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## ***Performance of a RED system with Ammonium Hydrogen Carbonate solutions***

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**Abstract.** The use of closed-loop salinity gradient power (SGP) technologies has been recently presented as a viable option to generate power using low-grade heat, by coupling a SGP unit with a thermally-driven regeneration process in a closed loop where artificial solutions can be adopted for the conversion of heat-into-power. Among these, the closed-loop reverse electrodialysis (RED) process presents a number of advantages such as the direct production of electricity, the extreme flexibility in operating conditions and the recently demonstrated large potentials for industrial scale-up. Ammonium hydrogen carbonate ( $\text{NH}_4\text{HCO}_3$ ) is a salt suitable for such closed-loop RED process thanks to its particular properties. At temperatures above 40-45 °C, it decomposes into a gaseous phase containing  $\text{NH}_3$ ,  $\text{CO}_2$  and water. Thus, the use of  $\text{NH}_4\text{HCO}_3$  solutions for feeding a RED unit would allow their easy regeneration (after the power generation step) just using low-temperature waste heat in a purposely designed regeneration unit. This work aims at presenting an experimental investigation performed on a RED system fed with  $\text{NH}_4\text{HCO}_3$  solutions. Laboratory tests were carried out to find the best conditions for maximizing the power density and process performances of a RED unit by investigating a number of operating parameters such as fluid velocity and feed solutions concentration.

**Keywords:** Reverse Electrodialysis; Salinity Gradient Power; Heat Engine; Heat-to-power; Ammonium hydrogen carbonate.

## 1 Introduction

Consumption of fossil fuels has dramatically increased in the last decades, reaching record levels year after year, with a global consumption often increasing more rapidly than production (e.g. 2.3% more in 2013) [1]. The spreading of renewable energy technologies is nowadays of paramount importance to meet the growing energy needs and reduce the use of fossil fuels. Within this context, energy from salinity gradients represents a promising source of sustainable energy [2,3]. A number of technologies have been proposed to harvest such energy for generating mechanical or electric energy. Among these, the most studied are pressure-retarded osmosis (PRO) and reverse electrodialysis (RED) [4,5]. In PRO, the salinity gradient is exploited to generate a water flux through a semi-permeable membrane, increasing the volume of the pressurised draw solution thus generating mechanical power by a hydraulic turbine [6,7]. Conversely, in RED process, the salinity gradient generates ion fluxes through ion exchange membranes; this ionic current is converted into electronic current on electrode surfaces, and finally collected by an external load [8–13].

Up to now, research activities for both PRO and RED have been mainly focused on the use of natural solutions as feed streams. In particular, for the case of RED, different options have been investigated so far, from the use of river water and seawater (e.g. [14–16]) to the use of brackish water and concentrated brines [17,18].

The exploitation of natural salinity gradients is very promising, especially in coastal areas, where both dilute and concentrate streams can be available in large amount. On the other hand, using natural streams in SGP technologies have some remarkable drawbacks, such as geographical constraints for plant location and extensive pre-treatment costs to avoid fouling/biofouling phenomena in membrane modules.

Recently, a different application for SGP technologies has been proposed, where the SGP unit (either RED or PRO) operates in a closed loop using artificial saline solutions as working fluids. The exhausted solutions can be then regenerated through a proper regeneration step (either via an electrically-driven or a thermally driven process, acting as energy storage or conversion technology, respectively) and sent back to the SGP stage [2]. Such “closed-loop SGP” system can be economically sustainable, for example, if a cheap source of thermal energy is available for the separation stage, e.g. waste heat from industrial processes. In this way, the system can be considered as a “SGP heat engine”, where low-grade heat is converted into electricity by means of a SGP technology.

This concept was firstly proposed in the 1975 by Loeb [19] and then by Reali [20], who suggested the development of a closed loop PRO system where waste heat or energy from geothermal and volcanic sites could be exploited as thermal energy source for the regeneration step.

The use of artificial salinity gradients also allows exploring new possibilities in terms of unconventional salts and solvents [21], aiming at increasing the performance of the SGP heat engine, which is related to the ratio between the energy produced and the thermal energy required. In this regard, the use of thermolytic salts, such as ammonium hydrogen carbonate ( $\text{NH}_4\text{HCO}_3$ ), has been recently presented as an interesting option for both RED [22–24] and PRO [25]. The peculiar property of  $\text{NH}_4\text{HCO}_3$  is that it can be decomposed into ammonia, carbon dioxide and water by heating above 40–45 °C [26], thus allowing in principle to operate the regeneration step of the SGP heat engine at low temperature (i.e. using very low-grade heat).

Up to now, three different applications have been proposed in the literature for the exploitation of  $\text{NH}_4\text{HCO}_3$  in SGP heat engines: the ammonia-carbon dioxide Osmotic Heat Engine (OHE) [25], the Thermal-Driven Electrochemical Generator (TDEG) [22] and the concept of Microbial Reverse electrodialysis Cell (MRC) [24].

The ammonia-carbon dioxide OHE proposed by McGinnis et al. (2007) is a closed-loop PRO system where a  $\text{NH}_4\text{HCO}_3$  solution is used as draw solution to create high osmotic pressures. A maximum thermal efficiency of 16% of the Carnot efficiency (likely corresponding to an actual energy conversion efficiency of 1.2%) has been predicted for an OHE that uses waste heat around  $50^\circ\text{C}$  [25].

The Thermal-Driven Electrochemical Generator (TDEG) presented in 2012 by Luo et al. [22] represents the first attempt to drive a RED process with  $\text{NH}_4\text{HCO}_3$  solutions (as working fluids). Using a laboratory RED unit with 10 cell pairs, a maximum power density of  $0.33 \text{ W/m}^2_{\text{membrane}}$  was obtained feeding the system with 0.02 M (dilute) – 1.5 M (concentrate)  $\text{NH}_4\text{HCO}_3$  solutions. Another recent application of  $\text{NH}_4\text{HCO}_3$  is represented by microbial RED systems in which a small RED stack is placed directly in contact with a microbial fuel cell (MFC), i.e. a biochemical reactor where exoelectrogenic bacteria are used to oxidize soluble organic matter, thus releasing electrons on an electrode surface. Using solutions with conductivity typical of domestic wastewater ( $\sim 1 \text{ mS/cm}$ ), a power density over  $3 \text{ W/m}^2$  of projected cathode area (i.e. over  $0.3 \text{ W/m}^2$  of membrane area installed in the 5 cell-pairs set-up) has been reported in an MFC [24].

