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Investigation of electrode material - redox couple systems for reverse electro dialysis processes. Part I: Iron redox couples.

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Abstract

The performances of electro dialysis (ED) and reverse electro dialysis (RED) processes depend on several factors, including the nature of the electrode material and of the redox couple adopted to make possible the conversion between electric power and chemical potential. In this paper, the possible utilization of iron-based redox couples ($\text{FeCl}_3/\text{FeCl}_2$, hexacyanoferrate(III)/hexacyanoferrate(II) and $\text{Fe(III)-EDTA}/\text{Fe(II)-EDTA}$) on graphite and DSA electrodes for RED processes was studied by a detailed experimental investigation.

The hexacyanoferrate(III)/hexacyanoferrate(II) system was stable for long time (more than 12 days) in the absence of light and oxygen at high redox couple concentrations and low current densities both at compact graphite and DSA electrodes. Perfluorinated Nafion cationic membranes were found to be impermeable to the components of the redox couple. Fe(II)-EDTA exhibited a limited electrochemical stability in long term electrolyses at all adopted operative conditions, which discourages the use of the $\text{Fe(III)-EDTA}/\text{Fe(II)-EDTA}$ for RED applications. The $\text{FeCl}_3/\text{FeCl}_2$ system was, on the other hand, stable for long times (more than 12 days) at acidic pH at compact

graphite electrodes. Selemion anionic membranes allowed to confine the redox couple in the electrode compartments with very slow passage of protons to the side compartment (“dilute or concentrated compartment”).

Keywords: Electrodialysis; Reverse Electrodialysis; Electrode reaction; Redox couple, Iron complexes

1. Introduction

Electrodialysis (ED) is a separation technology based on the alternate arrangement of cationic and anionic ion-exchange membranes in a direct current field. This unit operation has been intensively studied for many applications such as desalination or concentration of electrolyte solutions using conventional ED or inorganic/organic acid production/recovery with bipolar membranes (BMED) [1,2]. Conversely, in reverse electrodialysis (RED) electrical energy is directly extracted from chemical potential gradients arising from salinity differences, especially from sea and river water [3]. 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]. According to Post et al., it is possible to convert 85 % of this potential energy into useful electricity [3]. In spite of the fact that RED application was discussed theoretically by Pattle et al. in 1954 [5], the interest in this topic rapidly increased only in the last years as attested by new scientific papers, the involvement of a number of private companies in research activities and EU funds devoted to this topic since RED processes seems closer to a possible application from a technological point of view due mainly to the development of more effective membranes. On the other hand, in order to develop some plants on an applicative scale, various technological and scientific aspects have to be studied in more detail. In both ED and RED, there are at least four complementary elements: (1) electrodes, where electron transfer reactions occur to allow the transformation of the charge carrier from ion to electron; (2) ion selective exchange membranes, which allow the selective transport of ions; (3) solvents, which make a continuum for ion transport; (4) electrolytes, i.e. the current carriers between cathode and

