

Energy generation by reverse electro dialysis

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Abstract. In this work, the process of generating electricity from the water salinity gradient (RED) using the Russian produced ion exchange membranes MK-40 and MA-41 was investigated. The experiments were carried out with a saturated brine of sodium chloride in a chamber with salt water and with a solution of sodium chloride with a concentration range 0.017-3.39 g/l in a chamber with fresh water. The maximum value of the specific power obtained was 0.3 W/m². The dependence of the specific power of the salt content in the chamber with fresh water was investigated and its optimal value (0.5 – 1.5 g/l) was found. The dependence of the received power on the flow velocity in chamber with fresh water was studied. The RED process with three different RedOx systems was studied and their effect on the received power was determined. The highest power was obtained for the RedOx system of potassium ferrocyanide. In case of not using the ferro-ferricyanide system leads to a significant decrease in specific power and the release of gaseous chlorine in the anode chamber.

1. Introduction

Recently significant interest in technology of the direct conversion of the salt concentration gradient between salty and fresh water into electricity using Reverse Electrodialysis (RED) is not diminishing, due to the increased demand for alternative and autonomous energy sources. The gradient of salt concentration in salty and fresh water, separated by an ion selective membrane, leads to the formation of a potential difference on membrane assembly.

In the installation, shown in figure 1, consisting of alternating cation and anion exchange membranes, between which salty and fresh water flows, the potential difference appearing on the membranes is summed up and can be used as an energy source. To convert the ion current into the electricity a RedOx reaction must take place in the electrode chambers [2-4]. Thermodynamic calculations show that when 1 m³ of river water (1 g/l NaCl) is mixed with 1 m³ of sea water (30 g/l NaCl), 1.4 MJ of energy can be obtained (equivalent to 0.4 kWh). The obtained energy can be increases when using feed water more saline than seawater. In case of mixing 1 m³ saturated NaCl brine (350 g/l NaCl) and 1 m³ river water, approximately 17 MJ (equivalent to 4.7 kWh) can be obtained. Theoretically, 2400 GW of electric power can be obtained by mixing the global runoff of river water with sea water, 1000 GW from which can be technically used [5-7]. The main problem that prevents the mass use of the reverse electro dialysis process is the large internal electrical resistance of the apparatus, which limits the power received [8-10].



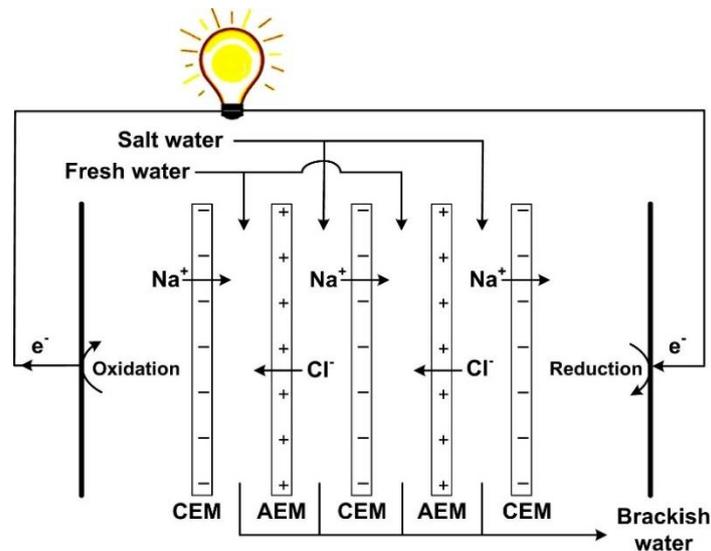


Figure 1. Principle of reverse electro-dialysis (RED) [1].

Of great importance is the selectivity of ion-exchange membranes, as well as the design of the separator, which provides turbulent flow and fixation of the intermembrane distance. As the thickness of the fresh water chamber increases, ohmic losses increase significantly, and with a small intermembrane distance partially filled with an inert separator, the cost of pumping the solution can exceed the useful work of the process [11, 12].

It is known that the efficiency of electricity production by reverse electro-dialysis can be improved using profiled membranes [7]. This allows to abandon the inert spacer and reduce the cost of pumping the solution [7, 13]. Also, the increased surface area positively affects the efficiency of the process. At the same time, it is possible to use highly efficient and inexpensive membrane materials for RED. As such materials, Russian produced heterogeneous ion-exchange membrane materials are promising, which are relatively inexpensive and at the same time have all the necessary properties, which will increase the specific power of the installation and reduce the cost of electricity.