All these works suggest that employing ammonium bicarbonate solutions can be an interesting alternative to generate power by means of SGP-heat engines. Notwithstanding these promising features, insufficient data have been so far collected on the performance of a RED unit fed by  $\text{NH}_4\text{HCO}_3$  solutions. The focus of the present work is on the experimental investigation of the performance of a lab-scale RED unit operated with  $\text{NH}_4\text{HCO}_3$  solutions. A number of different operating conditions including flow rates and salt concentrations were tested, thus providing more insight into the potential use of ammonium bicarbonate for RED closed-loop applications.

## 2 Experimental apparatus and procedures

### 2.1 Experimental apparatus

The experimental campaign was performed with a homemade reverse electrodialysis (RED) module with  $10 \times 10 \text{ cm}^2$  of membrane area. The repeating unit of the system (cell pair) is constituted by a cation exchange membrane (CEM), a dilute (LOW) compartment, an anion exchange membrane (AEM) and a concentrate (HIGH) compartment. The cell pair number was fixed at 10 for each test performed. During the operation, all the compartments are alternately fed with the two feed streams, thus generating a concentration gradient across all the membranes. The CEMs ideally allow only the transport of cations, rejecting anions; analogously, the AEMs allow the passage of anions, rejecting cations. Once the RED system is connected to a variable external electrical load, the resulting ionic currents is converted into electric current at the ends of the stack, where two electrodes are placed. A suitable redox couple (in this case,  $\text{K}_3\text{Fe}(\text{CN})_6 / \text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ) is used in the electrode compartments for this purpose.

Ion exchange membranes provided by Fujifilm Manufacturing Europe BV (The Netherlands) and 270  $\mu\text{m}$  woven spacers (Deukum GmbH, Germany) were used as stack components. The properties of the used IEMs are reported in Table 1.

Table 1. Properties of the two sets of IEMs adopted in the experiments\*.

Membrane	Thickness ( $\mu\text{m}$ )	Areal resistance <sup>a</sup> ( $\Omega \text{ cm}^2$ )	Permselectivity <sup>b</sup> (%)	Ion Exchange Capacity (meq/g)
Fujifilm AEM RP1 80045-01	120	1.84	62 %	1.28
Fujifilm CEM RP1 80050-04	120	3.12	80 %	1.45

\* Nominal data provided by membrane manufacturer using conventional (NaCl) solutions.

<sup>a</sup> electrical resistance measured in 0.5 M NaCl solution at 25°C.

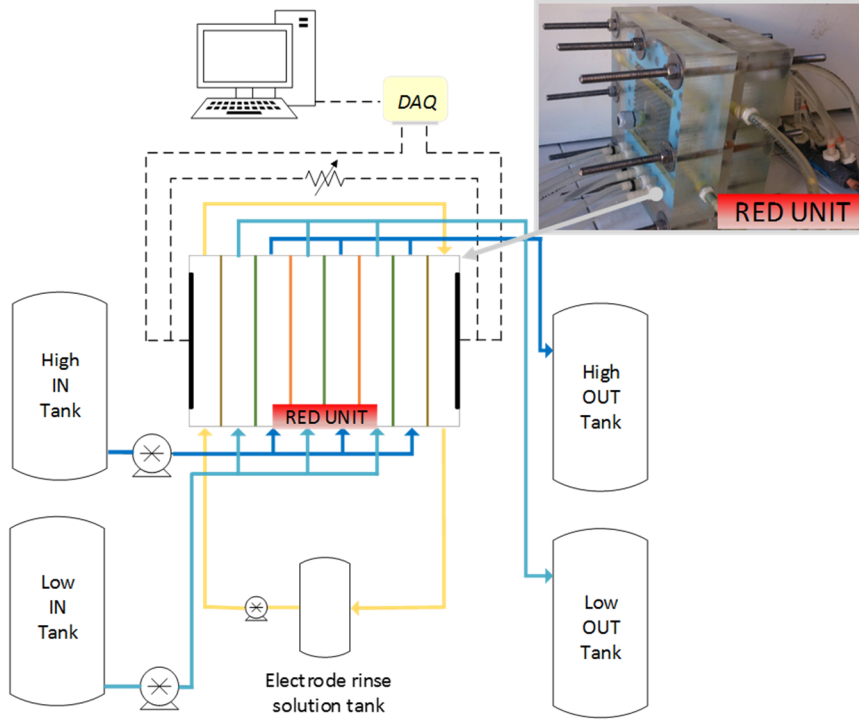
<sup>b</sup> permselectivity measured in 0.05 – 5 M NaCl conditions at 25°C.

Nafion® perfluorinated membranes (DuPont, USA) were employed in the electrode compartments, because of their very high selectivity towards the active redox species.

The electrode compartments contain Ru-Ir oxide-coated Ti electrodes (Magneto Special Anodes BV, The Netherlands). The electrode rinse solution was composed of 0.1 M  $\text{K}_3\text{Fe}(\text{CN})_6$ , 0.1 M  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  (Chem-lab with purity 99.5%), adding 1 M  $\text{NH}_4\text{HCO}_3$  as supporting electrolyte. A flow rate of 225 ml/min in the electrode compartments was kept for all the tests.

The test rig is constituted by the RED unit, plus four inlet/outlet tanks (20 l capacity) for both solutions and the required monitoring device, as sketched in Figure 1.

Two peristaltic pumps (Cellai 530 U) were used to force the concentrate and the dilute solutions to flow within the RED unit. A similar peristaltic pump (Verderflex M025) was used for pumping the electrode rinse solution (ERS) from a glass tank covered by aluminium foil to avoid decomposition of the redox couple due to light exposure [27]. The relevant process variables (inlet-outlet pressure drops, stack voltage) were measured and collected via a data acquisition system (DAQ-National Instruments) and monitored through LabVIEW™ environment. The conductivity of the feed solutions (both at inlets and outlets) were measured by means of a conductivity meter (WTW LF196). A variable resistance (ranging between 0.7 – 54.8  $\Omega$ ) was connected to the RED unit for testing the system under different load conditions. The feed solutions were prepared with demineralized water and ammonium hydrogen carbonate (Sigma-Aldrich, purity 99%).



