Reverse Electrodialysis Power Production - Progress in the development of an innovative system

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Abstract

In this paper we are presenting an innovative salinity gradient power approach based on the reverse electrodialysis technology. The current focus on the combination of fresh water and seawater is limited by the overall electrical resistance, which is determined by the low conductivity of the freshwater compartment. However, we in the REAPower project (www.reapower.eu) are using sea water as the "low concentration" salt solution in combination with brine; a salt solution with a very high salt concentration. This offers a tremendous potential for the improvement of the electrical performance, as shown in several papers before. An inter-disciplinary and international team of specialists are working together since October 2010 for delivering the materials, components and processes that will allow to fully exploiting the potential of this very promising technology. This paper presents the project plan and progress achieved so far in the membrane development and the stack design and construction, with results from the process simulation.

Keywords: brine, ion exchange membranes, modelling, reverse electrodialysis, seawater, stack,

1. Introduction

Salinity gradient power (SGP), also called "osmotic energy" is the chemical energy potential associated with the "controlled" mixing of two salt solutions at different concentrations. The concept of SGP is already known in the literature and was described for the first time in 1954 by Pattle [1]. There are two main techniques considered currently for recovering the osmotic energy of a system and convert it into a more exploitable form: pressure retarded osmosis (SGP-PRO) and reverse electrodialysis (SGP-RE). In the former, SGP is converted into mechanical energy and then to electrical energy by means of turbines using osmotic membranes, i.e. membranes allowing the passage of water and obstructing the passage of salts.

In this paper we are focusing on reverse electrodialysis, where cation and anion conductive membranes are placed in an alternating way in order to produce diluate and concentrate compartments. The concentrate compartment (HIGH) is then filled with the high concentration salt solution while the diluate compartment (LOW) is filled with the low concentration salt solution. The salt concentration difference (salt gradient) between both compartments in the cell pair invokes a Nernst potential across the cell pair which causes an electrical current to flow through the electrical load connected to the electrodes.

2. The REAPower Concept

Up to recently research focused mainly on the combination of fresh water as the low concentration solution (LOW) and seawater as the high concentration solution (HIGH) (see for example [2], [3] and [4]. However this approach has an important disadvantage: The electrical resistance within the LOW compartment filled with the fresh water (typical conductivity < 0.05 Sm-1) is very high when compared to the HIGH compartment filled with seawater (typical conductivity of 4.8 Sm-1). As a result the LOW compartment with the fresh water completely dictates the overall resistance of the cell pair. The LOW compartment resistance cannot be minimised by reducing its width, because of practical restrictions. This high resistance limits the power that can be extracted by the salinity gradient.

This restriction has led to the REAPower project and the idea of using sea or brackish water as the "low concentration" salt solution in combination with brine, a salt solution with a very high salt concentration. This offers a tremendous potential for the improvement of the electrical performance. Firstly, the conductivity in the "low salt concentration" compartment can be up to two orders of magnitude higher. As a result, the cell pair is no longer restricted by the resistance in its compartments and an optimization of the membrane and other elements with respect to their effect on the total resistance becomes of importance.

It is shown by model calculations [5] that a decrease of membrane thickness results in very low total cell pair internal resistance, which allows producing much higher power outputs (W/m²), by a factor of 10 or even more, compared to the combination of seawater with fresh water. The thinner membranes will not only improve the resistance but will use considerable less material, reducing the relevant costs.

Other factors that can help to increase further the power output are: (a) to decrease the seawater compartment width and (b) to increase the feed water temperature. The effects of each parameter as calculated in [5] are illustrated in Figure 1.

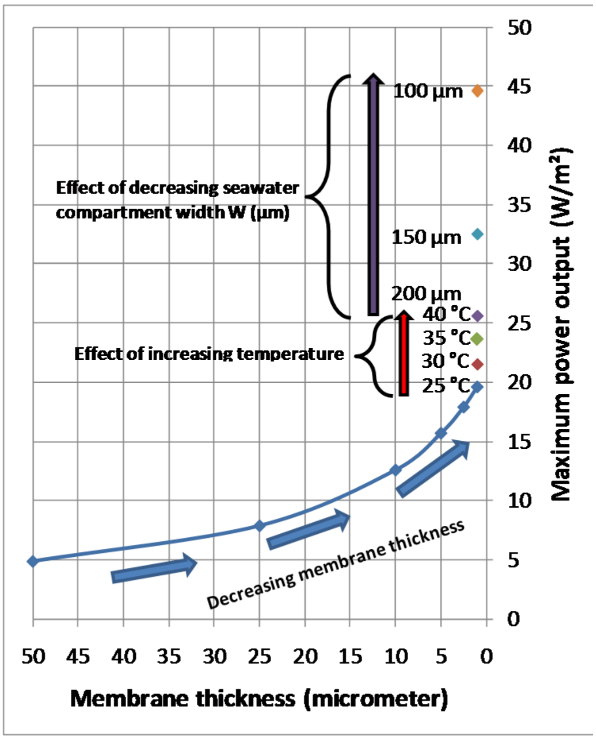

Figure 1: Effect of various parameters on the power output.

