

O. Scialdone, A. Albanese, A. D' Angelo, C. Guarisco, A. Galia, *Investigation of electrode material – Redox couple systems for reverse electro dialysis processes. Part II: experiments in a stack with 10-50 cell pairs*, Journal of Electroanalytical Chemistry 704 (2013) 1-9. Accepted 4 June 2013.

Investigation of electrode material - redox couple systems for reverse electro dialysis processes. Part II: experiments in a stack with 10-50 cell pairs

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Abstract

The performances of reverse electro dialysis depend on several factors, including the nature of the electrode material and of the redox processes adopted to make possible the conversion between chemical potential and electric power. In this paper the possible utilization of various redox processes (reduction/oxidation of iron species, oxidation and reduction of water, oxidation of chlorine and reduction of water) was studied in a stack equipped with 10-50 cell pairs and by focused electrolyses in a three compartment cell. The effect of selected redox processes on power density output and eventual contamination of saline solutions flowing in the stack was evaluated in detail. The effect of the number of cell pairs and of the concentration of saline solutions was also investigated.

Keywords: Electro dialysis; Reverse Electro dialysis; Electrode reaction; Redox processes, Stack

1. Introduction

In reverse electrodialysis (often named in literature with SGP-RE or RED acronyms) electrical energy is extracted from chemical potential gradients arising from salinity differences, especially from sea and river water [1-8]. The energy that theoretically can be generated per m³ river water is 1.7 MJ when mixed with a large surplus of sea water [4]. In this case, power output is limited by the low conductivity of freshwater, thus enhancing the resistance of the stack. As an alternative, seawater or brackish water can be used as the low salinity solution together with very concentrated waters from salt ponds or desalination plants. Furthermore, it has been recently proposed to use salinity gradients obtained by thermolytic solutions such as ammonium bicarbonate (NH₄HCO₃) [9] that can be concentrated with waste heat (> 40 °C) or with solar energy [3,6] with conventional technologies such as vacuum distillation [10]. In order to convert this potential energy in electric energy the following components are necessary [11]:

- (1) anion-exchange membranes (AEMs) and cation-exchange membranes (CEMs) used to selectively drive the flow of positive ions in one direction (toward the cathode) and the negatively charged ions in the opposite direction (toward the anode).
- (2) solvents, which make a continuum for ion transport;
- (3) electrolytes, i.e. the current carriers between cathode and anode;
- (4) electrodes, where electron transfer reactions occur to allow the transformation of the charge carrier from ion to electron.
- (5) end membranes to confine the special ions of the electrolyte (e.g. H⁺).
- (6) spacers, to ensure the feed of the stack with the low and high concentrated solutions.

In a recent paper, Veerman and co-authors have shown that a proper selection of redox species and of electrode materials is of paramount relevance in order to develop the SGP-RE process on an applicative scale [4]. However, very few experimental data are currently available on the selection of electrode materials and electrolytes. Electrode systems can be grouped in two categories: with or without opposite electrode reactions (e.g., the direct and the reversed reaction take place at the anode and the cathode, respectively) [4,11]. In the first case, when recirculation of electrode rinse

solution is adopted, no net modification of the chemical composition occurs and the electrodic thermodynamic voltage is null. The opposite electrode reactions can involve reactive electrodes or homogeneous redox couples with inert electrodes [4]. In the case of reactive electrodes, electrodes alternatively grow and dissolve thus being dimensionally not stable that is a major drawback for the electrochemical engineering of the stack. This reversal can be avoided, by using homogeneous redox couples with inert electrodes, thus leading to lower cost of electrodes, better energy efficiency of the device and a more easy design of the stack.

The most adopted electrode systems without opposite electrode reactions are based on gas evolving redox processes, such as in the case of water oxidation and reduction and chlorides oxidation. These processes are characterized by higher voltage losses and the necessity to stock electrogenerated gases preventing their mixing as they can form an explosive mixture.

Recently, some of the authors have carried out a preliminary evaluation of iron-based redox couples ($\text{FeCl}_3/\text{FeCl}_2$, hexacyanoferrate(III)/hexacyanoferrate(II) and Fe(III)-EDTA/Fe(II)-EDTA) on graphite and DSA electrodes for reverse electrodialysis processes by a series of cyclic voltammetric experiments and electrolyses [11]. Both hexacyanoferrate(III)/hexacyanoferrate(II) and $\text{FeCl}_3/\text{FeCl}_2$ systems were shown to be stable for long time in proper conditions while Fe(II)-EDTA exhibited a limited electrochemical stability in long term experiments at all adopted operative conditions. Perfluorinated Nafion cationic membranes and Selemion anionic membranes allowed to confine the redox couple in the electrode compartments for hexacyanoferrate(III)/hexacyanoferrate(II) and $\text{FeCl}_3/\text{FeCl}_2$ systems, respectively, thus avoiding the potential contamination of concentrated and dilutes solutions flowing in the stack [11].