**Figure 1.** Simplified scheme of the experimental apparatus. A picture of the RED unit used in the present work is reported in the upper-right corner of the figure.

## 2.2 Experimental procedures

### 2.2.1 Experimental measurement of power density

During the testing, the RED unit is connected to the calibrated external resistance ( $R_{ext}$ ), and the stack voltage ( $E_{stack}$ ) is recorded with a frequency of 1 Hz. Therefore, for each value of the external resistance ( $R_{ext}$ ), the corresponding stack current is calculated by Ohm's law:

$$I_{stack} = \frac{E_{stack}}{R_{ext}} \quad (1)$$

The stack voltage is also equal to:

$$E_{stack} = OCV - R_{stack} \cdot I_{stack} \quad (2)$$

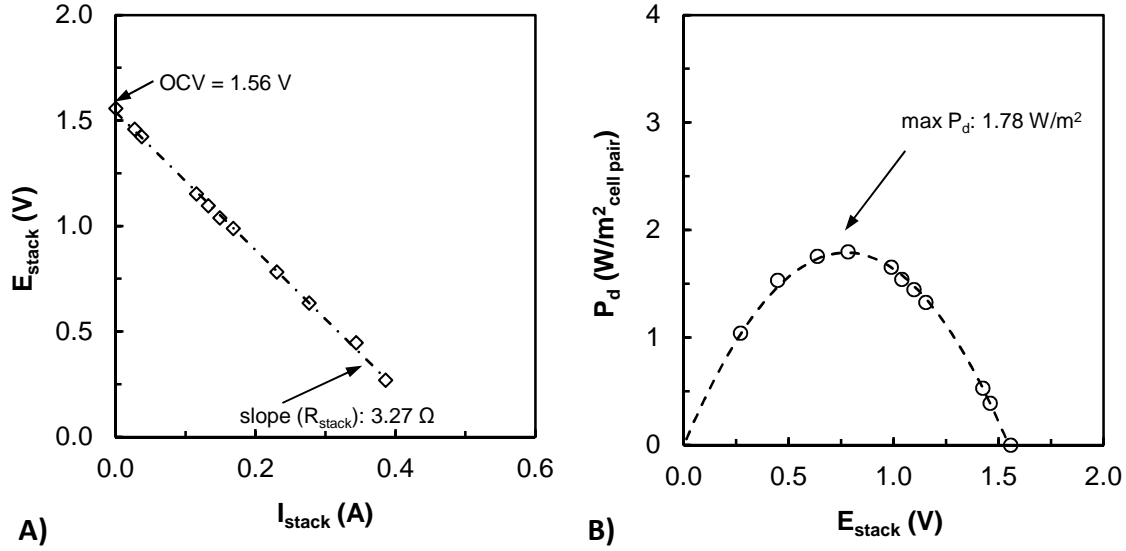
where  $OCV$  is the open circuit voltage (i.e. the stack voltage under zero-current conditions), and  $R_{stack}$  is the internal stack resistance (which can be assessed as the slope of the straight line in a  $E_{stack}$  vs  $I_{stack}$  graph, see Figure 3.A). Thus, the electric power ( $P$ ) is given by:

$$P = E_{stack} \cdot I_{stack} \quad (3)$$

The performance of a RED system is generally expressed as power density, i.e. the amount of power generated per cell pair area:

$$P_d = \frac{P}{N \cdot A} \quad (4)$$

where  $N$  is the number of cell pairs and  $A$  is the active area of one cell pair (Figure 2.B).



**Figure 2.** Example of data measured/inferred by the experimental procedure: A)  $E_{\text{stack}}$  vs  $I_{\text{stack}}$ ; B)  $P_d$  vs  $E_{\text{stack}}$ . RED stack (10x10 cm<sup>2</sup>, 10 cell pairs) equipped with Fujifilm membranes, 270  $\mu\text{m}$  woven spacers.  $C_{\text{HIGH}} = 2 \text{ M NH}_4\text{HCO}_3$ ;  $C_{\text{LOW}} = 0.02 \text{ M NH}_4\text{HCO}_3$ ;  $v = 1 \text{ cm/s}$ ,  $T = 293 \text{ K}$ .

The net power density is calculated as the gross power minus the pumping power required (assuming 100% pumping efficiency):

$$P_{d,\text{net}} = \frac{P - \Delta p_{\text{HIGH}} \cdot Q_{\text{HIGH}}^{\text{tot}} - \Delta p_{\text{LOW}} \cdot Q_{\text{LOW}}^{\text{tot}}}{N \cdot A} \quad (5)$$

where  $\Delta p$  are the pressure drops and  $Q^{\text{tot}}$  is the total (i.e. sum of each channel flow rate) feed flow rate; subscripts *HIGH* and *LOW* refer to concentrate and dilute, respectively. Notably, for each operating condition tested, the concentrate and dilute solution were always fed with the same flow rate (i.e.  $Q_{\text{HIGH}}^{\text{tot}} = Q_{\text{LOW}}^{\text{tot}}$ ). The corresponding pressure drops take into account the contribution relevant to the spacer-filled channel as well as that relevant to the inlet-outlet manifolds (e.g. distributor and collector) which in many cases may be the most prominent [28].

### 2.2.2 Evaluation of blank resistance and corrected power density

The power output values collected from laboratory-scale RED units are affected by the behaviour of the electrode compartments (generally identified with a so-called “blank-resistance”, blank). Despite this, contribution is negligible on full-scale systems (i.e. where hundreds of cell pairs are piled in a single stack), it can be significant for a laboratory-scale unit.

The blank resistance ( $R_{\text{blank}}$ ) can be estimated as the stack resistance when the number of cell pairs approaches zero [29]. For this reason, the stack resistance was experimentally measured by varying

the number of cell pairs (5, 10, 15 and 20), and a blank resistance of 1.07  $\Omega$  was obtained as intercept with y-axis on a  $R_{stack}$  versus N plot.

