



Effect of different aqueous solutions of pure salts and salt mixtures in reverse electro dialysis systems for closed-loop applications



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ABSTRACT

Reverse Electro dialysis (RED) in a closed-loop arrangement is a viable way to convert low-grade heat into electric power. The present work experimentally investigates the use of pure salt- and equimolar two salts-water solutions as feeds in a lab-scale RED unit. RED performances were analysed in terms of Open Circuit Voltage (OCV), stack resistance and corrected power density. The pure salts and the mixtures employed were chosen via a computational analysis. Effect of feed solution velocity and concentration was investigated. Results concerning the pure salt-water experiments show that NH_4Cl is the most performing salt in the concentration range probed, while higher power density values are expected with the use of LiCl at larger concentrations. As regards the salt binary mixtures, in some cases, the measured stack electrical resistance was found lower than both the two values measured for the corresponding pure salts, thus resulting into higher power density values for the mixtures. This surprising experimental evidence suggests that it is possible to increase the power produced by a conventional RED unit by adding an equivalent molar quantity of another suitable salt. Finally, among the mixtures tested, the NH_4Cl - LiCl mixture appears as the most promising, thanks to the combination of the favorable properties of these two salts.

1. Introduction

The continuous growth of the energy demand is giving impulse to the search and the development of new renewable energy sources. Among these, the energy deriving from salinity gradients (i.e. Salinity Gradient Power, SGP) represents a promising option [1]. This form of energy is available whenever two solutions at different concentration are put in contact and is progressively dissipated while the two solutions are naturally mixing together. Performing a “controlled mixing” between the two solutions to convert the chemical potential difference into available power is the goal of all the SGP technologies [2]. Among these, Pressure Retarded Osmosis (PRO) and Reverse Electro dialysis (RED) have reached the highest technology readiness level and are currently the most investigated [3].

Pressure Retarded Osmosis is based on the use of osmotic membranes to convert the salinity gradient energy into mechanical power [4–6], while Reverse Electro dialysis makes use of ionic exchange membranes (IEMs) to allow a direct conversion into electric power. More in detail, a RED stack is composed of a number of repeating units named cell pairs constituted by a cationic exchange membrane, a

channel fed by the dilute stream, an anionic exchange membranes and a channel fed by the concentrate solution. The chemical potential difference between the adjacent channels along with the presence of the two types of IEMs results into the spontaneous generation of separate ion fluxes: one positive and the other negative directed towards opposite directions. These are directly converted into electric current via red-ox reactions occurring at the end compartments of the unit where two electrodes are hosted.

The properties of IEMs represent one of the most crucial aspects affecting the performance of a RED unit [7]: the perm-selectivity (i.e. transport selective property) of an IEM towards its counter-ion dramatically affects the process driving force [8], while the IEM electrical resistance may significantly reduce the producible power [9] as it often represents the highest contribution to the stack resistance [10]. These two properties are affected by the swelling degree and the ion exchange capacity of the membrane, the first is a measure of the increase of the membrane volume in presence of a solution and the second represents the number of fixed charges per unit volume of dry membrane.

RED has been traditionally studied as a viable way to exploit either naturally existing salinity gradients as river estuaries [11] or artificial

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Nomenclature

A	membrane area [m ²]
A _β , α, b	Pitzer model constant [(kg/mol) ^{1/2}]
A _Λ , B _Λ , C _Λ	coefficients of Jones and Dole's equation [dimensionless]
C	solution molarity [mol/l]
m	solution molality [mol/kg]
I	ionic strength [mol/kg]
Z	modified ionic strength [mol/kg]
f _γ	coefficient of Pitzer's model [dimensionless]
B _γ , C _γ	coefficients of Pitzer's model for pure salt-water solutions [dimensionless]
B _{MX} , B' _{MX} , C _{MX}	coefficients of Pitzer's model for binary mixture-water solutions [dimensionless]
ΔV	stack voltage [V]
I	stack current [A]
N	number of cell pairs [dimensionless]
P _D	Power Density [W/(m ² N)]
P _{D,corr}	Corrected Power Density [W/(m ² N)]
R	universal gas constant (8.314 J/(mol K))
R _{blank}	blank resistance [Ω]
R _{BL}	electrical resistance of the boundary layer [Ω]
R _{IEM}	electrical resistance of ionic exchange membrane [Ω]
R _{stack}	stack electrical resistance [Ω]
R _u	electrical resistance of the external load [Ω]
r	Jone and Dole's viscosity coefficient [(l/mol) ⁻⁵]
s	Jone and Dole's viscosity coefficient [l/mol]
T	temperature [°C]
v	fluid velocity [cm/s]
z _M , z _X	cation and anion charge [dimensionless]