As a continuation of this work, we report here a study aimed to evaluate the performances of both iron redox couples ($\text{FeCl}_3/\text{FeCl}_2$, hexacyanoferrate(III)/hexacyanoferrate(II)) and some processes with gas evolution (water oxidation and reduction, chlorides oxidation and water reduction) in the frame of a reverse electrodialysis process in a stack. In particular, the possible utilisation of processes with gas evolution was first evaluated by coupling the information reported

in the literature with experimental studies performed in simple three compartments cells. Then, the possible utilization of both iron redox couples and processes with gas evolution was evaluated by carrying out a series of experiments in a stack equipped with 10-50 couples of membranes.

Table 1. Main characteristics of investigated redox processes.

Redox processes (V vs. SHE)	ΔV (V)	Stability of redox species and electrodes	Toxicity	Examples of applications
$\text{H}_2\text{O} \rightarrow \text{H}^+ + 0.5 \text{O}_2 + \text{e}^-$ (0.99 V at pH 2) $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + 0.5 \text{H}_2$ (-0.83 V at pH = 14)	2.4 – 2.5 ^a	Very high	No with suitable supporting electrolytes	Electrolytic splitting of water for hydrogen generation [14] Electro-dialysis (ED) Investigations for SGP-RE [4,12-13].
$\text{Cl}^- \rightarrow 0.5 \text{Cl}_2 + \text{e}^-$ (1.36 V) $\text{H}_2\text{O} + \text{e}^- \rightarrow 0.5 \text{H}_2 + \text{OH}^-$ (-0.83 V at pH = 14)	2.25 – 2.35 ^a	Very high	Possible concerns for chlorine, active chlorine, chlorate and perchlorate potential formation.	Production of chlorine and soda [14] ED Investigations for SGP-RE [4,16-17]
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ $E^\circ = 0.77 \text{ V}$	0.4 – 0.6 ^b	Very high for pH < 3 – 4 and in absence of air [11]	Very low in water solutions	Widely adopted in Fenton and electro- Fenton applications Investigations for SGP-RE [4,11]
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$ $E^\circ = 0.356 \text{ V}$	0.2 – 0.4 ^b	Very high in absence of air and light [11]	Very low toxicity Release of toxic gas after reaction with strong acids. Possible release of HCN under no proper operative conditions [11]	Widely adopted for studies on electrodes characterization. Investigations for SGP-RE [4,11]

^a computed by the sum of anode voltage on Ru at pH of 2, cathode voltage at Pt at pH 14 and ohmic drops in the anode and cathode compartment at 1 mA/cm² estimated on the bases of literature [14,15].

^b computed on the bases of electrolyses in undivided cells at 1 mA/cm² at graphite electrode for Fe(III)/Fe(II) and at Iridium based electrodes for $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ [11].

2. Experimentals

2.1 Electrolyses

Electrolyses were performed in a three compartments cell divided by ion-exchange membranes. Cationic (CEM) and anionic (AEM) membranes, thickness 120 μm , adopted to perform the experiments are reported in Table 2. SCE was used as reference electrode and all potentials reported in this study are referred to it or to SHE, Ti/IrO₂-Ta₂O₅ and Ti/RuO₂-IrO₂ from De Nora S.p.A were

used as anodes and Ni plates as cathode. The solutions used in anode and cathode compartments were stirred by magnetic stir bar and prepared using distilled water, Na₂SO₄ (Sigma Aldrich) or NaCl (Sigma-Aldrich) adjusting the pH value to the target one by adding proper amounts of H₂SO₄ (Sigma Aldrich), HCl (Sigma Aldrich) or NaOH (Applichem). The central compartment solution in the three compartment cell was constituted by an aqueous solution of NaCl. The volume of each compartment was generally of 50 ml. Amel 2055 potentiostat was used for electrolyses.

Table 2. Membranes used in this study

Name	Code	Company	Type
Selemion	CMV	AGC Engineering Co.	CEM
	AMV	AGC Engineering Co.	AEM
Fuji	C	FujiFilm	CEM
	A	FujiFilm	AEM
Nafion	324	Du Pont	CEM

^a Polymer matrix: Poly(styrene-co-divinybenzene) for Selemion and Perfluorinated bilayer membranes for Nafion membranes.