Therefore, the internal resistance due to the cell pairs only ( $R_{cells}$ ) can be calculated as:

$$R_{cells} = R_{stack} - R_{blank} \quad (6)$$

In this way, a corrected stack voltage can be estimated, disregarding the contribution of the blank resistance:

$$E_{stack,corr} = OCV - R_{cells} \cdot I_{corr} \quad (7)$$

where  $I_{corr}$  is the corrected current, calculated as:

$$I_{corr} = \frac{E_{stack,corr}}{R_{ext}} \quad (8)$$

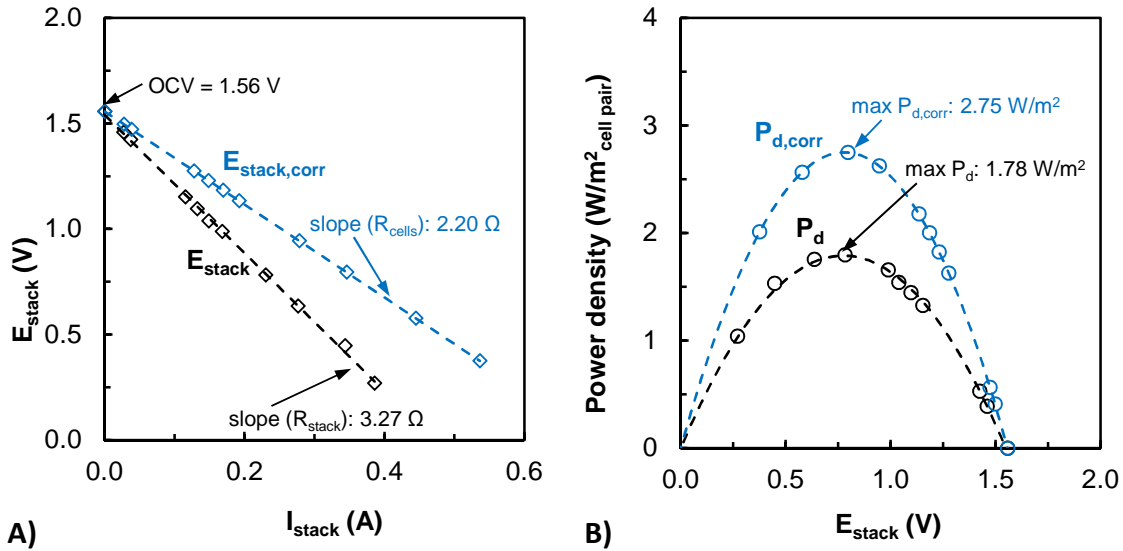
Substituting eq. (8) into eq. (7) and rearranging, the corrected stack voltage is given by:

$$E_{stack,corr} = OCV - E_{stack,corr} \frac{R_{cells}}{R_{ext}} \quad (9)$$

Rearranging eq. (3), eq. (4), eq. (8) and eq. (9), the corrected power density ( $P_{d,corr}$ ) can be calculated as:

$$P_{d,corr} = \frac{OCV^2}{N \cdot A \cdot R_{ext} \left( 1 + \frac{R_{cells}}{R_{ext}} \right)^2} \quad (10)$$

Eq. (10) provides the power density obtainable by a full-scale RED system operating under the same conditions of a laboratory-scale unit. Hence, it provides a reliable indication of the potential of the RED unit on a large scale (Figure 3). Figure 3 also shows the comparison between the relevant magnitudes of the corrected and uncorrected quantities previously described.



**Figure 3.** Example of data measured/inferred by the experimental procedure: A)  $E_{\text{stack}}$  vs  $I_{\text{stack}}$ ; B) Power density vs  $E_{\text{stack}}$ . Black dashed line case includes the blank resistance; blue dashed line case does not include the blank resistance. RED stack ( $10 \times 10 \text{ cm}^2$ , 10 cell pairs) equipped with Fujifilm membranes,  $270 \text{ }\mu\text{m}$  woven spacers.  $C_{\text{HIGH}} = 2 \text{ M NH}_4\text{HCO}_3$ ;  $C_{\text{LOW}} = 0.02 \text{ M NH}_4\text{HCO}_3$ ;  $v = 1 \text{ cm/s}$ ,  $T = 293 \text{ K}$ .

### 3 Results and discussion

The RED unit was tested under different operating conditions, changing the feed concentration of the dilute and the flow velocity of both solutions. For the concentrated solution, an inlet concentration of  $2 \text{ M NH}_4\text{HCO}_3$  was adopted as standard for all tests: this allows to keep a high salinity ratio (i.e. ratio between  $C_{\text{HIGH}}/C_{\text{LOW}}$ ), notwithstanding the relatively low solubility of ammonium bicarbonate in water ( $2.7 \text{ M}$  at  $298 \text{ K}$  [30]). A summary of the tests presented in this work is reported in Table 2.

Table 2. Summary of experimental tests presented in this work.\*

Relevant section	Main focus of the tests	Dilute concentration, $C_{\text{LOW}}$ (M $\text{NH}_4\text{HCO}_3$ )	Feed flow velocity, $v$ (cm/s)
3.1	Influence of dilute concentration ( $C_{\text{LOW}}$ )	0.01 - 0.02 - 0.04 - 0.06 - 0.1	1
3.2	Influence of feed flow velocity ( $v$ )	0.02 - 0.04	0.5 - 1 - 1.5 - 2

\*Overall conditions: RED stack ( $10 \times 10 \text{ cm}^2$ , 10 cell pairs) equipped with Fujifilm membranes,  $270 \text{ }\mu\text{m}$  woven spacers.  $C_{\text{HIGH}} = 2 \text{ M NH}_4\text{HCO}_3$ ;  $T = 293 \text{ K}$ .

#### 3.1 Influence of dilute concentration

The concentration of the dilute solution is a crucial factor for the performance of a RED system, since it affects both the driving force and the resistance of the stack. In particular, a careful selection of the feed dilute concentration can significantly enhance the power output. Notably, the electric resistance of the dilute can represent even the 50% of the whole stack resistance when fresh water ( $0.017 \text{ M NaCl}$ ) and seawater ( $0.5 \text{ M NaCl}$ ) are used as feed solutions [31].