anode. Many efforts have been developed in the last years to improve both electrodialysis [1,2] and reverse electrodialysis processes. In the last case, studies were mainly focused on membranes [6] but also on several other aspects including water composition and concentration [7], modeling [3,8] and fluid dynamics [9]. Less attention has been given to the selection of the electrodic material-redox couple system (for the purpose of this work defined electrode system) with very few exceptions [4,10], the most relevant being a very recent paper of Veerman and co-authors that carried out a very detailed comparative assessment of the suitability for RED of selected electrode systems described in literature [4]. On the other hand, the behavior of these systems was rarely experimentally investigated under operative conditions of interest for RED applications [4]. 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]. 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 such as in the systems Cu-CuSO₄ [5], Ag-AgCl [11], Zn-ZnSO₄ [12], or homogeneous redox couples with inert electrodes [4]. In the case of reactive electrodes, the electrodes alternatively grow and dissolve thus being dimensionally not stable that is a major drawback for the electrochemical engineering of the stack. In fact the use of such solution in RED requires periodical interchange of anode and cathode, a not very attractive option from an applicative point of view, or periodical interchange of feed waters to invert the direction of the electrical current and consequently the direction of electron transfer at the electrodes [4]. This would impose to use identical compartments for concentrated and dilute solutions. In all cases, the inversion of electrode reactions is expected to reduce drastically the service life of electrodes. This reversal can be avoided, as recently proposed by Veerman et al. [4], 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 with opposite electrode reactions are often based on gas evolving redox processes, such as in the case of electrode systems containing NaCl and Na₂SO₄ water solutions. These processes are characterized by higher voltage losses and the necessity to stock electrogenerated gases preventing their mixing as they can form, for example in the case of water electrolysis, an explosive mixture. The objective of this paper, carried out in the frame of the EU-funded REAPower program, is to present an investigation on the possible utilization of some iron-based redox couples for ED and RED applications by integrating the information reported in the literature with detailed experimental studies. The research was focused on RED applications, because of our specific interest in this field, but most of considerations and results can be considered of interest for some ED applications such as that in the food field. Other redox processes not involving opposite reactions are also under investigation in our laboratory and will be the object of another work that will constitute an ideal continuation of the present study.

2. Preliminary considerations on the selection of redox couples

A large number of studies was devoted in the last decades to the behaviour of redox couples for numerous applications such as the investigation of electrode properties, redox catalysis, redox flow batteries, RED, etc. so that a very large set of data is available in the literature. An electrodic material-redox couple systems for RED or for ED for food purposes should, in particular, present the following characteristics:

1. Low voltage drops at electrode-solution interphase. The utilisation of the same redox couple at both electrodes allows one to have zero equilibrium voltage. Hence, energetic losses at electrode surface are due to over potentials, which are strictly related to the choice of the electrode and to the concentration polarization. If aforementioned contributions are minimized and conductivity of the electrolytic solution is high enough, limited voltage drop at terminal compartments of the stack can be obtained. It is important to underline that for commonly proposed redox couples these terminal voltage drops are usually low with respect to the overall cell voltage generated in

a stack having an applicative scale [4,13] so that these aspects are often no crucial for the energetic optimization of the system. High enough separation between redox potential of the couple and of the solvent is furthermore required to make more difficult its involvement in electron transfer reactions.

2. Low cost of redox species and electrodes.
3. High solubility of the redox couple. This condition grants appreciable current densities sustained by the target redox processes with lower possibility of involvement of the solvent in electrodic processes.
4. Low toxicity of redox species. For RED and many food concern ED applications it is necessary to avoid the utilisation of toxic substances that could potentially pollute the effluent streams or the products. In RED applications, treated concentrated and dilute solutions are likely to be discharged in the natural reservoirs from where they were drained and post treatments have to be reduced or, possibly, avoided to achieve a cost effective process. Similarly, in the case of ED for food purposes, the utilisation of toxic substances has to be avoided to guarantee the quality of the final products.
5. Chemical and electrochemical stability of redox species. In order to avoid or to minimize the consumption of redox species, the latter has to be stable for long times. Furthermore, it is important to verify that redox species decomposition does not form hazardous or toxic products that can negatively affect the process also in low concentrations. The chemical stability of numerous redox couples is a function of various parameters, the most relevant being often the pH. Thus, redox species usually consist in complexes where the donor ligands are Lewis bases and the metal ions are Lewis acids. For example, in the pH range of 0 – 14, most of the common chelating agents exist in an equilibrium of both the protonated and unprotonated forms. In addition the complexes may be involved in hydrolysis and/or precipitation [14].

