


 Cite this: *RSC Adv.*, 2014, 4, 42617

# Potential of brackish water and brine for energy generation by salinity gradient power-reverse electrodialysis (SGP-RE)

Ramato Ashu Tufa,<sup>a</sup> Efrem Curcio,<sup>\*ab</sup> Willem van Baak,<sup>c</sup> Joost Veerman,<sup>d</sup> Simon Grasman,<sup>d</sup> Enrica Fontananova<sup>b</sup> and Gianluca Di Profio<sup>b</sup>

In the present work, a salinity gradient power-reverse electrodialysis (SGP-RE) unit was tested for the production of electrical energy by exploiting the chemical potential of real brackish water and exhaust brine from a solar pond. A cross-flow SGP-RE module (REDstack B.V.), equipped with AEM-80045 and CEM-80050 membranes specifically developed by Fujifilm Manufacturing Europe B.V. within the EU-funded project REAPOWEP ("Reverse Electrodialysis Alternative Power Production"), was able to generate a maximum power density (expressed in W m<sup>-2</sup> membrane pair – MP) of 3.04 W m<sup>-2</sup> MP when operated with pure NaCl aqueous solutions (0.1 M in low concentration compartment – LCC, 5 M in high concentration compartment – HCC) at 20 °C and at a recirculation rate of 20 L h<sup>-1</sup>. However, a drastic reduction to 1.13 W m<sup>-2</sup> (–63%) was observed when feeding the SGP-RE unit with artificial multi-ion solutions mimicking real brackish water and exhaust brine. Further experimental activity allowed to identify Mg<sup>2+</sup> ion as responsible for the significant increase in stack resistance and consequent depletion in SGP-RE performance. Therefore, specific softening treatments of the real solutions should be considered in order to maintain the process efficiency at practical level.

Received 19th June 2014  
Accepted 13th August 2014

DOI: 10.1039/c4ra05968a

www.rsc.org/advances

## Introduction

Global demand for energy is increasing at an unsustainable rate mainly due to global economic expansion, population growth and an increasing living standard in emerging countries. As a result, the extensive utilization of available fossil fuels is causing a progressive depletion of these resources and an increase in global CO<sub>2</sub> emissions. Renewable energy sources with limited thermal and environmental pollution, and absence of net emission of greenhouse gases and radioactive wastes, are attracting an increasing attention. In particular, reverse electrodialysis (RE) is an emerging technology having the potential to generate energy from salinity power gradients (SGP). In a typical SGP-RE module, cation exchange membranes (CEM) and anion exchange membranes (AEM) are stacked alternately in a module; driven by a concentration gradient, the diffusive flux of ions generates an electrochemical membrane potential recorded as a voltage across electrodes.<sup>1</sup> From a theoretical point of

view, the value of the voltage from an unloaded RE stack (open circuit voltage – OCV) is predicted by the following equation:<sup>2</sup>

$$OCV = \frac{2NRT}{F} \left[ \frac{\alpha_{AEM}}{z_a} \ln \left( \frac{\gamma_{a,HCC} C_{a,HCC}}{\gamma_{a,LCC} C_{a,LCC}} \right) + \frac{\alpha_{CEM}}{z_c} \ln \left( \frac{\gamma_{c,HCC} C_{c,HCC}}{\gamma_{c,LCC} C_{c,LCC}} \right) \right] \quad (1)$$

in which  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $N$  is the number of membrane pairs,  $T$  is the temperature (K),  $z$  is the valence,  $\alpha$  is the average transport number of counter-ions,  $F$  is the Faraday constant (96 485 C mol<sup>-1</sup>),  $\gamma$  is the activity coefficient of the ion, and  $C$  is the concentration (mol L<sup>-1</sup>); subscripts a, c, HCC and LCC refer to anion, cation, high concentration compartment and low concentration compartment, respectively.

Previous investigations carried out on aqueous NaCl solutions, which mimic seawater and river water salinity, reached a power density around 2 W m<sup>-2</sup> of membrane<sup>3–7</sup> and energy efficiency around 50%.<sup>8</sup> Vermaas *et al.* (2013) showed that the theoretically obtained Gibbs free energy of mixing seawater (30 g L<sup>-1</sup> NaCl) and river water (1 g L<sup>-1</sup> NaCl), both at a flow rate of 1 m<sup>3</sup> s<sup>-1</sup> is 1.39 MW.<sup>8</sup>

Advantages of SGP-RE operations carried out at high concentration in the HCC have been clearly envisaged in the work of Post *et al.* (2007); if LCC and HCC are fed with 0.05 M and 5 M NaCl, respectively, the theoretically available amount of

<sup>a</sup>Department of Environmental and Chemical Engineering, University of Calabria (DIATIC-UNICAL), via P. Bucci CUBO 45A, 87036 Rende, CS, Italy. E-mail: e.curcio@unical.it; Fax: +39 0984 496655; Tel: +39 0984 494013

<sup>b</sup>Institute on Membrane Technology of the National Research Council (ITM-CNR), c/o University of Calabria, via P. Bucci, cubo 17/C, 87036 Rende, CS, Italy

<sup>c</sup>Fujifilm Manufacturing Europe B.V., Oudenstaart 1, 5047 TK, Tilburg, The Netherlands

<sup>d</sup>REDstack B.V., Pieter Zeemanstraat 6, 8606 JR, Sneek, The Netherlands



energy from mixing 1 m<sup>3</sup> of diluted and 1 m<sup>3</sup> of a concentrated solution at 293 K increases to 15 MJ.<sup>9</sup>

