Exergy analysis of reverse electrodialysis

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ABSTRACT

Reverse electrodialysis in closed loop configurations is a promising membrane technology in the energy conversion and storage fields. One of the main advantages of closed-loop reverse electrodialysis is the possibility of using a wide range of operating concentrations, flow rates and different salts for generating the salinity gradient. In this work, an original exergy analysis of the reverse electrodialysis process was carried out in order to investigate reverse electrodialysis performance in terms of energetic and exergetic efficiency parameters in a wide range of operating conditions. A mono-dimensional model of the reverse electrodialysis process was developed, in which all sources of irreversibility are considered, such as non-ideal membranes permselectivity, ohmic losses and uncontrolled mixing phenomena (salt and water diffusive flux across membranes). For each of them, the influence on the exergy efficiency is quantified and compared. Results also indicate how exergetic and energetic performance are largely dependent on solutions concentration: when high salinity gradient differences are used within the unit, membrane water permeability heavily affects process performance, thus reducing exergy efficiency, though a larger power output can be normally achieved. The more performing flow arrangement for the stack has been found to be the counter-current, though significant differences are observed only for long channels. Finally, performance is improved when short residence time within the stack is attained for the low-concentration solution.

1. Introduction

1.1. Salinity gradient power technologies

Energy from salinity gradients (commonly indicated as Salinity Gradient Power, SGP) is a clean and sustainable form of energy related to the mixing of solutions at different concentrations. This form of energy was described for the first time in the 1954 by Pattle [1], who also proposed how to extract it by employing Ionic Exchange Membranes (IEM). An increasing attention has been paid to this renewable energy source in the last years. In particular, in the last decade many research efforts in industry and academia have been devoted to the development of the technologies able to convert such energy into electricity. Among the different SGP technologies, reverse electrodialysis (RED) and pressure retarded osmosis (PRO) have been the most widely investigated.

In PRO [2,3], osmotic membranes are interposed between two solutions at different concentration. The difference of the chemical potential between the two solutions produces an osmotic flux from the dilute solution channel to the concentrate one. As a difference from Forward Osmosis (FO), in PRO a hydrostatic pressure lower than the

osmotic pressure difference between the two channels is applied to the concentrate solution. The resulting water flux occurring from the dilute to the concentrate compartment is thus "retarded" yet pressurized. This pressure energy gained by the permeating water is subsequently converted into electrical energy by means of a hydro-turbine coupled with a generator.

Conversely, RED allows the direct conversion of salinity gradients into electricity. RED units consist of several repetitive unit called "cell pair". A cell pair consists of two IEMs, an anion and a cation exchange membrane (AEM and CEM), interposed between two channels where the solutions at different saline concentrations flow. The chemical potential difference between the two solutions generates a selective transport of cations and anions through the membranes resulting in an ionic current and an electric potential difference over each membrane. Then, this ionic current is converted into electricity by redox reactions, which occur at two electrodes placed at the end of the cell-pairs pile.

Applications of the RED process started for the case of open-loop configuration systems, where natural salinity gradients (i.e. generated by mixing river water, seawater, brine, or brackish water) are exploited to produce electricity and after released into the environment. Several