Thus, the production of renewable energy using sea and river water by the method of reverse electro-dialysis is very promising, but not well studied.

The aim of this work is to study the process of generating electrical energy by use of a salt concentration gradient using ion exchange membranes MK-40 and MA-40.

2. Materials and Methods

The objects of study in this work were Russian produced heterogeneous ion exchange membranes MK-40 – a polymer composition of cation exchange resin KU-2 (polystyrene, cross-linked by divinylbenzene), polyethylene and reinforcing fabric. Functional group $-\text{SO}_3^-$, and MA-41 – a polymer composition of anion exchange resin AB-17 (polystyrene, cross-linked by divinylbenzene), polyethylene and reinforcing fabric. Functional group $-\text{N}^+(\text{CH}_3)_3$.

Heterogeneous membranes MK-40, MA-41 passed standard conditioning [14]: the surface of the membrane was wiped with carbon tetrachloride, then it was treated for 24 hours each time with ethyl alcohol, saturated NaCl solution, NaCl solution with a concentration of 100 g/l, NaCl solution with a concentration of 30 g/l. Then the membrane was washed with distilled water until its constant resistance after a 24 h of contact with the membrane.

The experimental setup consisted of an electrochemical cell, 3 LS-301 peristaltic pumps, 2 Agilent U1252B multimeters, a resistance bridge (0.1 Ω – 100 k Ω) and solution containers. Working area of membranes was 5x20 cm². Electrodes were made of titanium covered with platinum. As a model solution of salt water saturated NaCl was used (approximately 350 g/l), model solution of fresh water:

NaCl with a concentration of from 0.017 to 3.39 g/l. The reverse electrodialysis process was carried out with a MK-40/MA-41 membranes with an electrode solution of 0.025 M $K_4Fe(CN)_6$, 0.025 M $K_3Fe(CN)_6$ and 0.25 M NaCl. The flow rate through all chambers varied within 72-384 ml/min.

The appearance of the experimental setup is shown in figure 2, the number of pair chambers in the cell varied from 5 to 20. Cation exchange membranes were placed at the both sides of the membrane package to prevent degradation of the anion exchange membranes because of contact with potassium hexanoferrate.



Figure 2. The appearance of the experimental setup.

To determine the power characteristics, a different load was connected to the cell under study and the current strength and voltage were measured. The load range was from 0 (Short circuit) to 500 Ω . In this way, power versus current density curves were obtained.

With increasing concentration of salt in fresh water, an increase in power occurs due to a decrease in the ohmic resistance of the cell. If the threshold concentration is exceeded, the power characteristics decrease due to a decrease in the concentration gradient.

3. Results and Discussion

The process of generating electrical energy by the reverse electrodialysis method using MK-40 and MA-41 membranes was studied. The power characteristics of an electrochemical generator with a different salinity of fresh water were determined.

The numbers on the right side of figure 3 shows the sodium chloride concentration in the chamber with fresh water. With an increase of the salt concentration in the chamber with fresh water, an increase in the obtained specific power occurs due to an increase of the electric conductivity of the solution. A further increase of the concentration of sodium chloride leads to a decrease of the received power due to a decrease in the concentration gradient in chambers with fresh and salt water.