At present, literature works on RE systems operated under high concentrated solutions like brine are less in number and, most of the work, refer to pure NaCl aqueous solutions. A power density up to 0.87 W m<sup>-2</sup> (all data are referred to total membrane area, unless otherwise specified) has been reported for a RE system operated with a standard grade electrodialysis membrane compartments filled with a coal-mine brine and fresh water.<sup>10</sup> Theoretical models predict that a power density up to 8.5 W m<sup>-2</sup> is achievable by appropriate optimization and use of specially developed AEM and CEM membranes in contact with brine and seawater solutions.<sup>1</sup> However, the behaviour of a RE system might vary significantly when operated with real solutions. From eqn (1) it is possible to roughly envisage the different levels of influence of the monovalent and multivalent ions on the open circuit voltage generated by SGP-RE. Assuming apparent membrane permselectivity and activity coefficients constant, the electrochemical potential generated by monovalent ions (almost all investigations in literature focus on Na<sup>+</sup> and Cl<sup>-</sup>) is about twice as large as the one produced by divalent ions (Mg<sup>2+</sup> and Ca<sup>2+</sup> are among the most abundant ions in natural water) when operating at equal ion concentration ratio. Therefore, the sensitivity of a SGP-RE system to real feed conditions is crucial for practical applications.

To date, literature lacks systematic and adequate information on the effect of the simultaneous presence of ions other than sodium and chloride on SGP-RE performance. Vermaas *et al.* (2014) observed that, when using a mixture with a molar fraction of 10% MgSO<sub>4</sub> and 90% of NaCl in both LCC and HCC, experimentally obtained power density in steady state decreased from 29% to 50% compared to the case, in which the feed solutions contained only NaCl as a salt.<sup>11</sup> An increase in stack resistance because of the addition of Mg<sup>2+</sup> ions into sodium chloride solution was also noticed by Post *et al.* (2009).<sup>12</sup> Further experimental investigation is needed in order to define clearly the potentialities of the SGP-RE technology and to take a decisive step towards real applications.

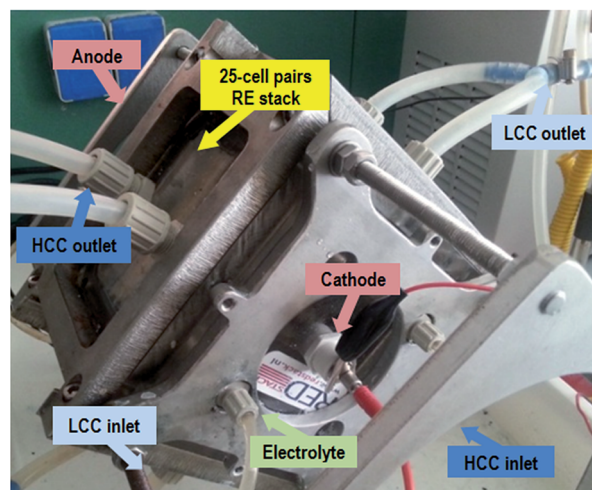
In the present work, with the aim to investigate realistic high-salinity conditions, in which sodium, magnesium, calcium, chloride, sulfate, and bicarbonate are the most common and abundant salt ions in natural waters, experiments have been carried out using brackish water and brine from solar ponds (Sicily, Italy) as a sources for low concentration compartment (LCC) and high concentration compartment (HCC) of a SGP-RE unit, respectively. The effect of ionic composition on SGP-RE was evaluated by the measurement of current, voltage and power density.

## Materials and methods

### Reverse electrodialysis stack

Experimental tests were carried out on a SGP-RE stack (Fig. 1a) provided by REDstack B.V (The Netherlands). The stack, operating in a cross-flow configuration, has an active membrane area of 0.01 m<sup>2</sup> (10 cm × 10 cm) and 25 cell pairs. The module was equipped with 270 μm polyethylene gaskets and PET

a)



b)

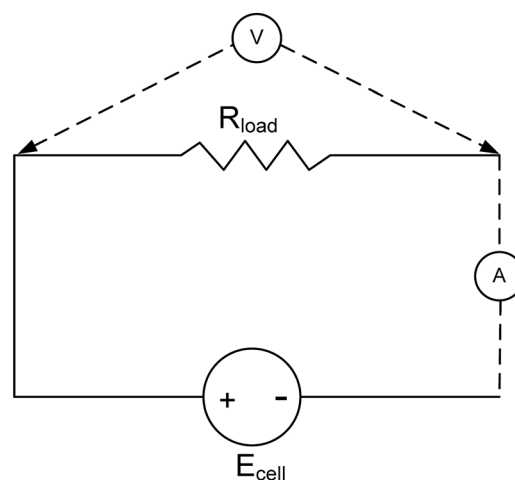


Fig. 1 a) The cross-flow stack used in SGP-RE experiments. (b) Electric circuit diagram of the experimental apparatus. The ammeter (A) is connected in series and voltmeter (V) connector in parallel with the resistance box ( $R_{load}$ ).

spacers (Deukum GMBH, Germany). Anode and cathode made of inert Ti-Ru/Ir mesh had a dimension of 10 cm × 10 cm (MAGNETO Special Anodes B.V., The Netherlands). All experiments were carried out at 20 °C.

### Membranes

The ion exchange membranes (IEM) used are AEM-80045 and CEM-80050 provided by Fujifilm Manufacturing Europe B.V (The Netherlands). The membranes were activated in a 0.1 M NaCl solution before use and stored in the same solution in the stack during the intervals of the testing periods. Membrane characteristics are summarized in Table 1.<sup>13</sup>

### Electrolyte and testing solutions

The electrolyte solution, recirculated throughout the electrolytic compartments at 30 L h<sup>-1</sup> by Masterflex L/S digital peristaltic



Table 1 Relevant properties of ion exchange membranes<sup>13</sup>

Membrane code	Thickness <sup>a</sup> (μm)	Ion exchange capacity (mmol g <sup>-1</sup> membrane)	Density of fixed charges <sup>a</sup> (mol L <sup>-1</sup> )	Membrane area resistance <sup>b</sup> (Ω cm <sup>2</sup> )
Fuji-AEM-80045	129 ± 2	1.4 ± 0.1	3.8 ± 0.2	1.551 ± 0.001
Fuji-CEM-80050	114 ± 2	1.1 ± 0.1	2.4 ± 0.2	2.974 ± 0.001

<sup>a</sup> Measurement conditions: NaCl 0.5 M, 20 °C. <sup>b</sup> Measurement conditions: NaCl 0.5 M, 20 °C, 2.8 cm s<sup>-1</sup>.

