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Mentor:

Institution: University of Arkansas

Classification: Junior

Grade Point Average:

Area of Study: Chemical Engineering

Title of Project: Reduction of Electrical Resistance as a Key to Improving Power Generation

Through Reverse Electrodialysis

Abstract: Due to the growing limitations in dependence on fossil fuels, attention has been turned towards searching for alternative means for harvesting energy. One emerging source is energy produced from natural salinity gradients between freshwater and saltwater. Two different processes used to accomplish this are pressure-retarded osmosis and reverse electrodialysis.

Significant amounts of research are currently under way regarding pressure-retarded osmosis, however very few studies have been conducted on reverse electrodialysis due to heavy resistance in the diluate chamber of a reverse electrodialysis cell. Current results from preliminary research conducted at the University of Arkansas show that the use of ion-exchange wafers does greatly reduce resistance; however the system used was not optimal for experimentation. The focus of further research is to optimize stack design for our reverse electrodialysis system, and reduce resistance in the diluate chamber by using ultra-thin wafers composed of ion-exchange beads to maximize overall power density.

Reduction of Electrical Resistance as a key to Improving Power Generation Through Reverse Electrodialysis

Introduction:

Recently, marine-based energy sources have become competitive options in the alternative energy sector in addition to existing major contributors such as solar power, wind, biomass, and hydroenergy¹. Salinity-gradient energy, or "blue energy"², is defined as the energy available from mixing two aqueous solutions of different salinities, and has a total global potential for power production of 2-2.6TW¹⁻⁹. Such technology has implications in harnessing power where seawater meets river water, as in estuaries³. Two forms of salinity-gradient energy are presently at the cusp of cutting-edge technology, and much debate has been focused on which has the more promising future. Pressure retarded osmosis (PRO) is driven by the osmotic pressure difference across a semipermeable membrane, and the useable work is extracted via a hydroelectric turbine⁶. For applications of mixing sea water and river water, reverse electrodialysis (RED) yields a higher average power density and energy recovery than pressure-retarded osmosis¹. Because of the lower pretreatment requirements and more chemically resistant membranes, it is also less susceptible to biofouling¹⁰. Several designs for a traditional RED stack have been considered, generally consisting of alternating cation and anion exchange membranes separated by spacers (or their equivalent) and terminated with an electrode at each end¹¹. In stacks consisting of multiple cells, a serial configuration is used to maximize power generation¹². Homogeneous ion exchange membranes are used for their exhibition of permselectivity for ions with opposing charge (counter ions) while passing ions with like charge¹³. Previous research has found solutions to common process losses in reverse electrodialysis including those for the spacer shadow effect ^{14,15}, fouling⁴, and resistance⁹.

In a traditional RED setup, the environment of the diluate chamber is considered relatively non-conductive, providing limited ionic diffusion. As a result, the diluate chamber resistance is the dominant restriction ^{16,17}, and no research to date has affectively solved this problem. The focus of this research is to provide a working solution by applying principles of Wafer Enhanced-Electrodeionization (WE-EDI)¹⁸ in hopes of greatly reducing resistance. A wafer is made by binding ion exchange resins with polymer¹⁸, and will be used as a spacer in the diluate chamber to stimulate ionic transport. Theoretical calculations show a possible increase in power density orders of magnitudes higher than what is achievable with current state-of-the-art technology. The largest reported experimental power density is 2.2W/m² using a stack composed of five cells, spacer thickness of 100µm, and specially manufactured membranes (30-40µm thick)⁵. Projected power output of this proposed research is more than 10W/m². Such overwhelming progress shows the enormous potential of this technology. As membrane area required for high power output is reduced, reverse electrodialysis will quickly become a more attractive option for harnessing salinity-gradient energy.

Previous Research Conducted on This Project

Reverse Electrodialysis Stack. The RED stack consisted of one cell, with alternating seawater and river water compartments. The cell began with one platinum electrode, followed by alternating cation and anion exchange membranes, and was terminated by another platinum electrode. Membranes were separated by gaskets, spacers, and woven plastic spacers used for turbulence enhancement. For preliminary research trials, the interelectrode distance was 0.9cm. After modifications, custom hybrid spacer-gaskets (500µm thick) were designed to minimize cell

length. Each one measured 500 microns in thickness. Furnatech homogeneous ion exchanged membranes were used for experimentation: FKS-30 for cation exchange membrane and FAS for anion exchange membrane.