2.2 Experiments in stack

The lab scale stack was provided by RedStack. Cathode and anode (10 cm x 10 cm x 2 mm) were placed in two electrode chambers (10 cm x 10 cm x 2 mm). Various cathode and anodes were used: carbon felt (Carbone Lorraine) or titanium meshes coated with Pt (Magneto) cathode and titanium meshes coated with IrO₂-Ta₂O₅ or RuO₂-IrO₂ (Magneto) anode (geometric surface area 100 cm²). The stack, assembled between the anode and cathode chambers, consisted of cation- and anion-exchange membranes (Fuji), gaskets integrated with spacers (Deukum, 0.28 mm thickness), two outer anionic (Selemion) or cationic (Nafion) membranes to separate electrodic compartments and side ones, creating 10-50 pairs of alternating high concentrated (HC) and low concentrated (LC) chambers. The LC solution entered from the cell next to the cathode chamber and flowed in parallel

through the LC cells in the stack, exiting from the cell next to the anode chamber (Fig. 1). The HC stream entered the stack near the anode and flowed serially through the HC cells in the stack, exiting from the cell next to the cathode chamber. One single passage for HC and LC solutions in the stack was achieved. Two peristaltic pumps (from General Control SpA) continuously fed the HC and LC solutions at a flow rate of 190 mL/min. Most of experiments were performed with one electrodic solution (about 0.3 L) continuously recirculated to both electrodic compartments and to a reservoir (Fig. 1c) fed with nitrogen by a peristaltic pump (from General Control SpA) with a flow rate of 75ml/min. For some experiments, two different electrodic solutions were fed to the cathodic and anodic compartments. Each solution was continuously recirculated to the electrodic compartment and to a reservoir by a peristaltic pump (General Control). During power density curve experiments, fresh HC and LC solution were pumped through the stack with the effluent collected in separate reservoirs. Solutions used in HC and LC compartments were prepared by dissolving NaCl (5 M or 0.5 M in HC and 0.5 M or 0.01 M in LC) from Sigma Aldrich or into deionized water. Electrodic solution for experiments in the stack was prepared by dissolving into deionized water:

- Na_2SO_4 (0.04 M) (Sigma Aldrich) for water/ Na_2SO_4 system;
- NaCl or KCl (Sigma Aldrich) for water/NaCl system;
- FeCl_2 and FeCl_3 (0.3 M) from Sigma Aldrich or $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ (0.3 M) from Labochem were used as received for iron redox couple systems.

All these chemicals were analytical grade. pH was adjusted to the target initial value by adding proper amounts of H_2SO_4 (Sigma Aldrich) or HCl (Sigma Aldrich).

2.3 Analysis.

Power production during power density curve experiments was determined by measuring the potential drop across a variable external resistance (1-160 range Ω) (Figure 1b) and the current intensity by a multimeter Simpson. Power was calculated by multiplying the electrical current and

total cell voltage. Power density can be computed by the ratio between the power and the total area of all membranes or the total area of cationic membranes (W per m² of membrane pair) (P_{mem}) or the geometric area of the electrode (P). In the first two cases, the power densities gives a measure of the power per invested euro because membranes form a substantial part of the price of a RED power plant [20] while in the last case the power density is more easily compared with other electrochemical devices used for the generation of electric energy such as fuel cells. In the paper we usually reported the power density P as the ratio between the power and the geometric area of the electrode even if in some cases also information on P_{mem} (W per m² of membrane pair) were given. The concentration of the partners of the redox couples and of active chlorine were estimated by photometric analyses (Ocean Optic DH-2000). Hexacyanoferrate(II) and hexacyanoferrate(III) were evaluated at 320 and 420 nm, respectively. The concentration of Fe(II) was evaluated for experiments performed with FeCl₂/FeCl₃ after treatment with phenatroline. The total concentration of iron was evaluated in the same way after treatment with ascorbic acid. In the case of active chlorine a Merck Chlorine test containing dipropyl, p-phenylenediamine (DPD) was used.