Table 2 Ion composition of real brackish water and brine from solar pond (20 °C). Source: Ettore Infera evaporation salt pond (Sicily, Italy)

		Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Brackish water	Concentration (mg L <sup>-1</sup> )	1520	49.7	101	323	3560	0.523	335
	Molar ratio		[Na <sup>+</sup> ]/[K <sup>+</sup> ] = 52.1	[Na <sup>+</sup> ]/[Ca <sup>2+</sup> ] = 26.4	[Na <sup>+</sup> ]/[Mg <sup>2+</sup> ] = 4.99		[Cl <sup>-</sup> ]/[HCO <sub>3</sub> <sup>-</sup> ] = 11 717	[Cl <sup>-</sup> ]/[SO <sub>4</sub> <sup>2-</sup> ] = 28.8
Brine from solar pond	Concentration (mg L <sup>-1</sup> )	66 000	7740	242	37 400	170 000	50.0	64 400
	Molar ratio		[Na <sup>+</sup> ]/[K <sup>+</sup> ] = 14.5	[Na <sup>+</sup> ]/[Ca <sup>2+</sup> ] = 474	[Na <sup>+</sup> ]/[Mg <sup>2+</sup> ] = 1.86		[Cl <sup>-</sup> ]/[HCO <sub>3</sub> <sup>-</sup> ] = 5841	[Cl <sup>-</sup> ]/[SO <sub>4</sub> <sup>2-</sup> ] = 7.15
	Theoretical voltage over membrane <sup>a</sup> (mV)	84	117	5	61	80	122	42

<sup>a</sup> Calculated from eqn (1). Activity coefficients calculated by PHREEQC v. 2.18.00 software.<sup>15</sup>

pumps (Cole-Palmer, US), was prepared by dissolving potassium hexacyanoferrate(II), potassium hexacyanoferrate(III) and sodium chloride (Sigma-Aldrich S.r.l., Italy) in deionized water (PURELAB, Elga LabWater®, 0.055 μS cm<sup>-1</sup>) up to a final concentration of 0.3 M K<sub>4</sub>Fe(CN)<sub>6</sub>, 0.3 M K<sub>3</sub>Fe(CN)<sub>6</sub> and 2.5 M NaCl.

Testing solutions (composition in Table 2) were prepared by dissolving the following reagent grade salts: NaHCO<sub>3</sub>, KCl and Na<sub>2</sub>SO<sub>4</sub> purchased from Sigma Aldrich S.r.l. (Italy); NaCl, CaCl<sub>2</sub>·2H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O from Carlo Erba Reagenti (Italy) in deionized water.

Salt solutions were recirculated throughout the SGP-RE system at a flow rate of 20 L h<sup>-1</sup> by Masterflex L/S digital peristaltic pumps Mod. no. 7528-10 6–600 rpm (Cole-Palmer, US). Heated circulating baths (PolyScience, US) were used to control the temperature of recirculating streams; temperature at the six inlets of the module was monitored by Multichannel data logging thermometers type K 800024 with high full scale accuracy of ±0.5% rdg (Sper Scientific, US). The conductivity of the solutions was measured by YSI (US) model 3200 Conductivity Instrument.

### Electrochemical measurements

A high dissipation five-decade resistance box in the range of 0.1–1000 Ω (CROPICO, Bracken Hill, US) was used to load the SGP-RE system. DC voltage drop across the load resistors was measured by a 3½ digital multimeter with accuracy of ±0.5% in the range of 200 mV to 200 V (Valleman, DVM760), and the current flowing across the load resistors was measured by Agilent 34422A 6½ digit multimeter, according to the circuit diagram provided in Fig. 1b. All the measurements were carried out under continuous operation. The performance of the

SGP-RE unit was evaluated in terms of voltage (*V*), current (*I*) and power density (*P<sub>d</sub>*). The experimental points *V* vs. *I* were fit by a straight line having the following equation:

$$V(I) = \text{OCV} - R_{\text{stack}} I \quad (2)$$

in which open circuit voltage OCV is evaluated at the intersection of *V(I)* with the voltage axis (*I* = 0), and *R<sub>stack</sub>* is the stack resistance (the slope of the straight line). The intercept of *V(I)* with the current axis (*V* = 0) represents the shortcut current *I<sub>shortcut</sub>*. The calculated electric power density *P<sub>d</sub>* (expressed in terms of W m<sup>-2</sup> of the AEM and CEM pair) plotted as a function of the current density *i* shows a typical parabolic trend.

It is noteworthy to mention that power density is equal to zero when the current is equal to zero (open circuit condition) or when the voltage is equal to zero (shortcut current condition).

Ion chromatography (IC) was used to evaluate the variation in the composition of LCC dilute solutions after one hour of SGP-RE operation in batch mode.

Cation and anion analysis were performed by 861 Advanced compact ion chromatograph (Metrohm Italiana SrL, Italy) and data processed by ICNet 2.3 software. For cation analysis, Metrosep A Supp 5 250/4.0 column and Metrosep A Supp 4/5 Guard precolumn were used with eluent solution 2 mM HNO<sub>3</sub>/0.25 mM oxalic acid. For anion analysis, Metrostep C4-250/4.0 column and Metrostep C 4 Guard precolumns were used, with 3.2 mM Na<sub>2</sub>CO<sub>3</sub>/1 mM NaHCO<sub>3</sub> as the eluent solution.

