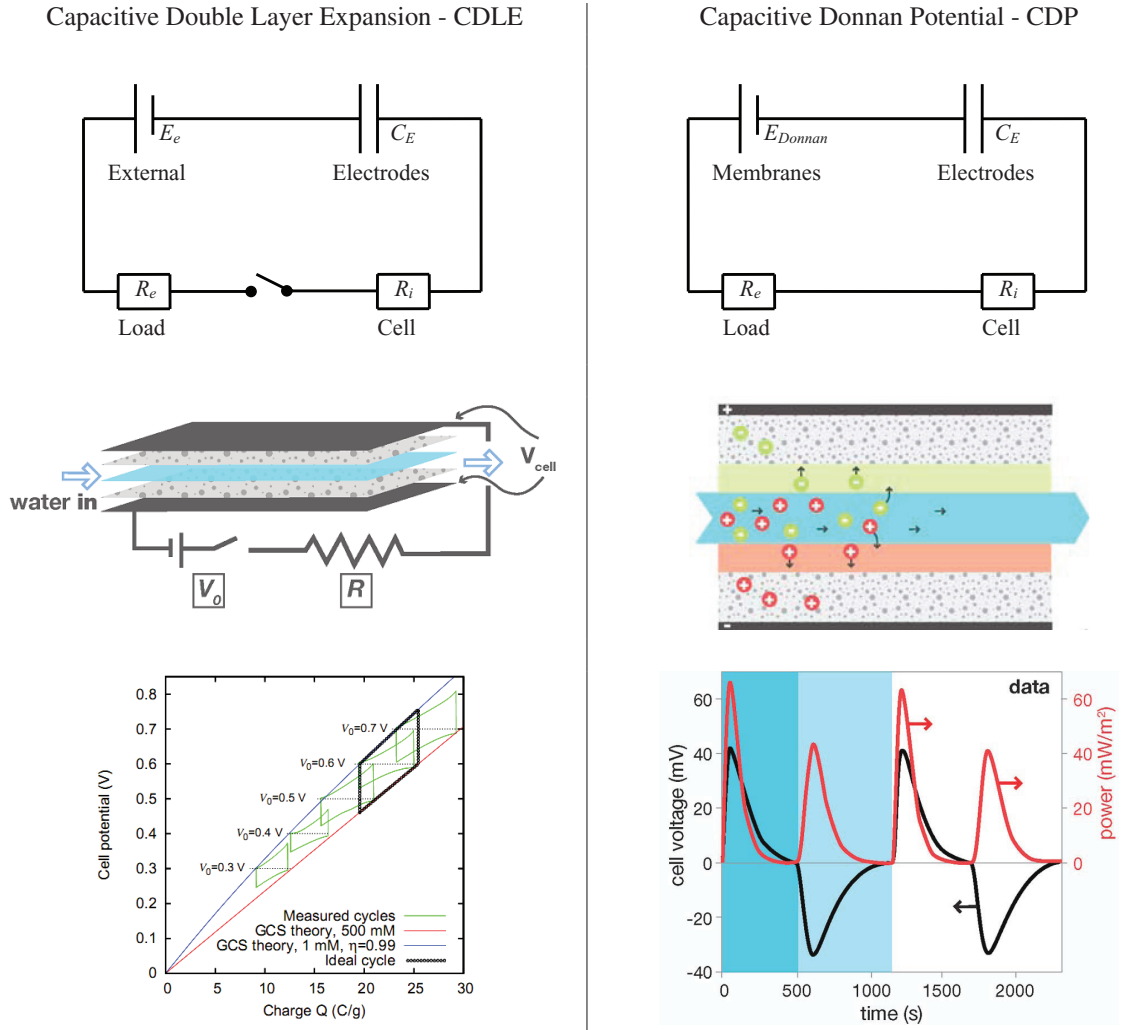
Capacitive Donnan Potential - CDP

Fig. 3: Circuit analogy (upper), sketch of cell design with black current collectors grey porous capacitive material and blue water flow compartment (middle) and potential/charge time response during operation (lower) for the CDLE (left) [27, 28] and the CDP (right) [29, 30], respectively.