In the case of RED process with  $\text{NaCl}$  solutions, the optimal dilute concentration to maximize the power output has been identified in the range of  $0.01\text{-}0.1 \text{ M NaCl}$ , depending on the stack design



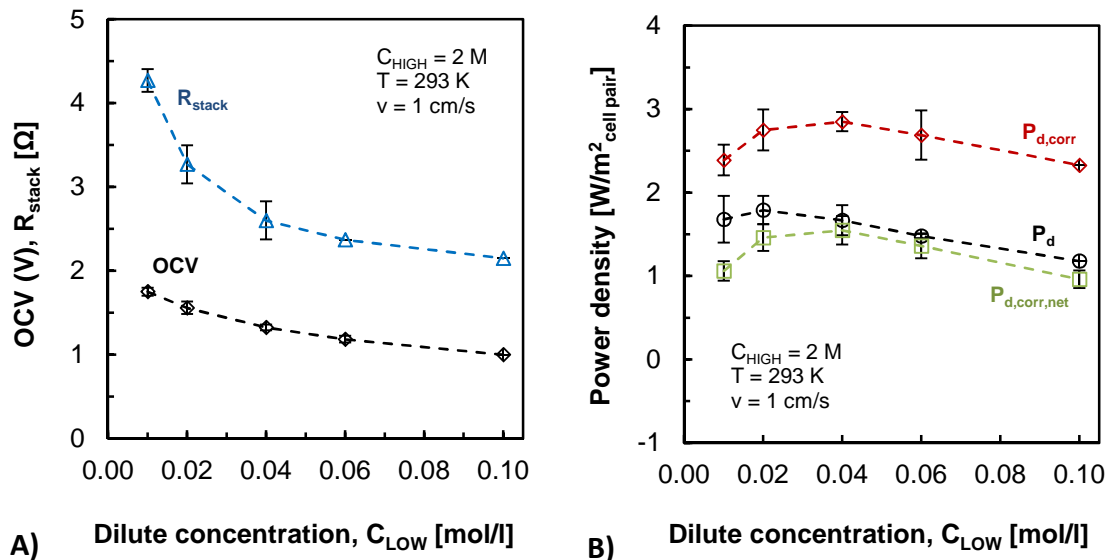
(e.g. channel thickness, membrane resistance) and operating conditions [32–34]. However, the use of unconventional salts such as ammonium bicarbonate requires a new investigation of the optimal concentration range maximizing the performance of the RED process. Moreover, when artificial solutions are used in a closed loop, feed concentrations are not dictated by those of natural sources, and can be purposely chosen for the process.

In this regard, the RED system was tested by changing the feed concentration of the dilute in the range of 0.01-0.1 M  $\text{NH}_4\text{HCO}_3$ . Relevant results are reported in Figure 4: in particular, open circuit voltage ( $OCV$ ) and stack resistance are shown in Figure 4.A, while the corresponding maximum values of power densities are reported in Figure 4.B.

In the investigated range, the lower the dilute concentration, the higher the  $OCV$  and the stack resistance are expected (Figure 4.A). As a matter of fact, the reduction of dilute concentration corresponds to a higher salinity ratio, thus resulting in an increase of the  $OCV$ . Similarly, lowering the feed concentration also causes an increase of the electric resistance in the dilute compartments, which is the main contribution to the stack resistance. These phenomena have a counteracting effect on the power output, leading to a maximum in the gross power density ( $P_d = 1.78 \text{ W/m}^2_{\text{cell pair}}$ ) at  $C_{LOW} = 0.02 \text{ M}$  (Figure 4.B).

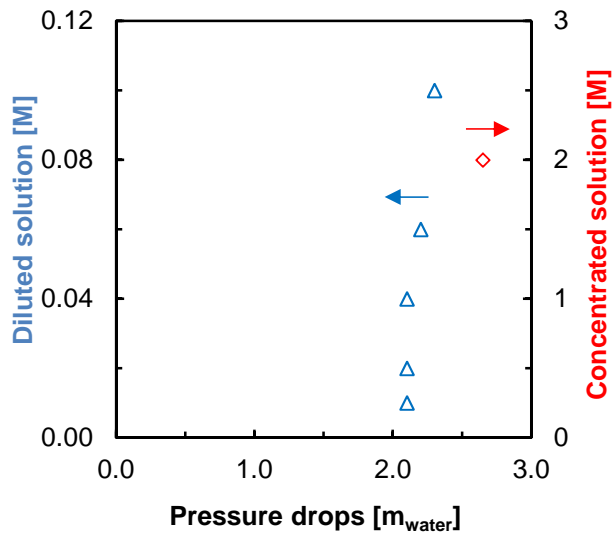
$OCV$  values and trend very similar to those presented here were found by Luo et al. [22]. Conversely, higher  $R_{stack}$  were reported by the same authors [22] allegedly due to the higher spacer thickness and to the different membranes employed (in their case: Selemion CMV and AMV, Asashi glass, Japan). Such a difference results in a  $P_d$  three times lower on average: they found a maximum  $P_d$  at  $C_{LOW} = 0.02$  as in the present case, but equal to  $0.66 \text{ W/m}^2_{\text{cell pair}}$ .

Looking at the corrected power density ( $P_{d,corr}$ ), a different (with respect to  $P_d$ ) optimal value of  $C_{LOW}$  was observed ( $\sim 0.04 \text{ M NH}_4\text{HCO}_3$ ), corresponding to a maximum value for  $P_{d,corr}$  of  $2.85 \text{ W/m}^2_{\text{cell pair}}$  (Figure 4.B).



**Figure 4.** Influence of dilute concentration on process performance. A)  $OCV$  and stack resistance. B) Gross power density, corrected gross power density, corrected net power density. RED stack ( $10 \times 10 \text{ cm}^2$ , 10 cell pairs) equipped with Fujifilm membranes,  $270 \mu\text{m}$  woven spacers.  $C_{HIGH} = 2 \text{ M NH}_4\text{HCO}_3$ ;  $v = 1 \text{ cm/s}$ ,  $T = 293 \text{ K}$ .