The project focuses on these issues by developing and testing membranes, components and stack designs, while using CFD simulation and modelling to better understand the process and support the system development.

3. Project Objectives and Progress

The overall objective of REAPower is to prove the concept of electricity production through SGP-RE using brine and seawater and to develop the necessary materials, components and processes. The specific scientific and technological objectives expected to be achieved within the life-time of the project are listed below:

(i) Create/select and optimise materials and components tailored to the requirements of the SGP-RE technology operating with high salinity brine and seawater. These include the membranes, spacers, electrodes and electrolytes.

(ii) Optimise the design of the SGP-RE cell pairs and stack using a computer modelling tool developed for that purpose

(iii) Verify the model, and assess the developed materials, components and design through tests on laboratory stacks.

(iv) Evaluate and improve the performance of the overall system through tests on a prototype fed with real brine from a salt pond

(v) Evaluate the results, analyse the economics and assess the perspectives of the technology

(vi) Define the next R&D activities that are needed aiming at an eventual commercialisation of the technology

At the moment objectives (i) and (ii) have been achieved, while work on (iii) is also on-going with promising results. The next three objectives are for the next stages of the project, which has another 2 years to be completed.

4. Membrane Development

Below there is a brief summary of the specifications agreed for the main characteristics of the membrane materials.

1) Ion conductivity: Areal Membrane Resistance; (AMR) = 1 Ω.cm² @ 100 µm membrane thickness..

2) Permselectvity (PS) (/ or transport number: “t”): the spec for t_{Na} and t_{Cl} was 0.8 for respectively the CEM and AEM. A t_X=0.8 corresponds to a PS=60 %.

3) For swelling no specific value was set as a target, but it was decided to wait for the measurement results and evaluate them in cooperation with the stack developers, based also on the preliminary stack design concept.

4) For stability issues it was decided to treat the membrane samples in brine, in high temperatures and with chlorine and then compare the resistance, permselectivity and mechanical properties to the non-treated samples.

The membrane manufactures of the consortium offered a pair of membranes each for testing. The initial results showed that all tested membrane materials could perform under the REAPower conditions. However, as the permselectivity was on the low side, FUJI worked on improving their membrane material and achieved to increase the Cation Exchange Membrane (CEM) permselectivity between 0.5M (sea) and 4M NaCl (brine) to 84%. For the Anion Exchange Membrane (AEM) steady progress was made and finally a permselectivity of 62 - 65% was achieved. Further improvement seemed to be hardly possible due to the fact that Cl^- is a bigger ion than Na^+. As a consequence, the co-ion Na^+ can more easily transfer the AEM, resulting in lower permselectivity values.

5. Selection of redox couples and electrode materials

UNIPA has studied numerous redox processes and electrode materials in order to select some processes/electrodes characterized by high chemical and electrochemical stability, fast electrochemical reaction of the redox couple, no poisoning of electrodes and membranes, low cost and absence or minimization of waste water treatment requirements.

In the first stage a detailed study of the state of the art was carried out, investigating a large number of processes used in numerous fields such as: water electrolysis, chlorine production, electrodialysis, reverse electrodialysis, investigation of electrodes properties, redox catalysis, redox flow batteries, etc. to select more promising redox processes and electrodes: The following redox systems were selected for the experimental investigation: $FeCl_2/FeCl_3$-graphite electrodes, Fe(II)EDTA/Fe(III)EDTA - graphite or DSA electrodes, Hexacyanoferrate(II) / Hexacyanoferrate(III) - graphite or DSA electrodes, water/Na_2SO_4,- DSA-O_2 and Ni electrodes, water/NaCl - DSA-Cl_2 and Ni electrodes.

Electroanalytical experiments, long term electrolyses, experiments in three-compartment cells and in a stack allowed to evaluate advantages and disadvantages of each couple and to select the more suitable systems for the project: $FeCl_2/FeCl_3$ at low pH and the H_2O/Na_2SO_4 redox systems.

6. Design and manufacturing of the first generation lab-stack

REDstack has worked on the design and manufacturing of the first generation lab-stack for the REAPower project, using as a starting point the concept for the reverse electrodialysis stack operating on seawater and freshwater. For the design of the lab-stack, several experiments have been performed by REDstack with the concept stack under REAPower conditions, highlighting some points for improvement.

The experience gained during the experiments and previous practical experience with handling and building of the stack, as well as stacking the membrane pile and positioning it inside the stack, has been incorporated in the REAPower adopted design. And with the input from the development work of the other partners this led to a list of 45 points describing the functionalities and boundary conditions/limitations of the new stack. Not all points could be implemented in the lab-stack design due to the size of the lab-stack. But those points will be included in the design for the bigger lab-stack that will follow in the project. In the picture is the first stack that was used in the REDstack experiments that helped define the final design.