Membrane) and the other electrode with a CSM (Cationic Selective Membrane), the driving potential of the process was entirely embedded inside the cell assembly, which means that the technology went from relying on an *externally* power source to become a completely *internally* driven power source. This made the process not only spontaneously driven but also removed the need of an external activation source. This is illustrated by the circuit analogy depicted to the upper right in Fig. 3. The process is typically reported to be run continuously at closed circuit, so that whenever a new concentration is introduced to the flow cell (middle right in Fig. 3) a stream of ions or from the electrodes (for sea and river water like solutions, correspondingly) is induced by the Donnan potential of Eq. 1 [30]. Hence, from the use of Capacitors and the Donnan Potential the technology goes by the acronym of CDP. The potential time dependency can be described by the Donnan potential times the capacitive time dependency as in Eq. 4.

$$\Delta\phi_{CDP}(t) = \Delta\phi_{Don}\exp\left(-\frac{t}{C_{cell}R_{cell}}\right) \qquad (4)$$

As can be seen from the lower right part of Fig. 3, one of the cycles gives off far less potential and power

Table 1: Overview of the four different technologies evaluated in this paper and some of their characteristics.

Name/ Abbrevation	Drive Potential	Membrane Characteristics	Process Power Characterisitcs	Auxiliary Energy Converter System
PRO	$\Delta\pi$	Water selective	Stationary	Hydraulic Turbine
RED	$\Delta\phi_{Don}$	Ionic Selective	Stationary	Red-ox Electrode Syst.
CDLE	$\Delta\phi_{initial}e^{-\frac{t}{\tau}}$	None	Transient	Porous Ultra Capacitor
CDP	$\Delta\phi_{Don}e^{-\frac{t}{\tau}}$	Ionic Selective	Transient	Porous Ultra Capacitor
NBE	$E^{rev}\left(\frac{SeaWater}{RiverWater}\right)$	None	Transient	Nano-Electrodes

than the other - this being the lower potential curves related to the river water feed cycle. As is indicated in Eq. 4, increasing the ohmic resistivity of the cell will lead to lowered transient discharge. Additionally, from Ohm's law it follows that due to the lower conductivity of river water, more of the potential free energy is subject to parasitic ohmic losses. For the sea water and the river water cycle steps, 60 and 40 mW m^{-2} were reported, correspondingly.

3.3. Material Design Development

As goes with development of materials for the two processes, CDLE and CDP, it can be seen from Eqs. 3-4 that modifying R_{cell} and C_{cell} are the two common key parameters in material design and process optimisation. As R_{cell} truly represents a parasitic loss in the two processes, this term needs to be lowered both for the electrodes and for the electrolyte compartment. This will simultaneously lead to a lower time dependency term, cf. Eqs. 3-4. Another thing to be optimised along with the resistivity of the cell is the capacitance. Lowering R_{cell} usually means lowering C_{cell}, simply because the amount of material in the electrode goes down. Increasing the conductivity of the porous electrode material, on the other hand, allows for lowered resistance with constant specific capacitance. Shortening the active porous layer thickness will again lead to a lowered storage of potential free energy, because the maximum charge that can be stored is lowered. Optimising the total capacitance and the resistivity is among the challenges yet to be properly addressed. Moreover, finding active materials with intrinsically optimised C_{cell}- and R_{cell} properties is another way around this subject.

3.4. Process Design

The final process design of the CDLE and the CDP is still a subject to development and future investigation. For Several of the cells that have been deployed this far, the only objective has been to give (improved) proof of principle [27, 28, 29] or to address the need for better cell design [30]. Moreover, it was shown that accounting for the losses due to non-optimal cell design, at least the CDP technology holds the same potential for current, potential and power density as the RED technology.

4. Blue Energy Overview

Up to this point we have presented several different reported technologies to exploit the Blue Energy potential. The approaches are diverse, which we have tried to illustrate in Table 1. The impact of the technological and, also, consortium and partnership diversity is yet to be seen, though diversity might prove to be important in making Blue Energy a benign source of pure and renewable electricity.