## Results and discussion

### Reference test with NaCl

SGP-RE performance was preliminarily checked by feeding aqueous NaCl solutions (LCC: 0.1 M; HCC: 5 M). According to



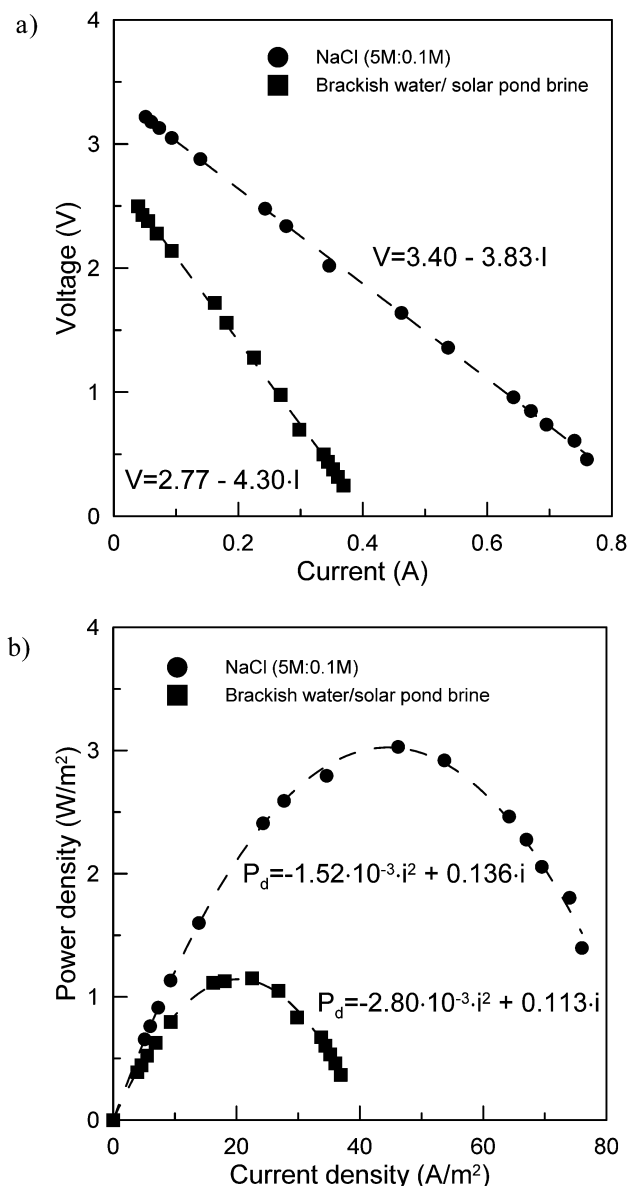


Fig. 2 a) Voltage vs. current; (b) gross power density vs. current density. Data collected under reference conditions: NaCl solution (0.1 M/0.5 M). Temperature: 20 °C. Margin of error within 10%.

Fig. 2a, the measured OCV was 3.4 V and  $I_{\text{shortcut}} = 0.89$  A. The power density curve shown in Fig. 2b is fitted by eqn (3) for  $a = 1.52 \times 10^{-3}$  and  $b = 0.136$ . Under these conditions, the system was able to provide a maximum gross power density of  $3.04 \text{ W m}^{-2}$  in correspondence to a current density of  $44.7 \text{ A m}^{-2}$ . The maximum gross power density generated under these conditions was assumed as a reference for the system operated with multi-ion solutions.

Kim and Logan (2011) showed an innovative microbial reverse-electrodialysis unit (5-cells stack), when operated with typical seawater (600 mM NaCl) and river water (12 mM NaCl) solutions at  $0.85 \text{ mL min}^{-1}$ , produced up to  $3.6 \text{ W m}^{-2}$  (cathode surface area) and 1.2–1.3 V with acetate as a substrate; a higher flow rate ( $1.55 \text{ mL min}^{-1}$ ) resulted in power densities up to  $4.3 \text{ W m}^{-2}$ .<sup>16</sup>

In a comparative study between reverse electrodialysis and pressure retarded osmosis, both considered for applications on seawater and river water, Post *et al.* (2007) calculated a potential maximum power density for SGP-RE in the range of  $2\text{--}4 \text{ W m}^{-2}$ .<sup>9</sup>

Using a 50-cells stack, a power density of  $0.93 \text{ W m}^{-2}$  was obtained by Veerman and colleagues (2009) with artificial river water ( $1 \text{ g L}^{-1}$  NaCl) and artificial sea water ( $30 \text{ g L}^{-1}$  NaCl).<sup>4</sup>

Daniilidis *et al.* (2014) achieved a power density of  $6.7 \text{ W m}^{-2}$  of total membrane area using 0.01 M NaCl solution against 5 M at 60 °C, in general, the power density was found to increase monotonically for highly concentrated feed solutions.<sup>17</sup>

Theoretical predictions on a 12-cells stack equipped with Fujifilm ion exchange membranes and operated with 0.5 M/5.4 M NaCl diluate/concentrate solutions resulted in a maximum gross power density of  $2.4 \text{ W m}^{-2}$ .<sup>4</sup> A maximum gross power density of  $2.2 \text{ W m}^{-2}$  was measured in a stack having an intermembrane distance of 100  $\mu\text{m}$  using 0.507 M NaCl as artificial seawater and 0.017 M NaCl as artificial river water.<sup>7</sup>

### Tests on brackish water/solar pond brine

SGP-RE performance was then evaluated using artificial brackish water (fed to LCC) and exhaust brine from a solar pond (fed to HCC) according to the composition detailed in Table 2. Experimental data reported in Fig. 2a and b show a significant reduction in the maximum gross power density generated by