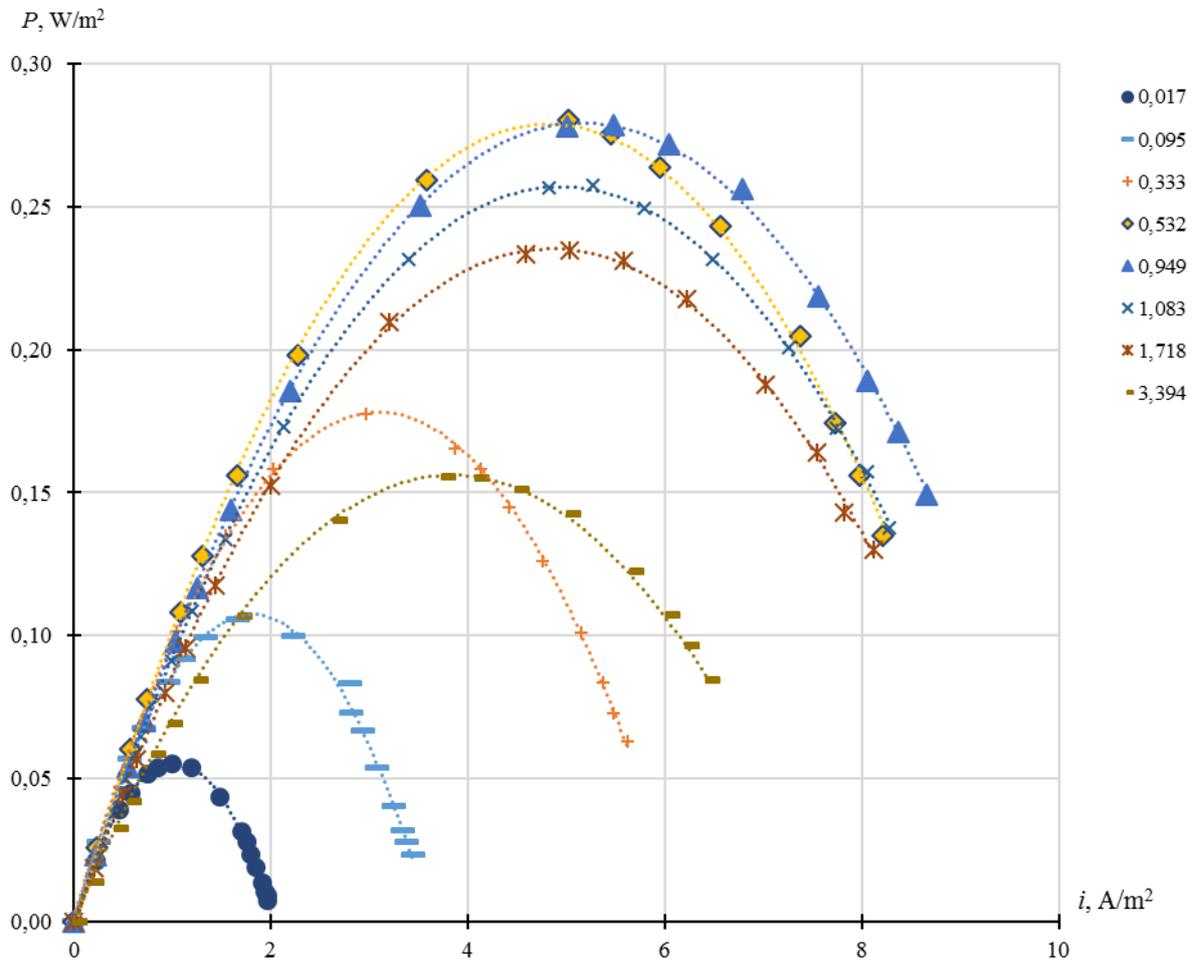


Figure 3. Specific power density versus load current for different salt concentration in “fresh” water.

The maximum specific power obtained was 0.28 W/m^2 with concentration of sodium chloride in fresh water in range 0.5-1 g/l.

Open circuit voltage (OCV) (with zero load) of RED cell with 5 pair chambers were measured (figure 3). Theoretical OCV can be calculated by (1).

$$E_{OCV} = \alpha \cdot N_m \cdot \frac{R \cdot T}{z \cdot F} \cdot \ln \left(\frac{\gamma_s \cdot c_s}{\gamma_f \cdot c_f} \right) \quad (1)$$

In which R is the universal gas constant ($8.314 \text{ J}/(\text{mol} \cdot \text{K})$), T is the absolute temperature (K), F is the Faraday constant ($96485 \text{ C}/\text{mol}$), z is the valence of the ion species (-), γ is the activity coefficient of the salt species (-) and c is the concentration of the salt (mol/liter). The subscripts (s) and (f) indicate salty water or fresh water, respectively.