Pressure losses were also measured and the relevant results are reported in Figure 5. This figure shows that the concentration has an effect on pressure drop as expected on the basis of the difference in solution viscosity. Clearly, when only the concentration of the dilute solution is changed (see Table 2) only a very slight variation in pressure drop occurs.



**Figure 5.** Influence of dilute concentration on pressure drops. RED stack ( $10 \times 10 \text{ cm}^2$ , 10 cell pairs) equipped with Fujifilm membranes,  $270 \text{ }\mu\text{m}$  woven spacers.  $C_{\text{HIGH}} = 2 \text{ M NH}_4\text{HCO}_3$ ;  $v = 1 \text{ cm/s}$ ,  $T = 293 \text{ K}$ .

By taking into account these hydraulic losses, the net corrected power density was estimated and reported in the same plot of  $P_{d,corr}$  (Figure 4.B): a maximum value of  $1.55 \text{ W/m}^2_{\text{cell pair}}$  was found at the same  $C_{\text{LOW}}$  of  $\sim 0.04 \text{ M}$  as expected. For all tests, each value is provided with an error bar calculated using the maximum discrepancy among results relevant to some reproducibility tests. For the net power density, the experimental uncertainty was estimated by adopting to the uncertainty definition given by Moffat [35,36].

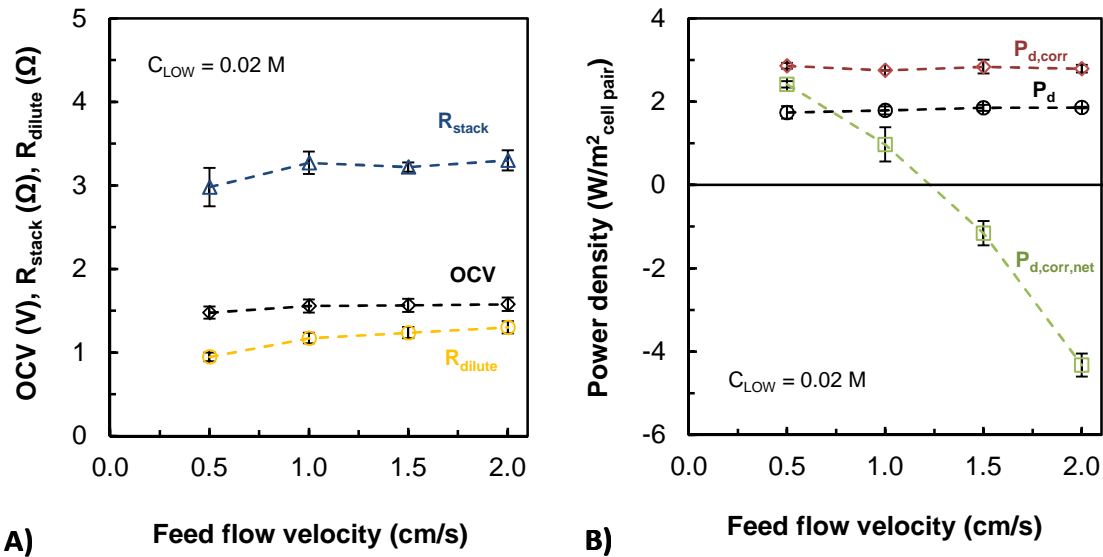
Since the maximum power density was found at  $0.02 \text{ M}$ , while the maximum corrected power density is at  $0.04 \text{ M}$ , the effect of dilute flow rate was investigated by fixing the dilute concentration at these two values (Table 2), as it will be presented in the next section.

### 3.2 Influence of feed flow velocity

In addition to the inlet concentration of feed solutions, another crucial parameter for the RED process is the flow velocity inside compartments, which also strongly affects the pressure drops, and hence the net power output.

The investigated RED system was tested assuming different flow velocities for both solutions, ranging from  $0.5$  up to  $2 \text{ cm/s}$ . Also, as mentioned above, two values of dilute concentration were tested (i.e.  $C_{\text{LOW}}$  equal to either  $0.02$  or  $0.04$ ): the results relevant to  $C_{\text{LOW}} = 0.02 \text{ M}$  are reported in Figure , while those at  $C_{\text{LOW}} = 0.04 \text{ M}$  are shown in Figure .

In Figure .A the effect of flow rate on  $OCV$  and relevant  $R_{stack}$  are reported. Notably, the former would be constant if membranes were ideal. In fact, its actual variation with flow rate is due to the non-perfect permselectivity of the membranes, which allow the passage of little amounts of salt and water. Results show that an increase of flow velocity provides a slight enhancement of the  $OCV$  in the first range (0.5 – 1 cm/s), until a plateau is reached (Figure .A). Such effect is mainly related to the lower residence time inside the stack that allows a practically constant driving force between inlet-outlet to be maintained. Higher flow rates also cause a reduction of polarization phenomena (especially in the dilute solution), which are, however, expected to be very low according to the very low fluxes occurring under open circuit conditions. Likewise, the flow rate has a double effect on  $R_{stack}$ : a low residence time corresponds to a small variation of the dilute channel conductivity thus leading to a high  $R_{stack}$ ; on the other hand, a higher flow rate reduces concentration polarization phenomena (i.e. non-ohmic resistance) thereby providing lower  $R_{stack}$ . For the present case, the first effect appears to be prominent as an increase of  $R_{stack}$  with the flow rate was recorded (Figure .A). As a matter of fact, the resistance due to the dilute compartment, as shown in Figure .A, represents around 30-40% of the stack resistance and its effect is determinant on the stack performance. Also Luo et al. [22] investigated the effect of feed flow rate on process performance. As already discussed for the case of Figure 4, they reported  $OCV$  similar to those of the present work, while the stack resistance was much higher, thus resulting in three times lower  $P_d$  [22].



**Figure 6.** Influence of feed flow velocity on process performance. A)  $OCV$ , stack resistance, resistance of the diluted compartment. B) Gross power density, corrected gross power density, corrected net power density. RED stack (10x10 cm<sup>2</sup>, 10 cell pairs) equipped with Fujifilm membranes, 270  $\mu$ m woven spacers.  $C_{HIGH} = 2$  M;  $C_{LOW} = 0.02$  M;  $T = 293$  K.

