

SELECTION OF REDOX SYSTEMS FOR REVERSE ELECTRODIALYSIS PROCESSES

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Introduction and aim of the work

In reverse electrodialysis (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 electrodialysis process. In spite of the large number of studies dedicated to reverse electrodialysis 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 electrodialysis processes and to study the behavior of these systems. This work was devoted to the study of the utilization of iron-based redox couples $FeCl_3/FeCl_2$, 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

Materials

REDOX COUPLES:

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

ION SELECTIVE EXCHANGE MEMBRANES:

- Fumasep (CEM-AEM)
- Selmem (CEM-AEM)
- Fuji (CEM-AEM)
- Nafion (CEM)

ANION EXCHANGE MEMBRANE

CATION EXCHANGE MEMBRANE

Experimental apparatuses

✓ Undivided cell (70 ml) for long time electrolyses (several days)

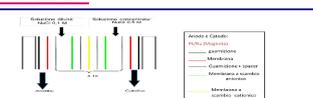
✓ Two- or three compartment cell to study the passage of species from/to the redox compartments and to evaluate the suitable membranes (several days)

Results

Redox couple	Advantages	Drawbacks
$[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$	<ul style="list-style-type: none"> 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-O₂ or graphite <p>Concentration vs. time plots for Hexacyanoferrate(III) and free cyanide from Kuhn, D.D. Young, T.C., Chemosphere 40 (2005) 1222-1230; Meeussen, J.C.L., Keizer, M.G. and de Haan, F.A.M., Environ. Sci. Technol., Vol. 26, No. 3, 1992.</p>	<ul style="list-style-type: none"> The accidental release of the redox couple has to be avoided since it gives rise to a coloration of the effluents and to the rapid formation of toxic species in the presence of light and air Decomposition of the hexacyanoferrate complexes to Fe and CN⁻ ions (dark green cloudy solution, observation of a blue deposit on the electrode surface, probably due to the formation of Prussian Blue complex) if too low concentrations or too high current densities are used Chemical decomposition of the complexes in the presence of air and/or light <p>Potential vs. time plots for two different current density values (9.3 and 39 mA/cm²) for a solution of redox couple (300 mM).</p>
$Fe(III)EDTA/Fe(II)EDTA$	<ul style="list-style-type: none"> No toxicity EDTA is widely used in food chemistry and in human diets against the iron deficiency anaemia <p>Cyclic voltammograms of $Fe(III)EDTA/Fe(II)EDTA$ performed at graphite in a 0.035 M Na₂SO₄ 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.</p>	<ul style="list-style-type: none"> Possible reaction of $Fe(II)EDTA$ with oxygen with formation of $Fe(III)EDTA$ Limited stability on a DSA-O₂ 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 operative conditions Disadvantageous use of the $Fe(II)EDTA/Fe(III)EDTA$ 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
$FeCl_3/FeCl_2$	<ul style="list-style-type: none"> 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 Selmem membranes. <p>Electrolyses performed with DSA electrodes with the redox couple $FeCl_3/FeCl_2$ in a three compartment cell in the presence of Fumasep, Selmem, 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.</p>	<ul style="list-style-type: none"> 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 <p>Electrolyses performed with compact graphite electrodes with the redox couple $FeCl_3/FeCl_2$ in a two compartment cell in the presence of Selmem 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.</p>

Future plans

• experiments in stack.



Acknowledgements

EC (7FP, Energy, REAPower project) is acknowledged for its financial support.

References

- ✓ J. Veerman, M. Saakes, S. J. Metz, G. J. Harnsen (2010) J. Appl. Electrochem. 40:1461
- ✓ Kuhn, D.D. Young, T.C., Chemosphere 60 (2005) 1222-1230;
- ✓ Meeussen, J.C.L., Keizer, M.G. and de Haan, F.A.M. Sci. Technol., Vol. 26, No. 3, 1992