3. Results and Discussion

3.1. Preliminary electrolyses in three compartments cells

3.1.1 Water/Na₂SO₄ system

Water oxidation and reduction are widely adopted as redox reactions for Electro Dialysis (ED) processes for food purposes (see Table 1) and they were used for some studies on reverse electrodialysis [4,12-13]. Indeed, in the presence of a suitable supporting-electrolyte such as Na₂SO₄, this system is not toxic for humans and quite cheap. Furthermore, a very large set of data is available in literature for these redox processes and electrode systems are very stables. Water electrolysis was widely studied and is a long-established technique for producing hydrogen [14] on a commercial scale. Electrolytic splitting of water ($\Delta G^0 = 241.9$ kJ/mol, $\Delta H^0 = 286.66$ kJ/mol) corresponds to a decomposition voltage of only 1.2 V. Most commonly used electrodes for the

cathode reaction are high surface area nickel layers, either Raney nickel or porous nickel coatings produced in situ by cathodic reduction of nickel sulfide coatings. Electrodes based on coatings of mixed oxides containing iridium oxide, cobalt oxide and iron – cobalt mixed spinel have proved to be relatively efficient electrocatalysts for anodic oxygen evolution [4,14]. As reported by Veerman and co-authors this system presents the following main disadvantages for reverse electrodialysis applications [4]: (i) quite high overvoltage; (ii) the generation of oxygen and hydrogen gas that have to be properly collected and stocked to avoid the formation of an explosive mixture; (iii) the presence of very high and low pH in the anode and cathode compartments, respectively, so that quite resistant membranes have to be used and the eventual passage of protons and hydroxyl ions to the confining compartments have to be checked.

To evaluate the passage of species between electrode and lateral compartments, some amperostatic electrolyses were performed in a three compartment cell equipped with cationic membranes to avoid/minimize the passage of chloride ions to the anode compartment and that of hydroxyl ions from the cathode to the confining one. In the lateral compartments, the anode and the cathode processes occurred in the presence of Na_2SO_4 as supporting electrolyte while the central compartment was filled with a 0.5 M NaCl solution. $\text{Ti}/\text{IrO}_2/\text{Ta}_2\text{O}_5$ was used as anode and Ni as cathode. In the anode compartment, a decrease of the pH was observed as a result of the anodic process (Fig. 2a for experiments performed with Nafion membranes) coupled with the formation of active chlorine (Fig. 2b) which is caused by slow but not null passage of chloride ions from the central compartment through the membrane. The formation of active chlorine in the anode compartment was dependent on the nature of the membrane and it was minimized when Nafion membranes were used. Water oxidation is thermodynamically favoured with respect to that of the chloride ions. On the other hand, chloride ions oxidation present lower overvoltages also in the presence of more suitable electrodes for oxygen evolution such as DSA- O_2 and the presence of acidic pH makes more difficult the water oxidation, thus favouring the chlorine evolution [15]. The formation of chlorine can decrease the quality of the oxygen formed and prevent its utilisation in a

fuel cell. The passage of protons from the anodic compartment to the central one caused a slow decrease of the pH also in the central compartment (Fig. 2a). With all the tested membranes, the concentration of active chlorine was always very low in the central compartment also after many hours with respect to the law limits for discharged waters (Fig. 2c). Interestingly, no formation of chlorite, chlorate and toxic perchlorate was detected both in the anode and central compartments.

Some electrolyses were repeated with an initial pH of the anode compartment of 14 but also in this case the pH dramatically decreased with the time passed and the formation of appreciable amounts of active chlorine in the anode compartment were detected. To evaluate the resistance of the membrane in the presence of concentrated NaCl, some experiments were repeated with a concentration of NaCl in the central compartment of 5 M. Also in this case very low concentrations of active chlorine were detected in the central compartment after many hours, thus confirming the well known ability of Nafion membranes to work in the presence of high concentrations of NaCl.

3.1.2 Water/NaCl system

The system water/NaCl is widely used in the literature pertaining both electro dialysis and reverse electro dialysis [16-17]. It is characterized by the formation of products such as gaseous chlorine, active chlorine, hydroxyl ions and hydrogen. The involved reactions were studied in a deep detail since they are involved in the larger electrochemical production of commodities, namely chlorine and NaOH [14]. Electrodes and membranes for this process were studied for many years by both academic and private research institutes and very interesting solutions are commercially available. Ruthenium oxides and Ni based electrodes are, as an example, widely used for anodes and cathodes, respectively. From an environmental point of view, the main problem arise in the possible release of active chlorine from the anodic compartment to diluted and concentrated solutions. Furthermore, chlorine can be potentially oxidized to toxic chlorate and perchlorate.