Greek letters

α _p	permselectivity [dimensionless]
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η	solution viscosity [Pa s]
γ _{MX}	salt activity coefficient [dimensionless]
β ⁰ _{MX} , β ¹ _{MX} , φ ¹ _{cc} , φ ¹ _{aa}	Pitzer model second order interaction parameters [dimensionless]
ψ _{Mca} , ψ _{Xca}	Pitzer model third order interaction parameters [dimensionless]
ΔΦ _{cell}	cell potential difference [V]
ν _M , ν _X	cation and anion stoichiometric coefficients [dimensionless]
Λ ₀	salt equivalent conductivity at infinite dilution [mS/(cm mol)]
Λ	salt equivalent conductivity [mS/(cm mol)]

Subscripts

HIGH	concentrate compartment
LOW	dilute compartment
c, c'	generic cation index
a, a'	generic anion index
cell	cell pair

Acronyms

AEM	anion exchange membrane
CEM	cation exchange membrane
IEM	ion exchange membrane
OCV	Open Circuit Voltage
PRO	pressure retarded osmosis
RED	reverse electrodialysis
SGP	salinity gradient power

gradients based on the use of industrial brines as those deriving from desalination plants [12] or saltworks [13]. In both cases, almost all studies have focused on the use of aqueous solutions with sodium-chloride as the main (or only) solute. IEMs have been progressively studied and developed in order to enhance their performance and capability to efficiently deal with this kind of solutions.

As an alternative to its traditional application, very recently, RED has been studied as a viable way to convert low-grade waste heat into electrical power by taking advantage of a closed-loop configuration [1,14]. The RED Heat Engine (REDHE) [15,16] is mainly composed of a RED stack and of a regeneration unit (Fig. 1): the RED stack is devoted to converting the salinity gradient into electric power by mixing the two solutions at different concentration, while the regeneration unit makes use of unworthy thermal power (temperature lower than 100 °C) to separate them and restore the initial salinity gradient.

Within the above closed-loop arrangement, it is not anymore necessary to locate the plant close to estuaries or industries producing brines, thus guaranteeing a higher versatility and flexibility of RED technology. More important, this application also allows the use of artificial solutions composed of any solvent-solute couple with the scope of maximizing the cycle efficiency. For instance, salts besides NaCl or mixtures of two or more salts may be used to generate and exploit a higher theoretical potential difference. Moreover, operating conditions in terms of solution concentration and velocity are no more dependent on the available stream but can be easily tuned to maximize the REDHE performance. The investigation of RED units fed by non-conventional (i.e. NaCl-water) solutions is nowadays a topic of crucial importance.

Surprisingly, only a very few studies have been presented so far on

the use of a RED unit fed with salts other than NaCl. Some of them regard the investigation of the performance of multivalent ions in a RED unit, mainly referring to the most common ions present in seawater (Mg²⁺, Ca²⁺ and SO₄²⁻) in order to predict the behaviour of a RED stack fed by natural seawater [17–19]. Other studies concern the use of thermolytic salts, such as ammonium hydrogen carbonate (NH₄HCO₃). These salts are able to decompose into ammonia, carbon dioxide and water at temperatures of about 40–45 °C. Thus, they can be used within a salt extraction regeneration strategy [20–22] in a REDHE. Unfortunately, power densities lower than those obtainable with NaCl solutions have been reported [20,23] so far. Other studies focus on the interaction between specific ions and IEMs without investigating the RED process performance: in particular these studies investigate how

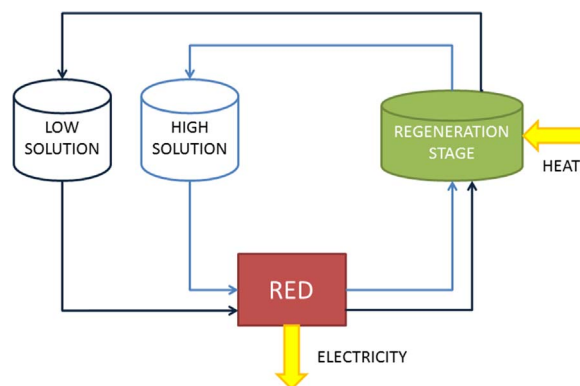


Fig. 1. Reverse Electrodialysis Heat Engine concept [15].

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