#### Journal of Electroanalytical Chemistry 704 (2013) 1-9

Contents lists available at SciVerse ScienceDirect

## Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

# Investigation of electrode material – redox couple systems for reverse electrodialysis processes. Part II: Experiments in a stack with 10–50 cell pairs

### O. Scialdone\*, A. Albanese, A. D'Angelo, A. Galia, C. Guarisco

Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy

#### ARTICLE INFO

Article history: Received 3 April 2013 Received in revised form 31 May 2013 Accepted 4 June 2013 Available online 14 June 2013

Keywords: Electrodialysis Reverse electrodialysis Electrode reaction Redox processes Stack

#### ABSTRACT

The performances of reverse electrodialysis 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.

© 2013 Elsevier B.V. All rights reserved.

#### 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 m<sup>3</sup> 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 (NH<sub>4</sub>HCO<sub>3</sub>) [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 anode and 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





CrossMark

<sup>\*</sup> Corresponding author. Tel.: +39 09123863754; fax: +39 09123860841. *E-mail address:* onofrio.scialdone@unipa.it (O. Scialdone).

<sup>1572-6657/\$ -</sup> see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jelechem.2013.06.001

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 (FeCl<sub>3</sub>/FeCl<sub>2</sub>, 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 FeCl<sub>3</sub>/ FeCl<sub>2</sub> 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 FeCl<sub>3</sub>/FeCl<sub>2</sub> systems, respectively, thus avoiding the potential contamination of concentrated and dilute 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 (FeCl<sub>3</sub>/FeCl<sub>2</sub>, hexacyanoferrate(III)/hexacyanoferrate(II)) and some processes with gas evolution (water oxidation and reduction, chlorides oxidation and water reduction) in the framework of a reverse electrodialysis process in a stack (Table 1). 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.

#### 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 um, 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 SpA 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, Na<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich) or NaCl (Sigma Aldrich) adjusting the pH value to the target one by adding proper amounts of H<sub>2</sub>SO<sub>4</sub> (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.

#### 2.2. Experiments in stack

The lab scale stack was provided by RedStack. Cathode and anode ( $10 \text{ cm} \times 10 \text{ cm} \times 2 \text{ mm}$ ) were placed in two electrode chambers ( $10 \text{ cm} \times 10 \text{ cm} \times 2 \text{ mm}$ ). Various cathode and anodes were used: carbon felt (Carbone Lorraine) or titanium meshes coated

with Pt (Magneto) cathode and titanium meshes coated with  $IrO_2-Ta_2O_5$  or  $RuO_2-IrO_2$  (Magneto) anode (geometric surface area 100 cm<sup>2</sup>). The stack, assembled between the anode and cathode chambers, consisted of cation- and anion-exchange membranes (Fuji), gaskets integrated with spacers [22] (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 75 mL/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 solutions 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 into deionized water. Electrodic solution for experiments in the stack was prepared by dissolving into deionized water:

- Na<sub>2</sub>SO<sub>4</sub> (0.04 M) (Sigma Aldrich) for water/Na<sub>2</sub>SO<sub>4</sub> system;
- NaCl or KCl (0.01-01-0.5 M) (Sigma Aldrich) for water/NaCl system;
- FeCl<sub>2</sub> and FeCl<sub>3</sub> (0.3 M) from Sigma Aldrich or K<sub>3</sub>[Fe(CN)<sub>6</sub>] and K<sub>4</sub>[Fe(CN)<sub>6</sub>] (0.3 M) from Labochem 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<sub>2</sub>SO<sub>4</sub> (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  $(1-160 \text{ range } \Omega)$  (Fig. 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 m<sup>2</sup> of membrane pair) ( $P_{mem}$ ) or the geometric area of cathode (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 m<sup>2</sup> of membrane pair) are 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)

Download English Version:

https://daneshyari.com/en/article/219040

Download Persian Version:

https://daneshyari.com/article/219040

Daneshyari.com