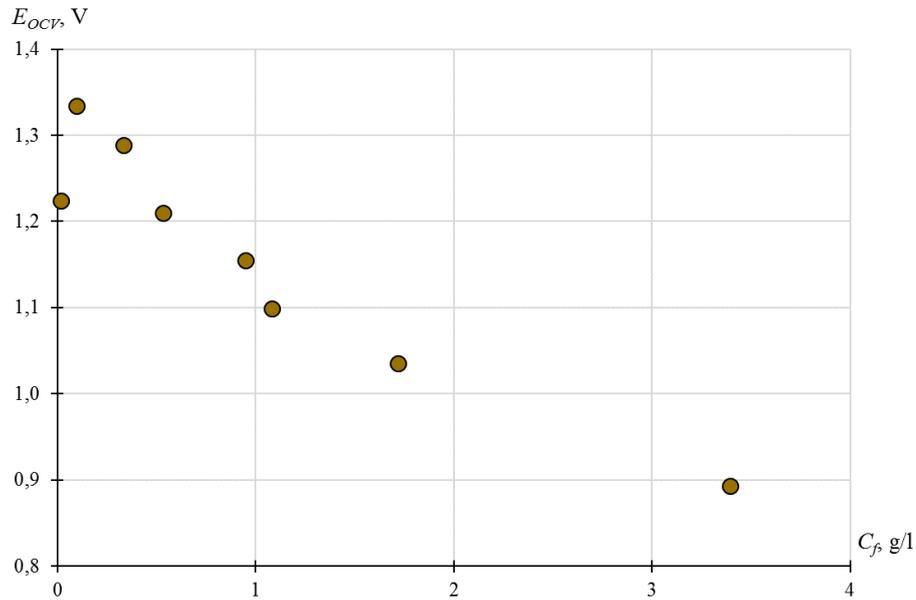


Figure 4. Open circuit voltage dependence of salt concentration in fresh water.

The value of OCV decreases with increasing salt concentration in the chamber with fresh water due to a decrease in the salt concentration gradient. The maximum value was 1.34 V (0.11 V per membrane).

3.1. Specific power dependence of flow rate

The dependence of the specific power of the flow velocity in the chamber with fresh water was investigated. It was shown that with an increase in the flow rate from 72 ml/min to 384 ml/min, the resulting power increases by 15%, however, the energy consumption of pumping the solution significantly increases.

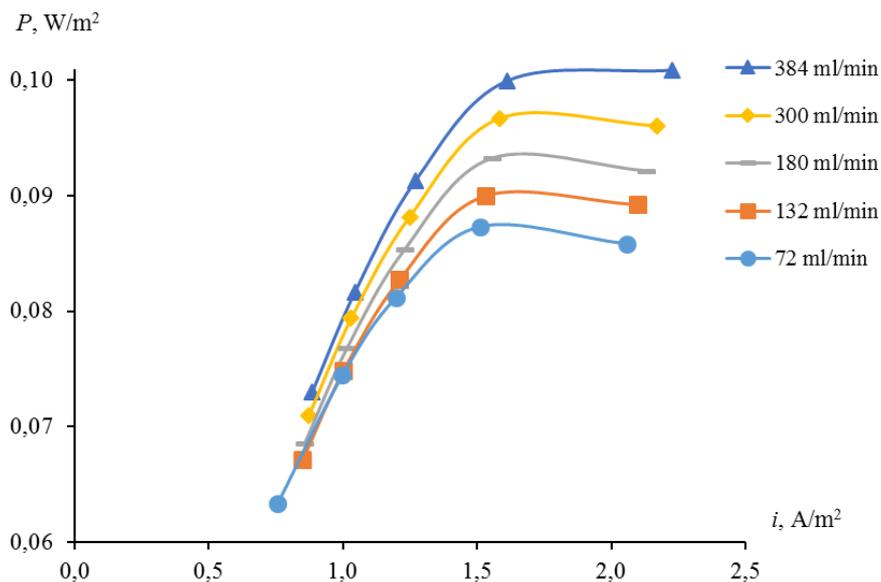
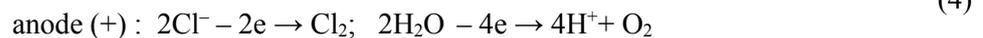
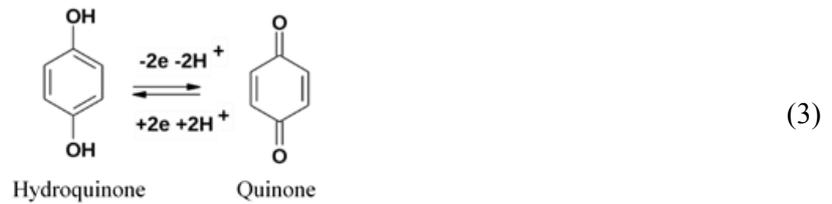


Figure 5. Specific power density versus load current for different flow rates of "fresh" water.