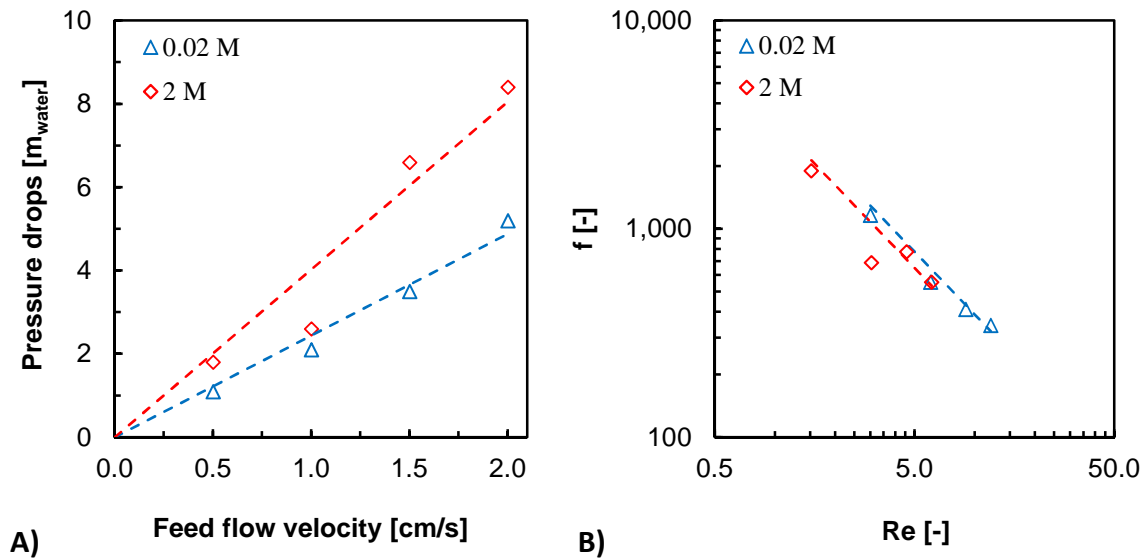
As a result of the simultaneous increase of competing variables as  $OCV$  and  $R_{stack}$ , the power density was found only slightly dependent on the flow rate: an average value of 1.81 and 2.81 W/m<sup>2</sup>cell pair for  $P_d$  and  $P_{d,corr}$  was found, respectively (Figure .B). As already discussed, the net corrected power density (eq. 5) can be calculated considering the pressure drops inside the dilute and concentrate compartments. As seen in Figure .A, the experimental pressure drops

increase as the feed flow velocity increases, but with a different slope depending on the solution concentration (i.e. different fluid-dynamic properties as density and viscosity). The two trends are linear, thus suggesting the existence of a stationary regime at the flow rate range investigated. The two trends were reported also in terms of non-dimensional numbers in Figure .B: the void-channel Reynolds number ( $Re$ ) and the void-channel fanning friction factor ( $f$ ) defined as [10,37]:

$$Re = \frac{\rho \cdot v_{m,void} \cdot d_{h,void}}{\mu} = \frac{2 \cdot \rho \cdot v_{m,void} \cdot H}{\mu} \quad (11)$$

$$f = \frac{\Delta p}{l} \frac{d_{h,void}}{2 \cdot \rho \cdot v_{m,void}^2} \quad (12)$$

where  $v_m$  is the average velocity along the main flow direction in a corresponding spacer-less (void) channel,  $d_{h,void}$  is twice the channel thickness  $H$  (270  $\mu\text{m}$  in our case) and  $m$  is the fluid viscosity (0.9 cP for the dilute solution and 1.88 cP for the concentrate). As it can be seen, the two trends are very similar to each other, being indeed almost. As a consequence, the  $P_{d,corr,net}$  values were calculated using the linear trend instead of the experimental points.

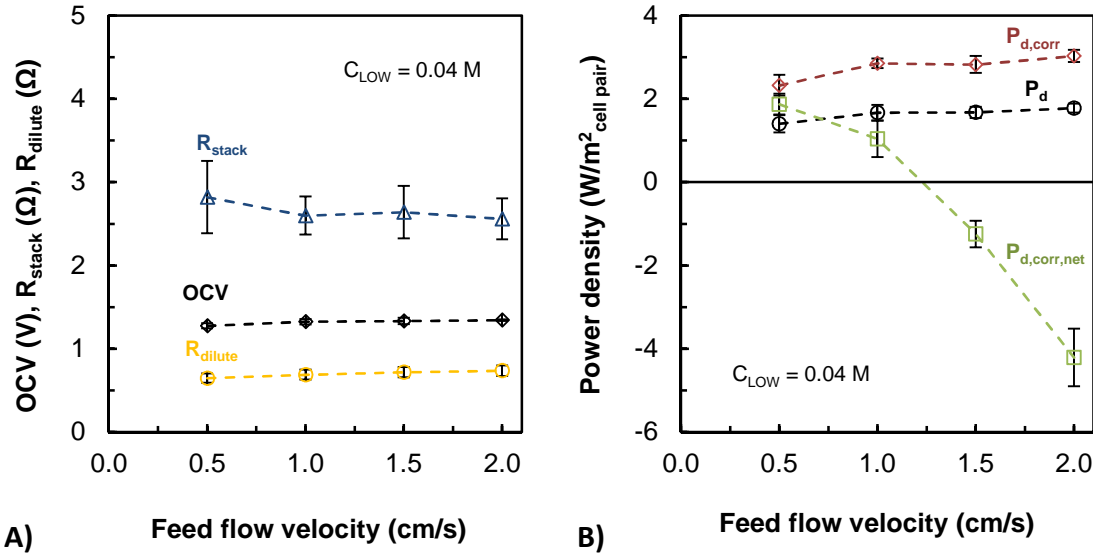


**Figure 7.** Influence of feed flow velocity on the experimental pressure drops. A) Experimental pressure drops values. B) Fanning friction factor as a function of Reynolds number. RED stack (10x10 cm<sup>2</sup>, 10 cell pairs) equipped with Fujifilm membranes, 270  $\mu\text{m}$  woven spacers.  $C_{HIGH} = 2 \text{ M}$ ;  $C_{LOW} = 0.02 \text{ M}$ ;  $T = 293 \text{ K}$ .