To evaluate the passage of species between electrode and lateral compartments, some amperostatic electrolyses were performed in a three compartment cell equipped with Nafion cationic membranes that, according to the literature, can resist to the very aggressive media present

at both anode and cathode compartments and that should allow to avoid/minimize the passage of hydroxyl ions from the cathode to the confining one. The anode process occurred in the presence of NaCl (1 M) and HCl (initial pH =2.5 to favor the chloride oxidation with respect to oxygen evolution) while the central and cathode compartments were filled with a 0.5 and 0.1 M NaCl solutions, respectively. In the central compartment, a fast decrease of pH was observed as a result of the passage of protons through the cationic membrane. Also the passage of active chlorine was observed that presented in the central compartment higher concentrations with respect to the limits (Fig. 3). Anyway, one has to take in account that contact times expected in a stack are very low (of few seconds) and an high dilution is expected since about one thousand of cells is expected to be used for applicative purposes. Interestingly, no appreciable concentrations of chlorate and perchlorate were found neither in the central nor in the anodic compartment. When experiments were repeated with an initial pH of 7, a fast decrease of the pH in the anode compartment occurred as a result of the lateral water oxidation and the consequent release of protons.

3.2. Experiments in stack

3.2.1 Experiments with $FeCl_2/FeCl_3$ and effect of the number of cell pairs

The generation of electric energy was first studied in the presence of the redox couple $FeCl_2/FeCl_3$, in a stack (Fig. 1) equipped with carbon felt electrodes containing 10 membrane pairs fed with concentrated (0.5 M) and diluted solutions (0.01M) of NaCl at a fixed-solution flow rate (190 mL/min). This redox couple can be considered one of the best candidates for reverse electrodialysis applications for several reasons: (i) high stability under proper operative conditions in terms of high concentrations of $FeCl_2/FeCl_3$, low pH and absence of air; (ii) very low toxicity; (iii) very low energetic penalty; (iv) low cost of the redox components and electrodes [11].

The electrodic compartment was fed with a water solution of $FeCl_2/FeCl_3$ (0.3 M) and NaCl (0.1 M) at a pH of 2 to avoid the precipitation of iron(III) and under nitrogen atmosphere to avoid the oxidation of Fe(II) to Fe(III) by means of oxygen [11] with a flow rate of 75 ml/min. Anionic

Selemion were used as outer membranes according to the literature to minimize the passage of the components of the electrodic solution to concentrated (HC) and diluted (LC) solutions [11]. The maximum power was 0.039 W. The power density P with respect to the geometric area of the electrode was 3.9 W/m^2 (Fig. 4). The cell obtained peak power at a total cell voltage of 1 V and current density of 4.5 A/m^2 . When the number of membrane pairs was increased to 40 and 50, a drastic increase of power density output arisen at higher values of current density and cell voltage (Fig. 4) as a result of the lower impact of the energetic loss due to the redox processes compared with the overall power generation. Indeed, the cell voltage loss due to the electrode processes in the case of the Fe(II)/Fe(III) redox couple was estimated to assume, according to electrolyses experiments and cyclic voltammetries performed in the undivided cell, values of about 0.3 – 0.35 V at current densities of 10 A/m^2 . Hence, the power loss due to the redox processes at a current density of about 10 A/m^2 can be roughly estimate to be close to 0.03 - 0.035 W which represents an high value for the experiments carried out with 10 cell pairs (maximum power output 0.039 W) but quite small if compared with the maximum power output observed for experiments performed with 50 cell pairs (0.36 W).

With 50 membrane pairs a maximum power density P of 36 W/m^2 with respect to the geometric area of the electrode (corresponding to $P_{\text{mem}} = 0.73 \text{ W/m}^2$ computed as W per m^2 of membrane). Was, in particular, observed at 13.5 A/m^2 and 2.7 V.

For all above mentioned experiments, the passage of the components of the redox couple to the HC and LC solutions was negligible. Furthermore, the pH of HC, LC and electrode compartments did not change appreciably due to the good permselectivity of adopted outer membranes and no degradation of redox species components was observed according to the literature [11]. Hence, it is possible to conclude that $\text{FeCl}_2/\text{FeCl}_3$ can be considered as a suitable redox species for reverse electro dialysis processes.

3.2.2 Effect of the redox processes

Then measurements were repeated with other redox systems (namely $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$, water/ Na_2SO_4 and water/ KCl) in a stack equipped with 40 membrane pairs to evaluate the effect of redox processes on the performances of reverse electrodialysis with the same HC and LC solutions. As shown in fig. 5, the power output P was strongly dependent on the selected redox processes and increased with the following order: $P(\text{water}/\text{Na}_2\text{SO}_4 \text{ with Pt based cathode and Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5 \text{ anode}) < P(\text{water}/\text{KCl} \text{ with Pt based cathode and Ti}/\text{RuO}_2\text{-IrO}_2 \text{ anode}) \ll P(\text{FeCl}_2/\text{FeCl}_3 \text{ with carbon felt electrodes}) < P([\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-} \text{ with carbon felt cathode and Ti}/\text{RuO}_2\text{-IrO}_2 \text{ anode})$ which is consistent at least from a qualitative point of view with the trend of voltages required to drive the corresponding redox processes (Table 1). Indeed, for iron redox couples the thermodynamic potential required to drive the redox reactions is null (since opposite anodic and cathodic reactions are involved) and the electrode potentials are only given by overvoltages that, according to literature, at adopted electrodes are lower for $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ couple [11]. On the other hand, for water/ Na_2SO_4 and water/ KCl systems, redox reactions require relevant thermodynamic potentials coupled with high overvoltages. However, from an applicative point of view, the power output is only one of the relevant variables to be evaluated for redox processes. In particular, the possible pollution of HC and LC solutions of components coming from electrode compartments has to be evaluated in detail.