3.2. The effect of the RedOx system on RED process

In the present work, three RedOx systems were used: two reversible (equimolar mixture of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (2)) and Quinone/Hydroquinone (3). In the other case, in the absence of a special RedOx system, water and salt electrolysis occurred in the electrode chambers (4).



From literature data it is known [15] that potassium hexacyanoferrate is most often used, but it's quite toxic and can affect the electrical conductivity of anion exchange membranes.

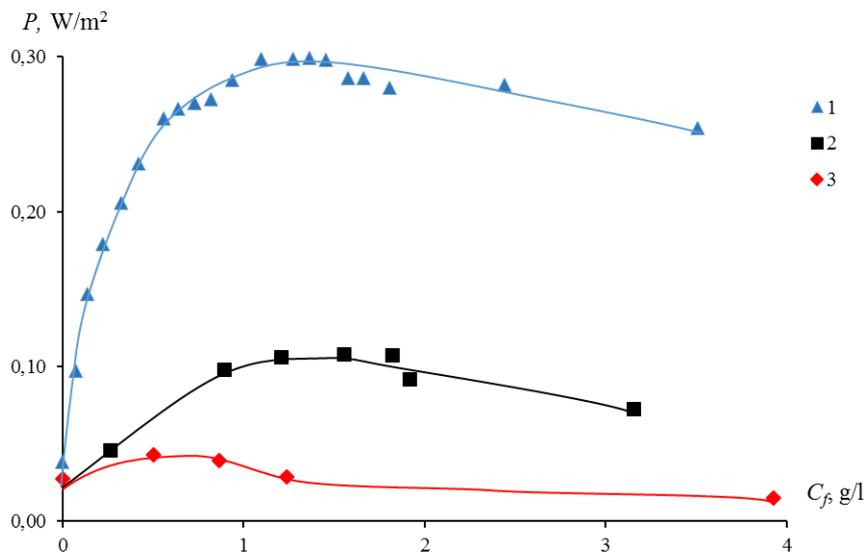


Figure 6. Specific power dependence of salt concentration in fresh water for different RedOx system: 1 - $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ 0.025+0.025 mol/l + NaCl 0.25 mol/l; 2 - NaCl 0.25 mol/l; 3 - Hydroquinone/Quinone (saturated + NaCl 0.25 mol/l).

RED process was carried out using various RedOx systems (Figure 6). For systems (1) and (3), a cell with 5 pair chambers was used. Since the potential drop on the cell is lower than the water decomposition voltage, the cell with 20 pair chambers was used for the RedOx system (2). Studies have shown that when using the Quinone/Hydroquinone system, the resulting specific power is reduced by

7 times, which makes this system unsuitable for RED process. It was also noted that when using RedOx systems (1) and (3) anion-exchange membranes significantly change their color after the experiments. When RED process carried out with water electrolysis in the electrode chambers, the power decreases by 3 times in comparison with the use of hexacyanoferrate, however, additional toxic components are not used. Also, the exception of a special RedOx system should increase the lifetime of the anion exchange membranes. However, in this case, it is also possible the evolution of chlorine gas due to electrolysis.

3.3. The effect of the hexacyanoferrate concentration on RED process

The effect of the concentration of the RedOx pair in the electrode solution on the obtained specific power was investigated. The experiments were carried out with a total concentration of the RedOx pair $K_3[Fe(CN)_6]$ and equimolar $K_4[Fe(CN)_6]$ in the electrode solution in the range of 0-0.1 mol/l with 0.25 M NaCl, the results are presented in table 1.

Table 1. Dependence of the specific power on the concentration of RedOx pair $K_3[Fe(CN)_6]$ + $K_4[Fe(CN)_6]$ in the electrode solution (concentration of sodium chloride in fresh water 1,94 g/l)

Concentration of redox pair, mol/l	Obtained power density
0.000	0.107
0.010	0.281
0.025	0.289
0.050	0.292
0.100	0.310

It was found that with increasing concentration of the RedOx system in the electrode solution, the resulting power slightly increases. However, to a certain value, then goes to a plateau. We can conclude that it's necessary to find an optimal concentration of hexacyanoferrate, and it will be possible to reduce the toxicity of the electrode solution by several times, while the power will change slightly.