The resulting  $P_{d,corr,net}$  reported in Figure .B were found to be lower than zero for all flow velocities being higher than 1.25 cm/s (see Figure .B). As it can be seen, the lowest flow velocity ( $\sim 0.5$  cm/s) among those tested, was found preferable to maximize the net power density under the investigated conditions (Figure .B). Actually, even lower flow rates should be investigated in the future in order to recognize the maximum value of  $P_{d,corr,net}$ .

A similar test was performed for the case of a dilute concentration of 0.04 M  $\text{NH}_4\text{HCO}_3$ , which was the value maximizing the corrected power density (Figure 4.B). Corresponding results are

shown in Figure . Trends quite similar to those relevant to  $C_{LOW} = 0.02$  M were found with the main difference concern the  $R_{stack}$  trend. As a difference from the case at  $C_{LOW} = 0.02$  M,  $R_{stack}$  exhibits here a decreasing trend as the flow rate increases. This is allegedly due to the influence of polarization phenomena, which are in this case more relevant than the resident time effect (Figure .A): at this higher concentration (than the previous case), the dilute channel resistance is poorly dependent on the residence time (Figure .A).



**Figure 8.** Influence of feed flow velocity on process performance. A) OCV, stack resistance, resistance of the diluted compartment. B) Gross power density, corrected gross power density, corrected net power density. RED stack (10x10 cm<sup>2</sup>, 10 cell pairs) equipped with Fujifilm membranes, 270  $\mu$ m woven spacers.  $C_{HIGH} = 2$  M;  $C_{LOW} = 0.04$  M;  $T = 293$  K.

The corrected net power density was calculated using the same procedure already described for the case of  $C_{LOW} = 0.02$  M and is not reported again here.

These results confirm that (i) the highest power density is achieved at the lowest flow rate and that (ii) flow velocities higher than 1 cm/s are unsuitable for generating electric power from the RED unit adopted in the present study.

## 4 Conclusions

Recent works have proved that  $NH_4HCO_3$ -water solutions may be conveniently used in a RED-closed loop for converting low-grade waste heat into electric current. Aim of the present work was to investigate the performance of a lab-scale (i.e. 10x10 cm<sup>2</sup>) RED unit fed by  $NH_4HCO_3$ -water solutions. In particular, the effect of dilute concentration and feed flow rate on gross power density were investigated. Pressure drops were also measured, thereby allowing the estimate of the net power density achievable. Results have shown that at a given flow rate (i.e. 1 cm/s) a dilute concentration of about 0.02-0.04M guarantees the largest power output. At these values of concentration, under the conditions here investigated, a maximum net power output of 2.42  $W/m^2_{cell\ pair}$  can be obtained at the lowest feed flow velocity (i.e. 0.5 cm/s). On the other hand, feed flow rates higher than 1 cm/s lead to negative power output being the power loss due to pressure drop larger than the power production.

Overall, the use of ammonium bicarbonate allowed to reach values of power density comparable with the state-of-the-art of the RED process with conventional (NaCl) solutions [33], although membranes are not optimized yet for the use of this salt. Such finding suggests that ammonium bicarbonate could be a promising salt for the RED process. Furthermore, results highlight that the power density achieved in this work is three times higher than that reported by Luo et al. in a similar work [22] where the same salt is used. The main difference has been identified in the much lower stack resistance, likely due to an improved formulation of IEMs with a lower thickness and higher ionic conductivity, thus also emphasizing the potential for further technological improvements. Future work will deal with the “regeneration” of the  $\text{NH}_4\text{HCO}_3$  solutions exiting from the RED-unit in order to assess the final feasibility of the RED heat engine for waste heat-to-power conversion.

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## Nomenclature

$A$	active area of one cell pair [ $\text{m}^2$ ]
$C$	molar concentration [ $\text{mol/l}$ ]
$d_{h,void}$	hydraulic diameter [ $\text{m}$ ]
$E_{stack}$	stack voltage [V]
$f$	void fanning friction factor [-]
$H$	channel thickness [ $\text{m}$ ]
$I_{stack}$	stack current [A]
$l$	channel length [ $\text{m}$ ]
$N$	cell pairs number [-]
$\Delta p$	pressure drops [Pa]
$P$	electric power [W]
$P_d$	electric power density [ $\text{W}/\text{m}^2_{\text{cell pair}}$ ]
$Q^{tot}$	total (i.e. inclusive of all channels) feed flow rate [ $\text{m}^3/\text{s}$ ]
$R_{blank}$	blank resistance [ $\Omega$ ]
$R_{cells}$	cell pairs resistance [ $\Omega$ ]
$R_{dilute}$	resistance of diluted solution [ $\Omega$ ]
$Re$	void Reynolds number [-]
$R_{ext}$	external resistance [ $\Omega$ ]

$R_{stack}$	internal stack resistance [ $\Omega$ ]
$T$	temperature [K]
$v$	velocity [cm/s]
$v_{m,void}$	mean velocity along the main flow direction (void channel) [cm/s]

### Greek letters

$\rho$	solution density [ $\text{kg m}^{-3}$ ]
$\mu$	solution dynamic viscosity [Pa s]

### Subscripts

<i>corr</i>	corrected value (of power output, stack voltage, stack current) obtained by using the stack resistance without the contribute of the blank resistance
<i>HIGH</i>	concentrate solution
<i>LOW</i>	dilute solution
<i>net</i>	net value (of power output) measured after subtracting the power losses due to the pumping of feed solutions

### Acronyms

<i>AEM</i>	anion exchange membrane
<i>CEM</i>	cation exchange membrane
<i>DAQ</i>	data acquisition system
<i>ERS</i>	electrode rise solution
<i>IEM</i>	ion exchange membrane
<i>MFC</i>	microbial fuel cell
<i>OCV</i>	open circuit voltage [V]
<i>OHE</i>	osmotic heat engine
<i>PRO</i>	pressure retarded osmosis
<i>RED</i>	reverse electrodialysis
<i>SGP</i>	salinity gradient power
<i>TDEG</i>	thermal driven electrochemical generator

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