Feed Water. The best experimental conditions were determined to be 3% NaCl concentration for the concentrate feed and 0.1% NaCl for the dilute feed. For each experiment, a 3% NaCl concentration was used for rinse feeds. All feed waters were run through the cell using peristaltic pumps, and different flow rates were tested. Initial and final conductivities of concentrate and dilute feed streams were measured with a Traceable® Expanded Range Conductivity Meter (Control Company).

Electrochemical Measurements. Readings were taken for both traditional RED conditions and our wafer-enhanced RED design with a digital Multimeter (Klein Tools) for preliminary research. Voltage potential, current, and resistance were measured directly from the instrument. For further experimentation, a potentiostat (Amel model 2053) was used to take voltage and current readings. Eventually, a power box (GWInstek) was used to apply voltage and measure current flux for different conditions.

Theory. Several equations were used for calculations. The first equation is for overall stack resistance:

$$R_{stack} = R_{aem} + R_{cem} + \frac{h_c}{\kappa_c} + \frac{h_d}{\kappa_d} + R_{electrode}$$
 (1)³

where R_{stack} refers to the overall stack resistance, R_{aem} to resistance of the anion exchange membrane, R_{cem} to resistance of the cation exchange membrane, h_c and h_d refer to concentrated and dilute feed channel heights respectively, k_c and k_d to concentrated and dilute conductivities respectively, and $R_{electrode}$ refers to resistance of the electrode. In addition, maximum voltage potential can be calculated with the following equation:

$$\Delta V = 2 \frac{\alpha R_g T}{F} \ln \frac{c_c}{c_d} \tag{2}$$

where ΔV is the maximum voltage potential across the membrane, α is the permselectivity, F is the Faraday constant, c_c and c_d are concentrate and dilute concentrations respectively, and T is temperature in Kelvin. A common form of measuring potential energy generation of a RED cell is through power density, which can be calculated by the following equation:

$$W_{max} = \frac{1}{2R_{stack}} \frac{\Delta V^2}{4} \tag{3}$$

where ΔV is the experimentally measured voltage, and R_{stack} is the measured stack resistance.

Preliminary Research. Initial experiments were conducted to analyze the effect of ion-exchange wafers on stack resistance for a single-cell system. Results showed a significant decrease in resistance for the wafer-enhanced design, indicating that the wafer did have a positive effect on stack performance. While resistances were greatly lowered under wafer-enhanced conditions, they were still much higher than those listed in literature. Figure 1 shows a comparison between the average power densities obtained under both wafer and non-wafer enhanced conditions.

Preliminary Effect of Ion-Exchange Wafers on Average Power Density

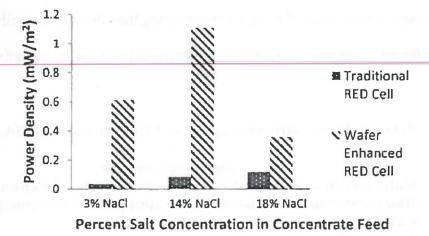


Figure 1. Average power densities for preliminary research conditions.

Since our stack was giving such high resistances, calculated power densities were on the order of mW/m² rather than W/m². Another contributing cause to the difference was our low voltage readings. These need to cross the 1V threshold for maximum power densities. Results of our preliminary research show that while the ion-exchange wafer does greatly reduce resistance, thus increasing power density, our calculated numbers were very low in comparison to listed literature values (highest power density reported is 2.2W/m²)⁵. This led us to examine possible reasons for such discrepancies.

Further Research. We proposed several probable causes for such high resistances, including internal cell leakage and inadequate stack design. Upon making comparisons across several experiments reported in literature, it was concluded that our cell length (interelectrode distance) was far too long, and our voltage potentials were lower because our stack only consisted of one cell as opposed to multiple cells connected in series. We have successfully designed and built a stack with minimal interelectrode distance and the ability to sustain a multi-cell design. The focus of further research to be conducted in the following semesters will be to pioneer a new technique of harvesting salinity-gradient energy. This will be done by placing thin ion-exchange wafers in each compartment of the new cell design and measuring the effects on overall obtained power density. If efforts are successful, reverse electrodialysis will become an attractive source of alternative energy.

