Recent Developments in Salinity Gradient Power

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Salinity Gradient Power (SGP)

- Sources of marine renewable energy include ocean currents, ocean waves, tides, thermal gradients, and salinity gradients.
- Salinity gradient energy, is an often overlooked source of marine energy, even though it possesses one of the highest energy concentration (i.e., energy density) of all the marine energy sources, comparable to that of ocean thermal gradient power.
- History of using salinity gradients for the production of power generation goes back to the 1930's.
- Its sustainable, in principal there is no fuel cost, produces no climate altering emissions, and the salts are not consumed in the process.
- Its renewable due to water evaporation by the sun and subsequent precipitation and its non-periodic, unlike wind or solar.

SGP General Discussion

- In 1954, Pattle suggested the use of the osmotic pressure differential between river water and seawater to generate power and actually constructed an apparatus that produced power.
- This energy source exists at the interface between waters of differing salinities and is particularly concentrated where fresh water rivers flow into the ocean or locations of subterranean brines and salt deposits.
- However, the solubility of NaCl is almost independent of temperature and, in accord with Le Chatelier's principle, it has a very small heat of dilution. As a consequence, this large source of energy occurs generally unnoticed.
- The equivalent pressure head between typically 35 ppt seawater (0.52M NaCl) and fresh water is about 24 atm; equivalent to a 240m water head, visualized as a 240m waterfall at the mouth of every river.
- To capture the energy of this potentially significant energy source, a suitable extraction device is required.

SGP Extraction Devices: Operation

- Although numerous techniques have been discussed over the past 80 years to recover this energy, two main techniques have stood out as to having the most potential for energy extraction.

- These are:

  - ✓ Reverse ElectroDialysis (RED) or called Dialytic Batteries, and
  - ✓ Pressure-Retarded Osmosis (PRO),

- Both RED and PRO require the use of selective membranes for their operation.

- Historically, high membrane costs and the large number of membranes required have limited Salinity Gradient Power development but this is changing with reductions in membrane costs.

Recent Large-Scale SGP Projects

- To date no appreciable amount of electricity has been generated from the fresh and seawater interface.
- The major hurdle for osmotic pressure technology is in the type and cost-effective manufacture of semi-membrane membranes.
- In 2002, KEMA, a Dutch company, started working on developing low cost membranes for RED under a project called “Blue Energy”.
- In 2003, the Norwegian company Statkraft opened a laboratory dedicated to saline gradient power research with a focus on high performance membranes for PRO – Saline Power (started in 1998).
- In April 2009, the Ijsselmeer – the largest lake in Western Europe – was created by building the Afsluuitdijk, a dyke closing off a vast expanse of water from the North Sea. RED related research using standard Anion/Cation exchange monopole membranes is planned for this site.
- http://www.youtube.com/watch?v=UwpY756Qa5U

ElectroDialysis

- ElectroDialysis (ED) - the most common electro-membrane process – is used for desalination and concentrating of aqueous solutions.

- ED depends on the following general principles:

  - ✓ Most dissolved salts are ionic, being positively (cationic) or negatively (anionic) charged.
  - ✓ When NaCl is dissolved in water, it freely dissociates into hydrated Na^+ and Cl^- ions.
  - ✓ These ions are attracted to electrodes with an opposite charge.

- ED uses an external electrical potential to move salts selectively through individual permselective membrane pairs, leaving behind fresh product water.

- ED is different from other membrane processes in that it is electrically driven rather than pressure driven. Thus, in ED, only ions and associated water is transferred.

ElectroDialysis

- Under the presence of an external electrical load, Cations, under the influence of the negative electrode move through the Cation Exchange Membranes (CEM) but are stopped at the Anion Exchange Membrane (AEM) interface.
- Similarly, anions under the influence of the positive electrode move through the AEM but are stopped at the CEM interface.
- AEM and CEM's are alternately arranged with a spacer sheet between to form a "cell". The basic ED unit consists of several hundred cell pairs bound together with electrodes on the outside and is referred to as a membrane stack.
- Pathways in ED units are separated by cation/anion membrane stacks and direct current provides the motive force for ion migration from the low concentration side to the higher concentration side.
- By this arrangement, concentrated and diluted solutions are created in the spaces between the alternating membrane pairs.