Table 3 Molar composition of binary LCC/HCC solutions used to investigate the effect of individual ions in the presence of NaCl

LCC solution composition	HCC solution composition	Parameters in eqn (2)	
		OCV (V)	$R_{\text{stack}}$ ( $\Omega$ )
0.1 M NaCl	5 M NaCl	3.40	3.83
$0.0999975 \text{ M NaCl} + 8.5 \times 10^{-6} \text{ M}$	$4.99915 \text{ M NaCl} + 8.5 \times 10^{-4} \text{ M}$	3.39	3.79
$\text{NaHCO}_3 [\text{Cl}^-]/[\text{HCO}_3^-] = 11.717$	$\text{NaHCO}_3 [\text{Cl}^-]/[\text{HCO}_3^-] = 5841$		
$0.098 \text{ M NaCl} + 0.002 \text{ M KCl} [\text{Na}^+]/$ $[\text{K}^+] = 52.1$	$4.68 \text{ M NaCl} + 0.32 \text{ M KCl} [\text{Na}^+]/$ $[\text{K}^+] = 14.5$	3.40	4.08
$0.096 \text{ M NaCl} + 0.004 \text{ M CaCl}_2 [\text{Na}^+]/$ $[\text{Ca}^{2+}] = 26.4$	$4.99 \text{ M NaCl} + 0.01 \text{ M CaCl}_2 [\text{Na}^+]/$ $[\text{Ca}^{2+}] = 474$	3.27	3.84
$0.0966 \text{ M NaCl} + 0.0034 \text{ M Na}_2\text{SO}_4$ $[\text{Cl}^-]/[\text{SO}_4^{2-}] = 28.8$	$4.39 \text{ M NaCl} + 0.61 \text{ M Na}_2\text{SO}_4 [\text{Cl}^-]/$ $[\text{SO}_4^{2-}] = 7.15$	3.40	4.15
$\text{NaCl } 0.083 \text{ M} + \text{MgCl}_2 \text{ } 0.017 \text{ M}$ $[\text{Na}^+]/[\text{Mg}^{2+}] = 4.99$	$\text{NaCl } 3.25 \text{ M} + \text{MgCl}_2 \text{ } 1.75 \text{ M} [\text{Na}^+]/$ $[\text{Mg}^{2+}] = 1.86$	2.73	6.69





the SGP-RE stack. Considering the value of  $3.04 \text{ W m}^{-2}$  as a reference (recorded when operating with pure NaCl solutions), it was found that  $P_{d,\max}$  decreased down to  $1.13 \text{ W m}^{-2}$  in correspondence to a current density of  $20.1 \text{ A m}^{-2}$  when operating with artificial brackish water/brine solutions. Moreover, the  $-63\%$  power density reduction was accompanied by an increase of  $76\%$  in stack resistance (from  $3.83$  to  $6.76 \Omega$ ), whereas OCV and shortcut current decreased to  $2.77 \text{ V}$  and  $0.41 \text{ A}$ , respectively.

### Effect of other ions

In order to discriminate the effect of multiple ions on the drastic reduction of power density generated by the SGP-RE unit operated with real solutions, the combined effect of each single cation ( $X^{n+}$ ) and anion ( $Y^{m-}$ ) in the presence of NaCl was investigated, and binary solutions were prepared according to the compositions reported in Table 3. The ratios  $[\text{Cl}^-]/[\text{Y}^{m-}]$  and  $[\text{Na}^+]/[\text{X}^{n+}]$  within solutions fed to LCC and HCC were maintained the same as in brackish water and brine, respectively. The trend of voltage, current and power density when the SGP-RE was operated with multi-ion solutions is shown in Fig. 3a and b. The observed effect of  $\text{HCO}_3^-$  on SGP-RE performance was negligible because of the very low concentration of bicarbonate ion in both LCC ( $8.5 \times 10^{-6} \text{ M}$ ) and HCC ( $8.5 \times 10^{-4} \text{ M}$ ). As a result, the OCV remained substantially unchanged ( $3.39 \text{ V}$ ), as well as  $I_{\text{shortcut}}$  ( $0.89 \text{ A}$ ) and  $P_{d,\max}$  ( $3.03 \text{ W m}^{-2}$ ).

Despite its significant concentration in the brine ( $0.32 \text{ M}$ ), the impact of  $\text{K}^+$  on the power density was quite limited because of the similar electrochemical properties of  $\text{Na}^+$  and  $\text{K}^+$  ions, listed as follows: ionic radii of unhydrated  $\text{Na}^+$  and  $\text{K}^+$  are  $1.17 \text{ \AA}$  and  $1.64 \text{ \AA}$ , respectively; ionic radii of hydrated  $\text{Na}^+$  and  $\text{K}^+$  are  $3.58 \text{ \AA}$  and  $3.32 \text{ \AA}$ , respectively;<sup>18</sup> ion diffusion coefficients in water for  $\text{Na}^+$  and  $\text{K}^+$  are  $1.334 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $1.957 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , respectively.<sup>19</sup> Although no appreciable difference in OCV was observed,  $I_{\text{shortcut}}$  moderately decreased to  $0.83 \text{ A}$  ( $-6.7\%$ ) and  $R_{\text{stack}}$  increased to  $4.08 \Omega$  ( $+6.5\%$ ). The maximum power density ( $2.84 \text{ W m}^{-2}$ ) was reached at a current density of  $41.8 \text{ A m}^{-2}$ .

