



# Investigation of electrode material - redox couple systems for reverse electro dialysis processes.

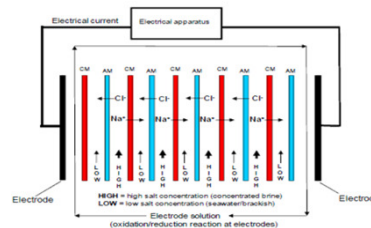
Onofrio Scialdone, Chiara Guarisco, Serena Grispo, Adriana D'Angelo, Roberta Riccobono

Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Viale delle Scienze, Palermo, +3909123863758, onofrio.scialdone@unipa.it

## Introduction and aim of the work

In reverse electro dialysis (RED) processes, electrical energy is directly extracted from chemical potential gradients arising from salinity differences, especially from sea and river water. A proper selection of redox processes and electrodes is necessary to perform successfully the reverse electro dialysis process. In spite of the large number of studies dedicated to reverse electro dialysis processes, very few investigations were focused on the selection of redox processes and of the electrode materials.

The objectives of this research are to identify the electrode material-redox couple systems for reverse electro dialysis processes and to study the behavior of these systems. This work was devoted to the study of the utilization of iron-based redox couples  $FeCl_2/FeCl_3$ , hexacyanoferrate(III)/hexacyanoferrate(II) and  $Fe(III)EDTA/Fe(II)EDTA$  on graphite and DSA electrodes for RED processes. To evaluate the advantages and disadvantages of these processes, numerous experiments were carried out in undivided and divided cells. The electrode material-redox couple system must have the following characteristics in order to be considered for a RED process: high chemical and electrochemical stability and low toxicity of the redox species, low voltages, absence of chemical poisoning of the electrodes and membranes, physical and chemical stability of electrodes, low cost of species and electrodes, absence or minimization of the treatments of effluents, no passage of redox species from electrode compartments to side ones.



## Experimental set-up

**REDOX COUPLES:**

- Hexacyanoferrate(III)/Hexacyanoferrate(II)
- $Fe(III)EDTA/Fe(II)EDTA$
- $FeCl_2/FeCl_3$

**ION SELECTIVE EXCHANGE MEMBRANES:**

Name	Company	Type	Polymer matrix
FUMASEP	Fumatech (Germany)	CEM	PET
	Fumatech (Germany)	AEM	PA
	Fumatech (Germany)	AEM	PEEK
SELEMION	Asahi Glass	CEM	POLY(STYRENE-CO-DIVINYLBENZENE)
	Asahi Glass	AEM	DIVINYLBENZENE
FUJI	FujiFilm	CEM	POLYETHYLENE
	FujiFilm	AEM	POLYETHYLENE
NAFION	Du Pont	CEM	PERFLUORINATED BILAYER

**MAIN CHARACTERISTICS:**

- Low electrical resistance
- High selectivity of permeation
- Good mechanical and chemical stability

## Results

**$[Fe(CN)_6]^{3-}$   
 $[Fe(CN)_6]^{4-}$**

- Low potential for redox processes
- Components of the redox couple not toxic
- Very good chemical stability under dark conditions in the absence of air
- Good electrochemical stability for low current density and high concentration of the redox couple
- Very low passage of redox couple to the side compartments with Nafion membranes
- Possibility to use DSA- $O_2$  or graphite

**Redox Couple (mM)**: 300, 300  
**Current Density (mA/cm²)**: 9.7, 39  
**Anode**: DSA- $O_2$   
**Solution**: Yellow transparent, Green

**Potential vs. time plots for two different current density values (9.7 and 39 mA/cm²) for a solution of redox couple (300 mM).**