Traditional RED Discussion

- RED relies on direct electrochemical conversion using ElectroDialysis cells operated as a concentration cell with no external voltage applied.
- Because concentration gradient driven systems force ion migration from the high concentration side to the low, they are sometimes referred to as Reverse ElectroDialysis or Dialytic systems.
- Since this ion movement consists, preferentially, of either cations or anions, it leads to a charge separation across the membrane, otherwise known as a membrane potential.
- Dialytic Power Generation Systems can be operated in the manor of a continuously fed fuel cell in which the chemical energy is converted directly into electrical energy.
- Nernst EQUATION – A thermodynamically derived equation relating the Open Circuit Voltage (OCV) potential of an electrochemical cell to the concentration or pressure of products and reactants.

  ✓OCV EMF = 0.059 V per 1 to 10 Concentration Difference (Theoretical maximum)
  ✓OCV EMF = 0.118 V per 1 to 100 Concentration Difference (Theoretical maximum)

Nernst Equation Basics

- The EMF Open Circuit Voltage (OCV) for a concentration cell is often described by the Nernst equation. Using an ideal monopolar permselective membrane as a salt bridge, a 1,1 valence electrolyte, and reversible electrodes in both compartments can be calculated as:

$$E = EMF = E^{\circ} - (\nu\ RT/F)\ \ln\ (a_{\pm}\ conc\ /\ a_{\pm}\ dil)$$

- Where $a_{\pm}$ = ionic activities (approx. concentrations), ν = charge on the active ion, R = Universal Gas Constant = 8.314 J/K, F = Faraday number = 96,500 C/mol, T = Absolute Temperature K (°C + 273), E^{o} = Galvanic Cell EMF = 0 because same electrode is used.

- For an ideal membrane (a = 1.0), monovalent active ion, and a 1:10 activity ratio for the two solutions (i.e., concentrated solution = 10 dilute) we get:

$$EMF = 0.0 - [1^{*}\ (8.314\ J\ K^{-1}\ mol^{-1} * 298K)\ /\ (96{,}500\ C\ mol^{-1})]\ \ln\ (10)$$

OCV EMF = 0.059 V per 1 to 10 Concentration Difference

OCV EMF = 0.118 V per 1 to 100 Concentration Difference

- Theoretical maximum – Actual voltage will be less because of Irreversible sources of voltage drop: e.g., Activation, Ohmic, and Polarization (Charge Double Layer).

Author's Research Focus

- Develop increased technical understanding into the membrane, ionic, environmental, and electrochemical effects on the generated membrane current and potential of a Bi-Polar membrane based, RED seawater concentration cell.
- A Bi-Polar membrane (BPM) consists of an anion (AEM) and a cation (CEM) selective membrane joined together in series across a region called the "transition or contact region".
- Although made up of well-defined AEM and CEM components, once combined the BPM acquires unique capabilities and the possibility of a simpler design with fewer membranes.
- These unique capabilities include:
  - ✓ An apparent variation in membrane potential depending upon which side is in contact with the more concentrated solution, which is not the case in monopolar ion-exchange membranes; and
  - ✓ Its use in converting water soluble salts to their corresponding acids and bases via the process of water dissociation (or splitting).

PhD Research Methodology

- Electrochemical methods such as Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) along with equivalent circuit modeling were used to establish membrane, electrode processes, and kinetics corresponding to changes in parameters.

- A Design of Experiment (DoE) based fractional factorial design analyses with accompanying performance testing to determine a predictive cell output performance optimized model in terms of pertinent input parameters tested.

- Using synthetic seawater, standard atmospheric pressure testing was conducted for the following variables:

  - ✓ Temperature
  - ✓ Concentration
  - ✓ Bi-polar membrane type
  - ✓ Solution pumping speed
  - ✓ Bi-polar membrane orientation
  - ✓ Electrode surface area

Select PhD Research Findings

- Of the variables tested, temperature was the primary driving factor in terms of the cell output potential.
- Determined that the seawater concentration cell operation under external loading is not described adequately by the Nernst equation.
- Confirmed that for maximum potential output, there is a preferred membrane orientation.
- The seawater concentration cell when operated under an external electrical load produced repeatable output results across the load conditions tested.
- The results confirmed that the average single membrane cell output value of nominally 400 picoWatts, which although extremely small, is within the power range utilized by some low power draw devices.

Continuing Research Focus and Future

- In general, although small in output power, when under external load, the cell was found to produce repeatable results while relatively invariant to concentration variations and overall motion.
- All good characteristics for a Dialytic based sea water concentration cell power generator for low power draw devices.
- Additional research is ongoing to continue this process further to develop the concept into a functioning energy generation system.
- This research entails investigating output performance changes through:
  - ✓ Changes in cell design;
  - ✓ Size scalability;
  - ✓ Differing configuration combinations.
- A patent resulting from this research was awarded on June 15, 2010.
- Dialytics, Inc. has a license agreement in place with USF to develop and commercialize this technology.

Questions/Comments