Blue Energy technologies are all likely to become viable if included into an appropriate business plan with suitable partners. Table 1 furthermore is meant to illustrate this and it aims to give an overview of what the qualitative properties of Blue Energy that first meets the eyes are. Here, we intend not to discuss power densities too extensively as this alone may not necessarily be justified in a comparison. For instance, the reported power density of CDLE, in terms of referring to the electrode area, is currently not really peaking

the list of output power density among the Blue Energy technological family, but on the contrary the material investments are rather low as no membranes are required.

Moreover, the three most recently reported technologies give a transient power output, i.e. the power is not constant or stationary. This means that e.g. a pulse of river water is fed to the electrode compartment and thus induces a power output for some period of time. Alternating the feed of sea and river water, like for these technologies, might at first appear inconvenient for a large scale industrial process. This is as one might think that a stationary system is easier to manage and sustain. On the contrary, however, several fouling studies have demonstrated that reverting the flow, both the inlet/outlet directions and the concentration in each compartment (sea/river water), can significantly impede fouling mechanisms and to a great extent restore the performance of Blue Energy Systems, e.g [33, 34, 35, 36, 37, 3]. This is yet another example, that the complexity which the Blue Energy technologies are subject to opens for a great diversity within technological possibilities.

5. Concluding Remarks

Although the CDLE and the CDP at this point are far from being competitive with the more developed RED and PRO on a commercial level, the first reported efforts have shown promising results and by developing the CDLE and the CDP in parallel as a collaboration effort several commercial opportunities may emerge.

In general, Blue Energy holds a great diversity in technological aspects and challenges. Each technology has its advantages and disadvantages that can be taken advantage of if in the hands of the right consortium. CAPMIX is an appropriate European union effort to deploy porous capacitors for Blue Energy development.

Acknowledgement

References

[1] R. E. Pattle, Production of electric power by mixing fresh and salt water in the hydroelectric pile, Nature 174 (1954) 660.

[2] J. W. Post, J. Veerman, H. V. M. Hamelers, G. J. W. Euverink, S. J. Metz, K. Nijmeijer, C. J. N. Buisman, Salinity gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis, Journal of Membrane Science 288 (2007) 218–230.

[3] J. W. Post, Blue energy: Electric production from Salinity Gradients by Reverse Electrodialysis, PhD thesis Wageningen University, 2009.

[4] A. Achilli, A. E. Childress, Pressure retarded osmosis: From the vision of sidney loeb to the fist prototype installation – review, Desalination 261 (2010) 205–211.

[5] J. N. Weinstein, F. B. Leitz, Electric power from differences in salinity: the dialytic battery, Science 191 (1976) 558.

[6] G. L. Wick, W. R. Schmitt, Power from salinity gradients, Mar. Technol. Soc. J. 11 (1977) 16–21.

[7] I. I. E. Agency, Annual report.

[8] R. E. Lacey, Energy by reverse electrodialysis, Ocean Engineering 7 (1980) 1–47.

[9] A. Achilli, T. Y. Cath, A. E. Childress, Power generation with pressure retarded osmosis: An experimental and theoretical investigation, Journal of Membrane Science 343 (2009) 42–52.

[10] N. Y. Yip, A. Tiraferri, W. A. Phillip, J. D. Schiffman, L. A. Hoover, Y. C. Kim, M. Elimelech, Thin-film composite pressure retarded osmosis membranes for sustainable power generation from salinity gradients, Environ. Sci. Technol. 45 (2011) 4360–4369.

[11] J. W. Post, C. H. Goeting, J. Valk, S. Goinga, J. Veerman, H. V. M. Hamelers, P. J. F. M. Hack, Towards implementation of reverse electrodialysis for power generation from salinity gradients, Desalination and Water Treatment 16 (2010) 192–193.

[12] G. L. Wick, Power from salinity gradients, Energy 3 (1978) 95–100.