6. Physical and chemical stability of electrodes. This feature is highly important to grant stable electrocatalytic properties and to avoid contamination of electrolytic solution by metal ions that can affect both the safety profile of the process and the long term performances of the stack.
7. No mass transfer of species from and to the electrode compartments. Only the transport of the ions necessary to sustain the electric current drained from the stack should ideally take place between electrodic and side compartments. This ideal condition would allow the operator to minimize the consumption of the redox species, to avoid contamination of dilute and concentrated solutions, to prevent drift in the permselectivity of ion-exchange membranes and to avoid a change of the electrode solution composition that may affect the performances of the redox processes or the stability of the components of the electrode systems. Of course, this aspect does not depend only on the composition of the electrode compartment solutions but also on the nature of the outer membranes – confining the electrode system – that may present different characteristics with respect to the other membranes mounted in the stack.

Quite interestingly, when one try to meet all the above mentioned requirements, most of the redox couples cited in the literature have to be discarded, thus reducing the choice to a very limited number of possibilities. Thus, numerous couples that potentially present a very high stability, such as those based on Cr, Ce, Co or V are likely to be discarded due to the high toxicity of these transition metals in some redox states potentially involved in the process. Within this regard, numerous complexes of iron are regarded as very promising for their low toxicity coupled with high stability. Iron is highly abundant and is often non-toxic in low concentrations. Fe(III) – Fe (II) couple is widely used in Fenton and electro-Fenton processes as the catalytic system, in the presence of sulphate and chloride ions, to favour the conversion of hydrogen peroxide to hydroxyl radicals [15]. These couples are used at $\text{pH} < 3$ to avoid the precipitation of ferric oxyhydroxides. The utilisation of an airtight system is also required for RED applications [4] to avoid the oxidation of Fe^{2+} to Fe^{3+} by molecular oxygen. However, the control of pH in a RED process is difficult

because anion exchange membranes exhibit not negligible transport number for protons, thus potentially allowing an increase of the pH of the electrode solution accompanied by a decrease of the pH of the effluent which can be not acceptable from an environmental point of view if too marked. In this perspective, a regular supply of an acid and of a base may be necessary for the electrolyte and the output stream, thus increasing the complexity and the cost of the process [4]. The use of ligands to complex Fe(II) and Fe(III) ions can be a good strategy to enlarge the pH stability range of the couple. Ligands have not to be consumed during the process and the resulting complexes should present low toxicity. Many examples of iron complexes are reported in literature [4,14-15]. However, most of them do not fulfil the set of properties requested for a redox couple previously summarized. Thus, very few examples are stable in a large range of pH close to the neutrality and present high chemical and electrochemical stability coupled with high solubility and low toxicity. In particular, in this work we have selected $\text{FeCl}_3/\text{FeCl}_2$, $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ and Fe(III)-EDTA/Fe(II)-EDTA for a detailed experimental study since these couples are likely to present, according to available literature data, a good potential for RED application [1,4,14-15]. Thus, at low pH values, the first cited presents very high stability coupled with low toxicity while the other two, according to the literature, can fulfill most of the above mentioned requirements and in particular are expected to be stable under a pH close to 7 (see Table 1). On the other hand, the behavior of these couples was studied on very small time scales, under operative conditions quite different from that involved in applicative ED and RED processes and/or on very costly electrodes such as Pt. Hence, a large set of experiments was carried out in our lab under experimental conditions of interest for RED processes. DSA electrodes were adopted for their limited cost, high dimensional stability and service life. Also graphite was used with the main aim of lowering the cost of the electrodes.

Table 1. Main characteristics of investigated iron redox couples.