For water/ Na_2SO_4 system, two different electrodic patterns were first used for anode and cathode compartments in order to avoid the possible formation of hazardous gaseous mixtures of hydrogen and oxygen, thus leading to a very fast increase of pH in the cathodic compartment and to a corresponding decrease in the anodic one as an effect of water reduction and oxidation reactions, respectively. Cationic Nafion outer membranes were chosen to minimize the passage of chloride ions to the anode compartment and of OH^- from the cathodic compartment to the side one, thus allowing the passage of protons from anodic compartment to the side one. Thus, a drastic decrease of pH of HC and LC was observed. pH of both solutions rapidly decreased to reach a plateau value close to 3 after about an hour of operations. In this context, it is useful to remember that a stack for

applicative purposes should be equipped with a high number of membrane pairs (at least about one thousand [4]) and as a consequence with very large diluted and concentrated flow rates to achieve a significant power output, thus leading to a strong dilution of solutions and to a lower decrease of pH. However, to avoid the strong acidification of diluted and concentrated solutions, some experiments were performed with the water/ Na_2SO_4 system with only one electrodic system, in order to avoid strong variations of pH, equipped with two reservoirs where oxygen and hydrogen gas were removed by nitrogen flux. In this case the pH of diluted and concentrated solutions did not change appreciably. Hence, also this system can be potentially used for SGP-RE applications even if with higher energetic penalties with respect to iron systems. In this context, it can be useful to stress the fact that the water- Na_2SO_4 system presents the advantage to use very safe chemical species and as a consequence has to be considered as an interesting alternative when diluted and concentrated solution have to be discharged in very sensitive environments such a salt ponds used for alimentary purposes.

In the case of water-KCl system, the passage of protons and active chlorine from the anode compartment to the rest of the stack was carefully evaluated since high passages of these specie were observed in the experiments performed in the three compartments cell. Quite interestingly, pH in HC and LC solutions after the passage in the stack was between 6 and 7. On the other hand, a concentration of active chlorine of few ppm was detected in these solutions. Please, consider anyway that in a stack for applicative purposes a very large number of cells is likely to be used so that an effective dilution is expected thus leading to concentrations of active chlorine lower than the law limits. Of course, it is useful to remember that the utilization of the system water-KCl could be particularly suitable if the anodically generated active chlorine could be used for applicative purposes, including the treatment of the diluted and concentrated waters to avoid or reduce bio-fouling [4].

For the hexacyanoferrate (II)/ hexacyanoferrate (III) system the electrodic circuit was fed with a water solution of $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ (0.3 M) and NaCl (0.1 M) under dark to avoid the

hexacyanoferrate (II) conversion to cyanides and under nitrogen atmosphere to avoid the oxidation of hexacyanoferrate (II) to hexacyanoferrate (III) by means of oxygen [11]. Cationic Nafion were used as outer membranes according to the literature to minimize the passage of the components of the electrodic solution to HC and LC solutions [11]. Indeed, no passage of cyanides in both HC and LC solutions was observed. Hence, this redox couple seems particularly suitable for reverse electrodiagnosis application. On the other hand, a potential accidental release of hexacyanoferrate in the concentrated and dilute solutions caused by an accidental rupture of the outer membrane could lead to the formation under sunlight of toxic HCN [11]. To avoid this potential risk, it could be possible to provide a guard cell between electrode compartments and the rest of the stack that, however, could lead to an enhancement of costs and complexity of operations.

3.2.3 Effect of other operative parameters.

The power output of a stack is expected to depend on a large set of other operative parameters. In particular, here we wanted to briefly analyze the effect of the concentration of redox specie and of salts present in HC and LC solutions by a series of experiments performed in a stack equipped with 40 cell pairs. We first focused our attention on the concentration of chlorides in the frame of the anodic evolution of chlorine. In this case, KCl serves as both supporting electrolyte and redox specie. As shown in figure 6, an increase of KCl concentration gave rise to higher power output. This is probably due to two concomitant effects: (i) higher concentrations of KCl enhance the conductivity of the electrode compartment lowering the resistance of the stack; (ii) higher concentrations of KCl avoid energetic penalties due to concentration polarization of chlorides in the anodic diffusion layer.