Because of its propensity to form sparingly soluble  $\text{CaSO}_4$  and to precipitate from solution,  $\text{Ca}^{2+}$  is generally present in natural waters only at relatively low concentration. As a consequence, for the investigated LCC/HCC composition of  $0.004 \text{ M}/0.096 \text{ M CaCl}_2$ , both OCV and power density were affected in a limited extent ( $-4\%$  and  $-6.6\%$  with respect to pure NaCl, respectively). The concentration of sulphate and magnesium ions is typically highest after  $\text{Na}^+$  and  $\text{Cl}^-$  in brine, seawater and brackish water. However, the presence of  $\text{SO}_4^{2-}$  did not significantly change OCV and resulted in a moderate decrease of  $I_{\text{shortcut}}$  ( $0.82 \text{ A}$ ) and  $P_{d,\max}$  ( $2.79 \text{ W m}^{-2}$ ,  $-8.2\%$  with respect to pure NaCl).

On the other hand, the presence of magnesium drastically decreased both OCV ( $2.73 \text{ V}$ ,  $-20\%$  with respect to pure NaCl) and power density ( $1.11 \text{ W m}^{-2}$ ,  $-64\%$  with respect to pure NaCl). The measured value of  $i_{\text{Pd,max}} = 20.2 \text{ A m}^{-2}$  was lowest. The effect of magnesium valence on the reduced electrical potential difference has been already anticipated when introducing eqn (1).

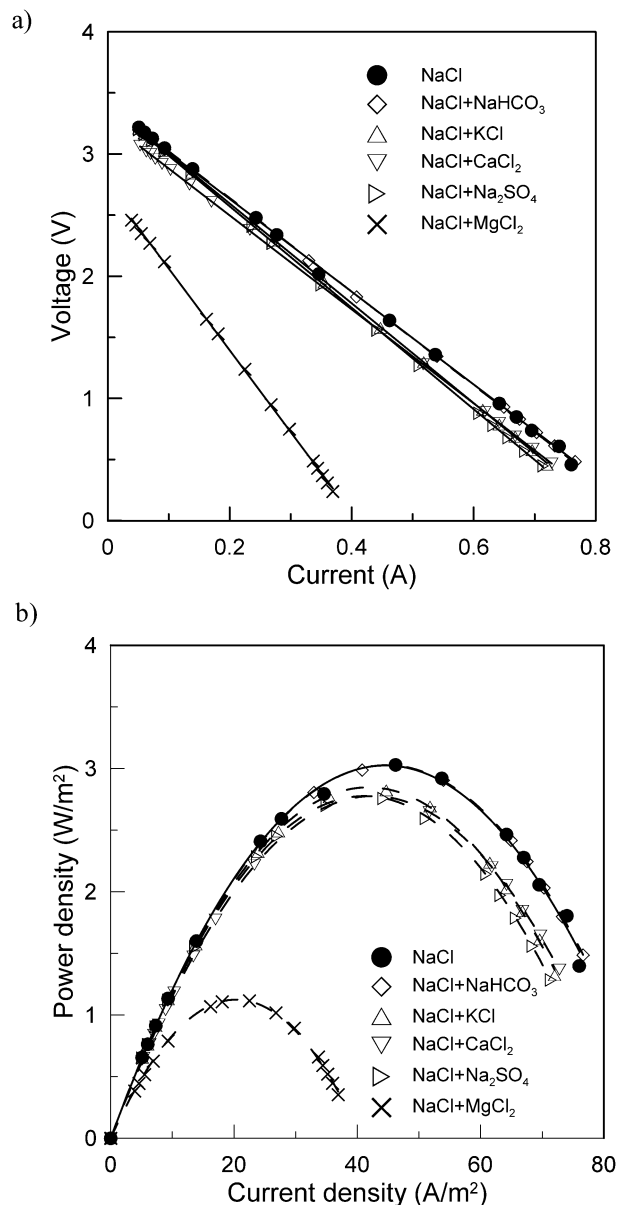


Fig. 3 a) Voltage vs. current; (b) gross power density vs. current density for multi-ion solutions. Compositions are detailed in Table 3. Temperature:  $20^\circ \text{C}$ . Margin of error within  $10\%$  (average of 3 tests).

Moreover, the significant enhancement of the cell resistance may be attributed to an increase in membrane resistance in the presence of  $\text{Mg}^{2+}$ . Sata (2004) reported a two- to three-fold increase in electrical resistance for different commercial cation exchange membranes (NEOSEPTA CL-25T, AMFion C-310, Ionac MC-3470) when using  $\text{MgCl}_2$  instead of NaCl. An enhancement in the electrical resistance of the membranes with the concentration of the electrolyte solution was also because of the increase in Donnan adsorbed salts and shrinking of the membranes.<sup>20</sup>

A systematic investigation of this aspect, based on the electrochemical impedance spectroscopy,<sup>13,14</sup> will be the objective of future communications.



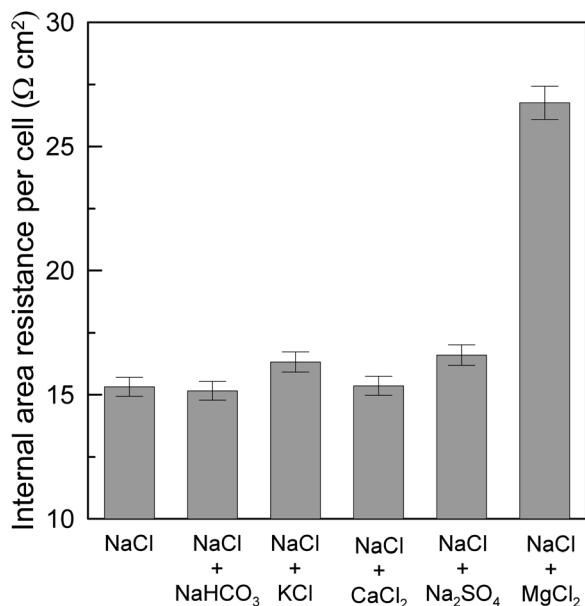


Fig. 4 Internal area resistance per cell for the binary solutions investigated (single membrane area: 100 cm<sup>2</sup>; number of cell pairs: 25).