Timeline. Research will be conducted during the spring and fall semesters of 2014.

Month
January-February
March-May
August-October
November-December
Optimization of wafer-making process for minimal thickness.
Run experiment with ion-exchange wafers and observe power densities.
Collect any final necessary data for publication.
Publish article in a scientific journal.

Budget \$750- materials for experimentation (ion-exchange resins, chemicals) \$750- travel allowance to attend 2014 National AIChE meeting in Atlanta, GA

References

- 1. Post, J.W., et al. Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis. *Journal of Membrane Science*. **288**, 218-230. (2007)
- 2. Post, J.W., Hamelers, H.V.M, & Buiman, C.J.N. Energy Recovery from Controlled Mixing Salt and Fresh Water with a Reverse Electrodialysis System. *Environmental Science and Technology*. 42, 5785-5790. (2008)
- 3. Ramon, G., Feinberg, B., & Hoek, E. Membrane-based production of salinity-gradient power. Energy and Environmental Science. 4423-4434 (2011)
- 4. Vermaas, D.A., Kunteng, D., Saakes, M., & Nijmeijer, K. Fouling in reverse electrodialysis under natural conditions. *Water Research*. 47, 1289-1298 (2013)
- 5. Vermaas, D.A., Saakes, M., & Nijmeijer, K. Doubled Power Density From Salinity Gradients at Reduced Intermembrane Distance. *Environmental Science and Technology*. 45, 7089-7095 (2011)
- 6. Yip, N.Y. & Elimelech, M. Thermodynamic and Energy Efficiency Analysis of Power Generation from Natural Salinity Gradients by Pressure Retarded Osmosis. *Environmental Science and Technology.* 46, 5230-5239 (2012)
- 7. Veerman, J., Saakes, M., Mets, S.J., & Harmsen, G.J. Electrical Power from Sea and River Water by Reverse Electrodialysis: A first Step from the Laboratory to a Real Power Plant. Environmental Science and Technology. 44, 9207-9212 (2010)
- 8. Dlugolecki, P., Gambier, A., Nijmeijer, K., & Wessling, M. Practical Potential of Reverse Electrodialysis As Process for Sustainable Energy Generation. *Environmental Science and Technology*. 43, 6888-6894 (2009)
- 9. Veerman, J., Saakes, M., Metz, S.J., & Harmsen, G.J. Reverse electrodialysis: Performance of a stack with 50 cells on the mixing of sea and river water. *Journal of Membrane Science*. 327, 136-144 (2009)
- 10. Post, J.W. "Blue Energy: electricity production from salinity gradients by reverse electrodialysis." 5-201 (2009)
- 11. Veerman, J., de Jong, R.M., Saakes, M., Metz, S.J., & Harmsen, G.J. Reverse electrodialysis: Comparison of six commercial membrane pairs on the thermodynamic efficiency and power density. *Journal of Membrane Science*. 343, 7-15 (2009)
- 12. Kim, K.S., Ryoo, W., Chun, M., & Chung, G. Simulation of enhanced power generation by reverse electrodialysis stack module in serial configuration. *Desalination*. 318, 79-87 (2013)

- Sadeghian, R.B., Pantchenko, O., Tate, D., & Shakouri, A. Miniaturized concentration cells for small-scale energy harvesting based on reverse electrodialysis. *Appl. Phys. Lett.* 99 (2011)
- Dlugolecki, P., Dabrowska, J., Nijmeijer, K., & Wessling, M. Ion conductive spacers for increased power generation in reverse electrodialysis. *Journal of Membrane Science*. 343, 101-107 (2009)
- 15. Vermaas, D.A., Saakes, M., & Nijmeijer, K. Power generation using profiled membranes in reverse electrodialysis. *Journal of Membrane Science*. **385-386**, 234-242 (2011)
- Dlugolecki, P., et al. On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport. *Journal of Membrane Science*. 349, 369-379 (2010)
- 17. Dlugolecki, P., Anet, B., Metz, S., Nijmeijer, K., & Wessling, M. Transport limitations in ion exchange membranes at low salt concentrations. *Journal of Membrane Science*. 346, 163-171 (2010)
- Ho, T., Kurup, A., Davis, T., & Hestekin, J. Wafer Chemistry and Properties for Ion Removal by Wafer Enhanced Electrodeionization. Separation Science and Technology. 45, 433-446 (2010)