**$Fe(III)EDTA$   
 $Fe(II)EDTA$**

- No toxicity
- EDTA is widely used in food chemistry and in human diets against the iron deficiency anaemia
- Possible reaction of  $Fe(II)EDTA$  with oxygen with formation of  $Fe(III)EDTA$
- Limited stability on a DSA- $O_2$  electrode when the redox couple is cycled for 5 hours
- Partial conversion of  $Fe(II)EDTA$  to  $Fe(III)EDTA$  at graphite anodes in long time electrolyses
- $Fe(II)EDTA$  exhibited a limited electrochemical stability in long term electrolyses at all adopted operational conditions
- Disadvantageous use of the  $Fe(III)EDTA/Fe(II)EDTA$  for RED applications
- Are electrochemically stable in a suitable range of pH (3-7); below pH 3, the complex decomposes, while at pH greater than 7, the solution becomes cloudy

**Time concentration profiles for long time electrolyses performed with an initial concentration of the couple of about 80 mM at compact graphite electrodes in undivided cell with 0.1 mol dm⁻³ Na₂SO₄ aqueous solution under amperostatic alimentation with a current density of 2 mA cm⁻² under dark and nitrogen atmosphere.**

**Cyclic voltammograms of  $Fe(II)EDTA/Fe(III)EDTA$  performed at graphite in a 0.035 M  $Na_2SO_4$  aqueous solution under dark in nitrogen purged solution. Cyclic voltammogram snapshots taken at 1 h intervals during potential cycling in 10 mM  $Fe(III)EDTA/Fe(II)EDTA$  solution (pH = 7) with a scan rate of 0.1 V s⁻¹, T = 25 °C, V = 50 mL.**

**$FeCl_2$   
 $FeCl_3$**

- Low potential for redox processes
- Components of the redox couple not toxic
- Good chemical stability at low pH in the absence of air
- Good electrochemical stability
- Utilization of cheap graphite electrodes
- No relevant passage of redox couple and active chlorine to the side compartments with Selemion membranes.
- Eventual leakages could lead to the formation of precipitates in the rest of the stack.
- passage of protons to the NaCl compartment by ion exchange membrane

**Electrolyses performed with DSA electrodes with the redox couple  $FeCl_2/FeCl_3$  in a three compartment cell in the presence of Fumasep, Selemion, and Fuji anionic membranes with the following configuration under nitrogen atmosphere: 1) Lateral compartments: aqueous solution of the redox couple (0.3 mol dm⁻³), NaCl and HCl (initial pH = 2); 2) Central compartment: aqueous solution of 0.5 mol dm⁻³ NaCl. Fig. A) reports the concentrations of Fe(III) in the central compartment. Fig. B) reports the plot pH vs. time in the lateral and central compartments.**

**Electrolyses performed with compact graphite electrodes with the redox couple  $FeCl_2/FeCl_3$  in a two compartment cell in the presence of Selemion anionic membrane with the following configuration under nitrogen atmosphere: 1) one compartment: aqueous solution of the redox couple (0.3 mol dm⁻³), NaCl and HCl (initial pH = 2); 2) the other compartment: aqueous solution of 0.1 mol dm⁻³ NaCl. The fig. reports the plot pH vs. time.**

**EXPERIMENT STACK**

**A reverse electro dialysis stack structure with one cell**

**Electro dialysis performed with a RED stack with 10 cells that used carbon felt as electrodes and redox couple  $FeCl_2/FeCl_3$  (0.3 M, pH=2 with NaCl 0.1M) as electrode solution. The figure A) plot current density and E (cell) vs. External variable resistance; figure B) show the power density's trend vs. Current density. The maximum power obtained occurs when the internal resistance corresponds to the external resistance.**

**Generated power density of a RED stack with 10 and 40 cells with Fuji anionic and cationic membranes and Selemion Anionic membranes.**

Acknowledgements  
EC (FPF, Energy, REAPower project) is acknowledged for its financial support.

References  
 ✓ J. Veerman, M. Saakes, S. J. Metz, G. J. Harmsen (2010) J. Appl. Electrochem. 40:1461  
 ✓ Kuhn, D.D. Young, T.C., Chemosphere 60 (2005) 1229-1230;  
 ✓ Meeussen, J.C.L., Keizer, M.G. and de Haan, F.A.M. Sci. Technol., Vol. 26, No. 3, 1992