### Stack resistance

A significant advantage gained when operating SGP-RE at high salt concentration is the reduction of the electrical resistance compared to the extensively studied case of low salt concentration (*i.e.* combination river water/seawater). The extent of the internal area resistance (IAR) per cell for the different tested solutions is presented in Fig. 4.

These results show a lower IAR per cell of SGP-RE stack (below 26.8 Ω cm<sup>2</sup>) compared to previous investigations on RE operated with a river water/seawater solutions pair, which was above 50 Ω cm<sup>2</sup> in most cases.<sup>3,4,18</sup> With respect to the reference NaCl solutions ( $R_{\text{stack}} = 3.83 \Omega$ , IAR = 15.32 Ω cm<sup>2</sup>), significant variations in electrical resistance were observed only for NaCl + MgCl<sub>2</sub> solutions. In this case, the presence of magnesium increased the resistance of the stack (6.69 Ω) and IAR (26.8 Ω cm<sup>2</sup>) by 75%, resulting in a drastic decrease of 64% in power density.

### Transport of ions

Ion chromatography was used to check the variation of ion composition in feed solutions as a result of the migration of ions through IEM driven by an electrochemical potential. Experimental tests were carried out in batch mode by recycling both artificial brackish water and artificial brine over the stack under open-circuit conditions (absence of net flux of electrical charges) and collecting the samples after 1 hour.

Only the solution flowing in the low concentration compartment was analyzed because of the large measurement errors related to the small variations in the highly concentrated brine.

Results reported in Table 4 show an increase in the overall concentration of LCC in the investigated interval of time, and the total mass of the dissolved ions increases by 164% from 6970 to 18 400 mg L<sup>-1</sup>. Within a narrow margin of measurement error (2%), the charge balance after migration of ions is satisfied (total positive charge = 329 meq L<sup>-1</sup>. Total negative charge = 323 meq L<sup>-1</sup>).

Fig. 5 illustrates the transport rate of each ion as a function of its concentration in HCC compartment.

Because of the nonideal behavior of the membranes, having permselectivity lower than 100%, a combined transport of both cations and anions can occur. It is interesting to compare transport rate and theoretical voltage over membrane for each ion reported in Table 2. The measured OCV for the SGP-RE stack operated with brackish water/solar pond brine was 2.77 V (Fig. 2a), thus implying a membrane voltage of 55 mV. Most of the voltages reported in Table 2 are higher than 55 mV, indicating a forward transport. Exceptions are for divalent ions Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>, in which expected back-transport is not observed because of the effect of multiple co-ion transport. When considering all ions, the overall electrochemical balance is satisfied within an acceptable confidence interval (7%).

The diffusion of Na<sup>+</sup> resulted in a concentration increase of 155% for an initial HCC/LCC Na<sup>+</sup> concentration ratio of 34; a similar concentration increase (+152%) was found for chlorine with an initial HCC/LCC Cl<sup>-</sup> concentration ratio of 47.8. These data seem to confirm that ion migration through ion exchange membranes is substantially driven by a concentration gradient.

Table 4 Ion composition (from Ion Chromatography analysis) of the low-concentration stream in SGP-RE batch operation (LCC: artificial brackish water; HCC: artificial brine)<sup>a</sup>

Ion	HCC	LCC		
	Initial concentration (mg L <sup>-1</sup> )	Initial concentration (mg L <sup>-1</sup> )	Concentration after 1 hour (mg L <sup>-1</sup> )	Concentration increase (mmol L <sup>-1</sup> )
Na <sup>+</sup>	66 000	1520	3870	102
K <sup>+</sup>	7740	49.7	478	11
Mg <sup>2+</sup>	37 400	323	1740	58
Ca <sup>2+</sup>	242	101	115	0.35
Cl <sup>-</sup>	170 000	3560	8960	152
SO <sub>4</sub> <sup>2-</sup>	64 400	335	3380	32

<sup>a</sup> Volume of low conc. compartment: 5 L; volume of high conc. compartment: 5 L. Solutions recirculated at 20 L h<sup>-1</sup>. Temperature: 20 °C. Data averaged on 3 measurements.



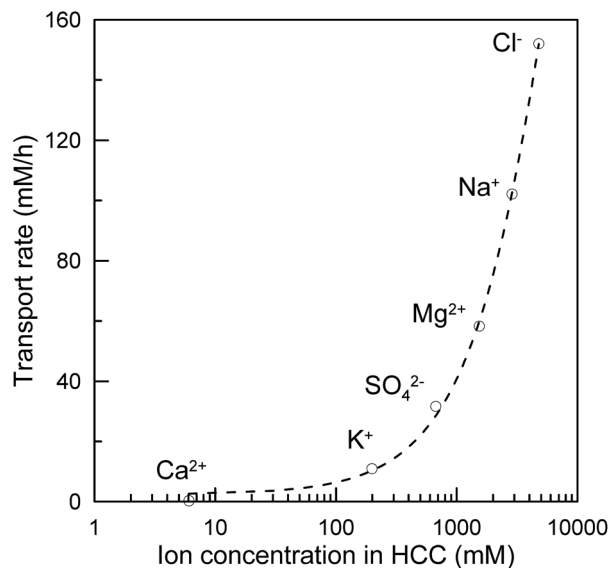


Fig. 5 Transport rate of single ions versus their concentration in brine compartment.