In order to evaluate the effect of the salt concentration of HC and LC compartments, it is useful to remember that the electromotive force for a stack assembly of N membrane pairs fed with water solutions of NaCl is expected to depend on the gradient concentration between HC and LC compartments according to eq. (1) [1,7,18].

$$E = 2 N \alpha RT \ln (a_c/a_d)/F \quad (1)$$

where R is the gas constant, T the temperature, α is the average permselectivity of the membrane pair, F the Faraday constant and a_c and a_d the solute activities in concentrated and diluted solutions, respectively.

If R_e and R_i are the load resistance external to the membrane stack and the stack resistance, respectively, the electric current through the load I will be given by:

$$I = E / (R_e + R_i) \quad (2)$$

Hence, the power output $P = I^2 R_e = E^2 R_e / (R_e + R_i)$ is expected to depend on several factors including the conductivity of concentrated and diluted solutions through their effect on the resistance of the stack R_i [7,19].

A very interesting and widely studied potential feedstocks is composed by sea (NaCl ~ 0.5 M) and river waters (NaCl ~0.01 M) which is characterized by an high ratio between the concentration of NaCl in HC e LC solutions $[NaCl]_{HC}/[NaCl]_{LC} \sim 50$ and by a correspondent ratio $a_c/a_d \sim 37$ [1] but also by a very low conductivity in the LC compartment ($\sim 500 \mu S/cm$) which lead to high values of R_i . Please, consider that the concentration of ions of diluted solutions increases during the passage in the stack but anyway a quite low overall conductivity is expected as an effect of the low residence time of the diluted solution inside the stack (lower than 1 min). Another interesting feedstock can be composed by brine (NaCl ~ 5 M) and seawater (NaCl ~ 0.5 M) which presents a lower ratio $[NaCl]_{HC}/[NaCl]_{LC} = 10$ but quite high conductivity in both HC ($\sim 250000 \mu S/cm$) and LC ($\sim 25000 \mu S/cm$) solutions [19]. Fig. 7 reports the power density achieved in a stack feeded with: (i) $[NaCl]_{HC} = 0.5 M$ and $[NaCl]_{LC} = 0.01 M$; (ii) $[NaCl]_{HC} = 5 M$ and $[NaCl]_{LC} = 0.5 M$ solutions. The stack was equipped with 40 cell pairs and the Fe(II)/Fe(III) redox couple. It is possible to observe that the utilization of NaCl concentrations similar to that of salt pond/seawater

solutions allows to achieve a drastic increase of the power output in spite of the lower $[\text{NaCl}]_{\text{HC}}/[\text{NaCl}]_{\text{LC}}$ ratio as a result of the the higher conductivity of LC solution [19].

It was also studied the response of the power output as a function of the time passed. Experiments were carried out with the 40 cell pairs and the Fe(II)/Fe(III) redox couple. It was observed that the power output increases with time reaching a stable value after about 20 minutes (Fig. 7).

4. Conclusions

Various redox processes were tested in a stack for reverse electrodialysis processes and by focused electrolyses. It was shown that all tested redox processes (namely, reduction/oxidation of $\text{FeCl}_3/\text{FeCl}_2$, reduction/oxidation of hexacyanoferrate(III)/hexacyanoferrate(II), oxidation and reduction of water, oxidation of chlorine and reduction of water) can be used for reverse electrodialysis applications with proper external membranes and electrodes. The nature of redox processes affects the external output and different proper external membranes have to be selected for each redox process to avoid the contamination of concentrated and diluted solution by the components of electrodic solution. Power density was shown to depend also on concentration of redox specie and on the number of cell pairs. It was shown that the utilization of NaCl concentrations for concentrated (HC) and diluted (LC) compartments similar to that of salt pond and seawater solutions allowed to achieve a drastic increase of the power output with respect to that achieved feeding HC and LC compartments with NaCl concentrations similar to that of seawater and riverwater.

Acknowledgments

EC (7FP, Energy, REAPower project, www.reapower.eu) is acknowledged for its financial support. E. Brauns and J. Veerman are acknowledged for precious comments and discussions.