[13] S. K. Ratkje, T. Holt, L. Fiksdal, Effect of biofilm formation on salinity power plant output on a laboratory scale, AIChE symposium series 248 (1986) 39–44.

[14] S. Loeb, T. Honda, M. Reali, Comparative mechanical efficiency of several plant configurations using a pressure-retarded osmosis energy converter, Journal of Membrane Science 51 (1990) 323–335.

[15] K. V. Peinemann, S. E. Skilhagen, T. Thorsen, T. Holt, Membrane processes in energy supply for an osmotic power plant, Desalination 224 (2008) 64–70.

[16] 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.

[17] J. Veerman, M. Saakes, S. J. Metz, G. J. Harmsen, Reverse electrodialysis: evaluation of suitable electrode systems, J Appl Electrochem 40 (2010) 1461–1474.

[18] S. R. deGroot, P. Mazuur, Non-equilibrium Thermodynamics, 2nd Edition, Dover, 1985.

[19] S. Kjelstrup, D. Bedeaux, Non-Eqilibrium Thermodynamics of Heterogeneous Systems, World Scientific - Series on Advances in Statistical Mechanics - Volume 16, 2008.

[20] D. A. Vermaas, M. Saakes, K. Nijmeijer, Doubled power density from salinity gradients at reduced intermembrane distance, Environ. Sci. Technol. 45 (2011) 7089–7095.

[21] K. Gerstandt, K. V. Peinemann, S. E. Skilhagen, T. Thorsen, T. Holt, Membrane processes in energy supply for an osmotic power plant, Desalination 224 (2008) 64–70.

[22] Atkins, Physical Chemistry, 7th Edition, Oxford University Press, 2002.

[23] S. E. Skilhagen, J. E. Dugstad, R. J. Aaberg, Osmotic power–power production based on the osmotic pressure difference between waters with varying salt gradients, Desalination 220 (2008) 476–482.

[24] F. La Mantia, M. Pasta, H. D. Deshazer, B. E. Logan, Y. Cui, Batteries for efficient energy extraction from a water salinity difference, Nano Lett. 11 (2011) 1810–1813.

[25] ISI web of knowledge, http://isiknowledge.com/, November 11, 2011.

[26] Scopus, www.scopus.com, November 11, 2011.

[27] D. Brogioli, Extracting renewable energy from a salinity difference using a capacitor, Physical Review Letters 103 (2009) 058501 (1–4).

[28] D. Brogioli, R. Zhao, P. M. Biesheuvel, A prototype cell for extracting energy from a water salinity difference by means of double layer expansion of double layer in nanoporous carbon electrodes, Energy Environ. Sci. 4 (2011) 772–777.

[29] B. B. Sales, M. Saakes, J. W. Post, C. J. N. Buisman, P. M. Biesheuvel, H. V. M. Hamelers, Direct power production from a water salinity difference in a membrane-modified supercapacitor flow cell, Environ. Sci. Technol. 44 (2010) 5661–5665.

[30] O. S. Burheim, B. B. Sales, O. Schaetzle, F. Liu, H. V. M. Hamelers, Auto generative capacitive mixing for power conversion of sea and river water by the use of membranes, Submitted to: Journal of Energy Resources Technology December (2011) 1–10.

[31] P. M. Biesheuvel, M. van Soestbergen, Counterion volume effects in mixed electrical double layers, Journal of Colloid and Interface Science 316 (2007) 490–499.

[32] R. J. Hunter, Foundation of Colloid Science, Clarendon Press, Oxford, 1993.

[33] H. C. Flemming, Reverse Osmosis: Mechanistic aspects of reveres osmosis biofouling and prevention, van Nostrand Reinhold, Ch. 6, 1993.

[34] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, Journal of Membrane Science 320 (2008) 292–302.

[35] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents, Journal of Membrane Science 348 (2010) 337–345.

[36] W. Thelin, Fouling in Pressure Retarded Osmosis, Doctoral Theses at NTNU, 2006:178.

[37] H. Vrouwenvelder, Biofouling of Spiral Wound Membrane Systems, PhD thesis Delft University of Technology, 2009.