Couple	Redox potential	Stability	Toxicity	Examples of applications
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	(V vs. SCE)			
FeCl ₃ /FeCl ₂ Na ₂ SO ₄ /NaCl	0.54	Very high for pH < 3 – 4 and in absence of air [4]	Very low in water solutions	<ul style="list-style-type: none"> - Widely adopted in Fenton and electro-Fenton applications - Investigations for RED with Ti/RuIr electrodes [4]
[Fe(CN) ₆] ³⁻ / [Fe(CN) ₆] ⁴⁻	0.4	Very high in absence of air and light [16-21,25,27,28]	Very low toxicity [30]. Release of toxic gas after reaction with strong acids	<ul style="list-style-type: none"> - Widely adopted for studies on electrode characterization - Investigations for RED with Ti/RuIr electrodes [4]
Fe(III)-EDTA/ Fe(II)-EDTA	-0.08	Stable in the absence of light [32-34] for pH between 5.5 – 7 ^a and 3-7 ^{b,c}	EDTA widely used in foods and medicine (to remove excess iron from the body). Iron EDTA is recognized as safe for the food uses [31].	Foods and medicine

^a The CV of a test sample was stable for at least 20 weeks at these pH [14]. ^b Stability tested by a serie of CV. [15]. ^c Below a pH of 3, the complex appeared to decompose whereas at higher pH than 7, the solution became turbid [15].

2. Experimentals

Electrolyses were performed both in a bench-scale batch undivided cell (50 ml) and in a three compartments cell divided by ion-exchange membranes. Cationic (CEM) and anionic (AEM) membranes 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. Compact graphite, Ti/IrO₂-Ta₂O₅ or in few cases Boron doped diamonds (BDD) and titanium mesh coated with platinum (wet surface area in most cases 6-7 cm²) were used as electrodes. The solutions used in the anode and cathode compartments were stirred by magnetic stir bar and were prepared using distilled water 0.035 M Na₂SO₄ (Sigma Aldrich) adjusting the pH value to the target one by adding proper amounts of H₂SO₄ (Sigma Aldrich) or NaOH (Applichem). The central compartment solution in the three compartment cell was constituted by an aqueous solution of NaCl (Sigma-Aldrich). The volume of each compartment was generally of 50 ml. Amel 2055 potentiostat was used for electrolyses. Cyclic voltammetry was performed at Compact graphite and Ti/IrO₂-Ta₂O₅ electrodes using an Autolab PGSTAT12 potentiostat. In some cases, scans were carried out with IR compensation.

The concentration of the partners of the redox couples and of active chlorine were estimated by photometric analyses (Ocean Optic DH-2000). Ferrocyanide and ferricyanide were evaluated at 320 and 420 nm, respectively. The concentration of Fe(II) was evaluated for experiments performed with FeCl₂/FeCl₃ or Fe(II)-EDTA/Fe(III)-EDTA after treatment with phenatroline. For these redox couples the total concentration of iron was evaluated in the same way after treatment with ascorbic acid. In the case of active chlorine a Merk Chlorine test containing dipropyl, p-phenylenediamine (DPD) was used.

FeCl₂ and FeCl₃ from Sigma Aldrich, K₃[Fe(CN)₆] and K₄[Fe(CN)₆] from Labochem and Fe(III)-EDTA sodium salt from Sigma Aldrich were used as received. Fe(II)-EDTA was prepared according to reference [14] with Na₂EDTA (Carlo Erba) and FeSO₄·7H₂O (Carlo Erba). The supporting electrolyte was composed by 0.035 mol dm⁻³ Na₂SO₄ (Sigma Aldrich) and H₂SO₄ (Sigma Aldrich) or NaOH (Applichem) or by NaCl (Sigma-Aldrich). All these chemicals were analytical grade. BDD and compact graphite were supplied by Condias and Carbone Lorraine, respectively, while Iridium anodes were kindly provided by De Nora S.p.A. (Milano, Italy). The thickness of the stagnant layer in the undivided cell in the adopted conditions was estimated trough a typical limiting-current essay as previously reported [26].

Table 2. Membranes used in this study.