4. Conclusion

In the present work the process of electric energy production by the RED process with using Russian produced heterogeneous ion-exchange membranes MK-40 and MA-41 with saturated solution of sodium chloride (approx. 350 g/l) and a solution of sodium chloride with a concentration of 0.017-3.39 g/l were investigated. The maximum obtained specific power was 0.3 W/m². The optimal salt concentration in the chamber with fresh water was 0.5-1.5 g/l. The effect of various RedOx systems on RED process was studied. Maximum power was obtained using potassium hexacyanoferrate. It was shown that the use of the Quinone-Hydroquinone system leads to a decrease in the resulting power by 7 times. In case of refusal to use a special RedOx system when using a sufficiently large number of membranes in a package, the electric current flows due to the electrolysis of water. The resulting power is about 3 times lower than when using potassium hexacyanoferrate, but there is a decrease in the ecological load on the environment.

Acknowledgments

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References

- [1] Vermaas D A, Kunteng D, Saakes M and Nijmeijer K 2013 Fouling in reverse electro dialysis under natural conditions *Water Research* **3** 1289-98
- [2] Han J, Hwang K, Jeong H, Byeon S, Nam J, Kim C, Kim H, Yang S, Choi J-Y and Jeong N 2019 Electrode system for large-scale reverse electro dialysis: water electrolysis, bubble resistance, and inorganic scaling *J. of Applied Electrochemistry* **49** 517-28
- [3] Daniilidis A, Vermaas D A, Herber R and Nijmeijer K 2014 Experimentally obtainable energy from mixing river water, seawater or brines with reverse electro dialysis *Renew Energy* **64** 123-31
- [4] Di S J, Cosenza A, Tamburini A, Micale G and Cipollina A 2018 Long-run operation of a reverse electro dialysis system fed with wastewaters *J. Environ Manag* **217** 871-87
- [5] Post J W, Hamelers H V M and Buisman C J N Energy 2008 Recovery from controlled mixing salt and fresh water with a reverse electro dialysis system *Environmental Science & Technology* **42(15)** 5785-90
- [6] Yip N Y and Elimelech M 2012 Thermodynamic and energy efficiency analysis of power generation from natural salinity gradients by pressure retarded osmosis *Environmental Science & Technology* **46(9)** 5230-9
- [7] Vermaas D A, Saakes M and Nijmeijer K 2011 Power generation using profiled membranes in reverse electro dialysis *J. Membr. Sci.* **385-386** 234-42
- [8] Zhu X, He W and Logan B E 2015 Reducing pumping energy by using different flow rates of high and low concentration solutions in reverse electro dialysis cells *J. Membr. Sci.* **486** 215-21
- [9] Pawlowski S, Crespo J G and Velizarov S 2014 Pressure drop in reverse electro dialysis: experimental and modeling studies for stacks with variable number of cell pairs *J. Membr. Sci.* **462** 96-111
- [10] Vermaas D A, Saakes M and Nijmeijer K 2014 Early detection of preferential channeling in reverse electro dialysis *Electrochim Acta* **117** 9-17
- [11] Post J, Goeting C, Valk J, Goinga S and Veerman J 2010 Towards implementation of reverse electro dialysis for power generation from salinity gradients *Desalination and Water Treatment* **16** 82-93
- [12] Ghaffour N, Lattemann S, Missimer T, Sinha S and Amy G 2014 Renewable energy – driven innovative energy – efficient desalination technologies *Appl. Energy* **1136** 1155-65
- [13] Zabolotskii V I, Loza S A and Sharafan M V 2005 Physicochemical properties of profiled heterogeneous ion-exchange membranes *Russian J. of Electrochemistry* **41(10)** 1053-60
- [14] Berezina N P, Kononenko N A, Dyomina O A and Gnusin N P 2008 Characterization of ion-exchange membrane materials: properties vs structure *Advances in Colloid and Interface Science* **139** 3-28
- [15] Veerman J, Jong R, Saakes M and Metz S J 2009 Reverse electro dialysis: Comparison of six commercial membrane pairs on the thermodynamic efficiency and power density *J. Membr. Sci.* **343** 7-15