In highlighting the experiments on ion transport carried out by Post *et al.* (2009), in which the LCC solution consisted of 3 mM NaCl + 2 mM MgSO<sub>4</sub> and the HCC of 0.45 M NaCl + 0.05 M MgSO<sub>4</sub>, an almost two-fold increase of sodium and chloride content in the LCC was observed after one hour when operating with standard-grade ion-exchange membranes.<sup>12</sup>

Moreover, our measurements indicate that sodium and magnesium are transported across CEM with a flux of 2.84 and 3.24 meq m<sup>-2</sup> s<sup>-1</sup>, respectively, whereas chlorine and sulfate diffuse across AEM with rates of 4.23 and 1.76 meq m<sup>-2</sup> s<sup>-1</sup>, respectively.

## Conclusions

A cross-flow SGP-RE stack equipped with AEM-80045 and CEM-80050 membranes, when operated with 0.1 M/5 M NaCl solutions, reached a maximum gross power density of 3.04 W m<sup>-2</sup> at 20 °C and recirculation rate of 20 L h<sup>-1</sup>. However, a remarkable increase of stack resistance (+75%) and a significant loss of maximum power density (−64%) were observed when the SGP-RE was operated with feed solutions containing Mg<sup>2+</sup> ions (HCC: NaCl 3.25 M + MgCl<sub>2</sub> 1.75 M; [Na<sup>+</sup>]/[Mg<sup>2+</sup>] = 1.86; LCC: NaCl 0.083 M + MgCl<sub>2</sub> 0.017 M; [Na<sup>+</sup>]/[Mg<sup>2+</sup>] = 4.99). The comparable decrease in power density observed for artificial multi-ion solutions, which mimic brackish water and exhaust brine from a solar pond (Ettore Infersa site, Sicily) depicts the necessity for specific softening strategies for a better performance of SGP-RE under real conditions. In this respect, the integration of SGP-RE within pretreatment schemes of typical SWRO desalination plants might represent a feasible and economically viable option for recovering the electrochemical energy intrinsically present into discharged brines.

Moreover, an urgent need for developing specific ion exchange membranes not suffering from magnesium effects is envisaged.

## Acknowledgements

The financial support of the European Union within the project REAPower – “Reverse Electrodialysis Alternative Power Production” under the EU-FP7 programme (Project no. 256736, <http://www.reapower.eu>), and the financial support of The Education, Audiovisual and Culture Executive Agency (EACEA) under the Program “Erasmus Mundus Doctorate in Membrane Engineering” – EUDIME (FPA 2011-0014, <http://www.eudime.unical.it>), are kindly acknowledged.

## Notes and references

- 1 M. Tedesco, A. Cipollina, A. Tamburini, W. van Baak and G. Micale, *Desalin. Water Treat.*, 2012, **49**, 404–424.
- 2 J. N. Weinstein and F. B. Leitz, *Science*, 1976, **191**, 557–559.
- 3 P. Dlugolecki, A. Gambier, K. Nijmeijer and M. Wessling, *Environ. Sci. Technol.*, 2009, **43**, 6888–6894.
- 4 J. Veerman, M. Saakes, S. J. Metz and G. J. Harmsen, *J. Membr. Sci.*, 2009, **327**, 136–144.
- 5 J. W. Post, C. H. Goeting, J. Valk, S. Goinga, J. Veerman, H. V. M. Hamelers and P. J. F. M. Hack, *Desalin. Water Treat.*, 2010, **16**, 182–193.
- 6 J. Veerman, M. Saakes, S. J. Metz and G. J. Harmsen, *Environ. Sci. Technol.*, 2010, **44**, 9207–9212.
- 7 D. A. Vermaas, M. Saakes and K. Nijmeijer, *Environ. Sci. Technol.*, 2011, **45**, 7089–7095.
- 8 D. A. Vermaas, J. Veerman, N. Y. Yip, M. Elimelech, M. Saakes and K. Nijmeijer, *ACS Sustainable Chem. Eng.*, 2013, **1**, 1295–1302.
- 9 J. W. Post, J. Veerman, H. V. M. Hamelers, G. J. W. Euverink, S. J. Metz, K. Nijmeijer and C. J. N. Buisman, *J. Membr. Sci.*, 2007, **288**, 218–230.
- 10 M. Turek, B. Bandura and P. Dydo, *Desalination*, 2008, **221**, 462–466.
- 11 D. A. Vermaas, J. Veerman, M. Saakes and K. Nijmeijer, *Energy Environ. Sci.*, 2014, **7**, 1434–1445.
- 12 J. W. Post, H. V. M. Hamelers and C. J. N. Buisman, *J. Membr. Sci.*, 2009, **330**, 65–72.
- 13 E. Fontananova, W. Zhang, I. Nicotera, C. Simari, W. van Baak, G. Di Profio, E. Curcio and E. Drioli, *J. Membr. Sci.*, 2014, **459**, 177–189.
- 14 P. Dlugolecki, P. Ogonowski, S. J. Metz, M. Saakes, K. Nijmeijer and M. Wessling, *J. Membr. Sci.*, 2010, **349**, 369–379.
- 15 D. L. Parkhurst and C. A. L. Appelo, *U. S. Geol. Surv., Water-Resour. Invest. Rep.*, 1999, **99–4259**, 1–312.
- 16 Y. Kim and B. E. Logan, *Environ. Sci. Technol.*, 2011, **45**, 5834–5839.
- 17 A. Daniilidis, D. A. Vermaas, R. Herber and K. Nijmeijer, *Renewable Energy*, 2014, **64**, 123–131.
- 18 A. G. Volkov, S. Paula and D. W. Deamer, *Bioelectrochem. Bioenerg.*, 1997, **42**, 153–160.
- 19 E. Samson, J. Marchand and K. A. Snyder, *Mater. Struct.*, 2003, **36**, 156–165.
- 20 T. Sata, *Ion Exchange Membrane*, Royal Society of Chemistry, Cambridge UK, 2004.