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Nomenclature

A_{cp}	area of a cell pair [m^2]
a_s	salt activity
a_w	water activity
b	membrane width (m)
$\dot{B}$	exergy flow (W$_{ex}$)
C_{conc}	concentrate molar concentration (M)
C_{dil}	dilute molar concentration (M)
Δx	discretization length (m)
E_{cell}	voltage generated by the cell pair (V)
E_{loss}	ohmic loss due to internal stack resistances (W)
E_{mix}	exergy destruction due to uncontrolled mixing phenomena (W)
E_{stack}	voltage generated by the pile (V)
F	Faraday constant (C/mol)
h	specific enthalpy (kJ/kg)
$\tilde{h}$	partial molar enthalpy of the "ith" species (kJ/kmol)
I	electric current (A)
IEM	Ionic Exchange Membrane
$I_{r,RED}$	exergy destruction within RED unit (W)
J	molar flux (mol/m^2 s)
m	molality (mol$_s$/kg$_{solv}$)
M_s	salt molecular weight (mol/kg)
M_w	water molecular weight (mol/kg)
N_{cp}	number of cell pair
N_k	number of discretization elements
OCV	Open Circuit Voltage (V)
p	pressure (kPa)
P_d	power density (W/m^2)
P_E	electric power (W)
P_s	membrane permeability to salt (m^2/s)
P_w	membrane permeability to water (m/Pa·s)
Q	volumetric flowrate (m^3/s)
R	gas constant (J/(K mol))
R_{AEM}	anionic membrane resistance (Ω m^2)
R_{blamk}	electrical resistance of the electrodic compartment (Ω)
R_{cell}	electrical resistance of the cell pair (Ω)
R_{CEM}	cationic membrane resistance (Ω m^2)
R_{conc}	electrical resistance of concentrate (Ω m^2)
R_{dil}	electrical resistance of dilute (Ω m^2)
RED	Reverse Electrodialysis
R_{int}	internal stack resistance (Ω)
R_L	load resistance (Ω)
R_u	universal constant of gases (kJ/(kmol K))
s	specific entropy (kJ/(kg K))
$\tilde{s}$	molar specific entropy (kJ/kmol)
T	temperature (°C or K)
v$_{conc}$	concentrate velocity (m/s)
v$_{dil}$	dilute velocity (m/s)
x_s	salt molar fraction (dimensionless)
x_w	water molar fraction (dimensionless)
z	ion charge

Greek symbols

α	permselectivity
γ	salt activity coefficient (dimensionless)
δ$_m$	membrane thickness (m)
η	performance (dimensionless)
μ$_{MX}$	chemical potential of the generic solute MX
ρ	density (kg/m^3)
ϕ	osmotic coefficient (dimensionless)

Subscripts

0	related to reference or "dead" state
in	related to inlet
M	related to cation
out	related to outlet
s	related to salt
sol	related to solution
X	related to anion
w	related to water

laboratory investigations have been performed and presented in literature, all focusing on how operating conditions and membrane properties can affect the main process performance parameters such as the power density and the process yield (i.e. energy generated per cubic meter of feed solutions). The first experiments related to RED process were carried-out in 1954 and reported a power density of 0.05 W/m^2 [1]. Several years later almost one order of magnitude higher values (i.e. 0.4 W/m^2) were found by Audinos [4] in 1983 and a further doubling (about 0.93 W/m^2) was reported by Veerman et al. [5]. The power density obtainable from these early tests was limited due to the lack of suitable IEMs. Only during the last decade, the development in membrane fabrication technology and stack design as well as the adoption of specific operating conditions [6,7] allowed significantly higher power density values to be obtained. For instance, power densities up to 6.7 W/m^2 [8] were found using high salinity solutions (e.g. brines) and higher temperatures (e.g. 60 °C). All these extensive research efforts have recently led to the successful design and operation of the first pilot scale prototypes fed with natural salinity gradients in real environment [9,10].

RED technology has been investigated also in a closed-loop configuration, with the aim to convert low-grade waste heat into electricity. This innovative *Reverse Electrodialysis-Heat Engine* (RED-HE) [11] consists of a traditional RED unit coupled with a Thermal Regeneration Unit (TRU). The TRU is provided with waste heat, which is used in a purposely-selected thermally-driven process to restore the initial concentrations of the solutions exiting from the RED unit. In this way the regenerated solutions can be fed again to the RED unit, thus closing the cycle. These systems could be profitably coupled to several industrial processes, like manufacturing or metallurgical industries, where low-grade waste heat is discarded into the environment. In this way, a reduction of fossil fuel consumptions could be achieved with economic and environmental benefits.

One of the most significant features of the RED-HE process is that there is no need for natural salinity gradients sources, thus overcoming the main restriction of implementation of the RED process which is obviously limited only to those sites where natural sources of SGP are available. The RED-HE can be in fact implemented in principle anywhere, thanks to the use of a limited quantity of artificial saline solutions suitably-selected for optimal process performance [12,13].

Another interesting application of closed-loop reverse electrodialysis systems is the development of a "salinity gradient based battery". Some examples of this application have been proposed so far both in scientific papers [14,15] and high-risk cooperation projects [16]. Both in open- and closed-loop configuration the enhancement of energy performance of RED units is a matter of crucial importance.

1.2. Exergy analysis

Exergy analysis represents a powerful method to identify the main sources of energy loss and quantify how much energy is effectively converted within the process. While in open-loop RED applications the process yield (i.e. how much energy is generated from the available