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FIGURE CAPTIONS

Figure 1. (A) Main components of the stack, showing the membranes between the electrodes, the electrodes, flow path of the HC and LC solutions and of electrolyte solution for an undivided electrodic circuit. (B) The electric circuit containing a load (resistor), an amperometer and a voltmeter. (C) Scheme of the device with three different circulating solutions: i) HC solution; ii) LC solution; iii) electrodic solution.

Figure 2. Electrolyses performed with Ti/IrO₂-Ta₂O₅ anode and Nickel cathode in the presence of Nafion, Selemion, and Fuji cationic membranes in a three-compartment cell with the following configuration: 1) Lateral compartments: water solution of Na₂SO₄ (20 mM); 2) Central compartment: water solution of 0.5 M NaCl. Fig. 2A reports the plot pH vs. time passed in anodic and central compartments while Figs. 2B and 2C report the concentrations of active chlorine detected in the anode and central compartment, respectively. Dashed lines represent the Italian law limits for active chlorine.

Figure 3. Electrolyses performed with Ti/RuIr anode and Nickel cathode in the presence of Nafion cationic membrane in a three-compartment cell with the following configuration: 1) Anode compartment: water solution of NaCl (1 M) and HCl (initial pH 2.5); 2) Central compartment: water solution of 0.5 M NaCl.; 3) Cathode compartment: water solution of NaCl (0.1 M). Current density: 100 A/m². The figure reports the plot of the concentration of active chlorine vs. time detected in the central compartment. Dashed lines represent the Italian law limits for active chlorine.

Figure 4. Plot of power densities (computed as the ratio between the power and the geometric area of electrode) vs. current density recorded in a stack equipped with 10 (◇), 40 (□) and 50 (●) membrane pairs for FeCl₂/FeCl₃ with carbon felt electrodes with an external resistance varied

between 1 and 160 ohm with fixed HC (NaCl 0.5 M) and LC (NaCl 0.01 M) compositions. The electrodic solution contained $\text{FeCl}_2/\text{FeCl}_3$ (0.3 M), NaCl (0.1 M) as supporting electrolyte and HCl (pH = 2) and was under nitrogen atmosphere. Flow rate of HC and LC solutions: 190 mL/min. Flow rate of electrodic solution: 75 mL/min. Outer membranes: Anionic-exchange Selemion. Inner membranes Fuji AEM and CEM.

Figure 5. Plot of power density (computed as the ratio between the power and the geometric area of electrode) vs. current density recorded in a stack of 40 cells pairs with different redox systems: (\diamond) water/ Na_2SO_4 (0,04 M) at Pt cathode and Ti/ $\text{IrO}_2\text{Ta}_2\text{O}_5$ anode (Cationic Nafion external membranes), (\blacktriangle) water/KCl (0,085 M) at Pt cathode and Ti/ $\text{RuO}_2\text{-IrO}_2$ anode (Cationic Nafion external membranes), (\square) $\text{FeCl}_2/\text{FeCl}_3$ (0.3 M) at Carbon Felt electrodes (Anionic Selemion external membranes), (\bullet) $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ (0.3 M) at Carbon Felt cathode and Ti/ $\text{IrO}_2\text{Ta}_2\text{O}_5$ anode (Cationic Nafion external membranes) with an external resistance varied between 1 and 160 ohm with fixed HC (NaCl 0.5 M) and LC (NaCl 0.01 M) compositions.

Figure 6. Plot of power density (computed as the ratio between the power and the geometric area of electrode) vs. current density recorded in a stack of 40 cells pairs with KCl at Pt cathode and Ti/ $\text{RuO}_2\text{-IrO}_2$ anode (Cationic Nafion external membranes). Concentration of KCl: 0.085(\blacktriangle), 0.1 (\square) and 0.5 M (\bullet). Anionic Selemion external membranes. External resistance varied between 1 and 160 ohm with fixed HC (NaCl 0.5 M) and LC (NaCl 0.01 M) compositions.

Figure 7. Plot of power densities (computed as the ratio between the power and the geometric area of electrode) vs. current density recorded in a stack equipped with 40 membrane pairs for $\text{FeCl}_2/\text{FeCl}_3$ (0.3 M) (\blacksquare, \square) and $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ (0.3 M) (\bullet, \circ) with an external resistance variable, with two different HC and LC compositions: HC (0.5 M) and LC (0.01 M) (white symbol), HC (5 M) and LC (0.5 M) (black symbol).

Figure 8. Plots of power densities (recorded as the ratio between the power and the geometric area of electrode) vs. current density recorded in a stack equipped with 40 membrane pairs for FeCl₂/FeCl₃ (0.3 M) with an external resistance variable recorded after 0 (□) and 20 minutes (●).