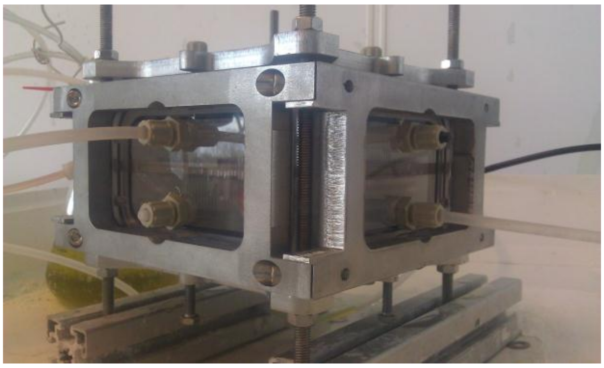

Figure 2: The lab-stack after assembling it for the first time.

Once the design was finalised, another 4 lab stacks have been constructed and are at the moment undergoing testing and evaluation by the project partners.

7. CFD Modelling and Process Simulation

UNIPA has studied the effects of spacer-filled channel geometry on the performance of the system via Computational Fluid Dynamics (CFD). CFD simulations were carried out to assess the influence of different parameters on the global process efficiency, such as the choice of spacer material and morphology, and the optimization of feed and blow-down distribution systems. Also, the possibility of choosing a porous medium to substitute the net-spacer was theoretically addressed. Both a unit cell approach and a full-length channel approach were adopted to investigate the effect of the different choices on the fluid flow along the channel. So far the following configurations were evaluated: (a) empty channel; (b) channel provided with a spacer; (c) channel filled with a purposely-manufactured fibre porous medium. Five types of spacers were investigated. A sensitivity analysis concerning computational grid size and topology was performed.

Concerning the dependence of pressure drops on the flow rate, the empty channel was found to guarantee the lowest pressure drops at a given fluid flow rate, as expected. The pressure drops along the channel 400 µm thick filled with a porous medium were very high even at low flow rates thus suggesting that this specific configuration is not suitable for this application. On the other hand, the overall pressure drops of the stack can be considered as resulting from different contributions: pressure drops relevant to the feed distributor, pressure drops inside the channel, pressure drops in the discharging collector. The choice of the optimal stack geometry is, therefore, strongly related to the need of both minimizing each of the above terms and obtaining the most uniform feed streams distribution among the stack channels. To this aim, simulations were performed on a simplified ideal planar stack with either 50 spacer-less or 50 spacer-filled channels. The effect of the distribution/collector channel thickness and geometry on single-channel flow rates and overall pressure drops in the system was analysed and a significant influence of distributor lay-out and size on the overall process performance was found [6] and [7].

The basic principles of the operation of the stack have been mathematically modelled by the implementation of a single cell-pair model. A reference literature work has been considered as a starting point and from this a novel and comprehensive cell-pair model has been developed and validated for the more complex case of REAPower process conditions (i.e. using seawater and brine concentrations in the two feed solutions). Chemical and electrochemical properties of the solutions have been estimated by purposely-selected thermodynamics equations, which allow good predicting capabilities up to solution concentrations of 5 M and more. Minor phenomena often neglected in other literature works, such as osmotic and electro-osmotic flux through the membranes, have been also considered and their effect on the overall efficiency evaluated.

The cell-pair model has been the starting point to construct a higher hierarchy model including a number of independent cell pairs and the two electrode compartments. The gPROMS® process simulator has been used, allowing a suitable mathematical model implementation taking into account all the specific features of the process. The implemented model has been already adopted to predict the influence of channel geometry and membrane features (e.g. resistance and permselectivity) on the final power density produced within the ideal stack. Moreover, thanks to the coupling with CFD modelling, the effect of distributor and cell-pair channel spacer size/geometry on flow rates distribution (in each cell-pair channels) and on pressure drops has been evaluated and considered in the prediction of net power output and overall process performance, providing input to the stack design work.

Model validation has already started by comparison of model predictions with experimental data and is showing good results [8]. Finally, the model has been used for performing some predictive performance analysis of the SGP-RE stack, indicating that the power density target of 8.4 W/m^2 of cell pair is achievable at the REAPower conditions.

8. Conclusions

The REAPower project has been working towards an innovative reverse electrodialysis system for power production from the salinity gradient of seawater and brine. Important progress has been achieved, with the development of new membranes, analysis of the most suitable redox couples and electrode materials and a new stack design. This new design has been implemented in 4 lab-scale stacks. At the same time, CFD modelling work and a simulation of the process have been performed that have provided valuable input for the design of the stack, the selection of the spacer etc. The first results from the testing of the lab-stacks are promising and are also validating the modelling and simulation work. The next steps within the next 2 years include further optimisation of the components, a larger lab-stack and a first pilot system that aims to reach 8.4 W/m^2.

Acknowledgements

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