Name	Code	Company	Type
Fumasep	FKS	Fumatech (Germany)	CEM
	FAD	Fumatech (Germany)	AEM
Selemion	CMV	Asahi Glass	CEM
	AMV	Asahi Glass	AEM
Fuji	C	FujiFilm	CEM
	A	FujiFilm	AEM
Nafion	324	Du Pont	CEM

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

3. Results and Discussion

3.1. Investigation of the redox couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$

3.1.1 Cyclic voltammetric investigations

The ferrocyanide/ferricyanide redox couple has been extensively studied and characterized by both electrochemical and spectroscopic techniques and is often used as model redox couple for characterization of new electrode materials and of mass transfer kinetics in electrochemical reactors. This quasi-reversible couple is reported to be very stable under the time scale of electroanalytical experiments. On the other hand, Kawiak and co-authors observed a significant change of the standard rate constant at Pt with the ferrocyanide concentration that was attributed to the partial coverage of the electrode surface by poorly soluble species [17]. Some authors suggested that Prussian Blue, an insoluble polymeric hexacyanoferrate (HCF) complex is likely to be adsorbed onto the surface of Pt and glassy carbon [17-20]. It was also proposed that ferricyanide and ferrocyanide can adsorb onto Pt and glassy carbon electrode surfaces [19-21].

In this work, the electroanalytical behavior of the couple $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ was studied in water solutions of Na_2SO_4 $0.035 \text{ mol dm}^{-3}$ at DSA and graphite electrodes at various scan rates ($0.01 - 1 \text{ V s}^{-1}$) and iron couple concentrations (2 - 30 mM). The cyclic voltammogram on a graphite electrode shows a symmetric wave for all the tested concentrations (Fig. 1a). The ΔE_p was about 80 mV for compensated scans and $i_{p,a}/i_{p,c}$ was close to 1, where $i_{p,a}$ and $i_{p,c}$ are anodic and cathodic peak current densities, respectively. Both $i_{p,a}$ and $i_{p,c}$ increased linearly with the concentration. When the anodic potential limit was extended to 1.1 V, the presence of an anodic peak at about 0.9 V and of two cathodic waves at about 0.75 e 0.5 V, was observed (Fig. 1b). An anodic peak at 0.9 V was also observed by Gomathi et al. at glassy carbon [20] and attributed to the formation of a redox

couple Prussian Blue/Berlin Green on the surface. On the other hand, Prussian Blue and Berlin Green, prepared in our lab did not generate a wave at graphite electrode at 0.9 V.

Pharr and Griffiths studied at Pt disk the effect of the potential cycling on the formation of HCF compounds in a system composed by 10 mM of potassium ferrocyanide and 1 mol dm⁻³ KCl. They have found that a soluble HCF complex is formed when potential is cyclically changed over large potential limits (from -0.33 to 1.04 V). Furthermore, a drastic reduction of the current of both anodic and cathodic peaks was observed by these authors when the electrode potential of the Pt disk was cycled for 6 h.

In our case, when the electric potential at the graphite electrodes was cycled for six hours in the presence of the ferro/ferricyanide couple, the peak currents did not decrease (Fig. 1b). On the contrary, a small increase of the peak currents associated to the ferricyanide/ferrocyanide couple was observed, probably arising from an enhancement of the active surface area owing to microerosion of the graphite surface. A slightly more marked increase of the second anodic peak and a decrease of the cathodic peak at 0.75 V were also observed (Fig. 1b).

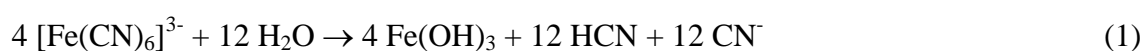
Cyclic voltammograms of the couple ferri-/ferrocyanide were repeated at DSA (Ti/IrO₂-RuO₂) electrodes that present a higher dimensional stability but higher costs than graphite. Also in this case, a symmetric wave at all tested concentrations (5 - 30 mM) and scan rates (0.01 - 1 V s⁻¹) was observed. The ΔE_p was about 80 mV for compensated scans but $i_{p,a}/i_{p,c}$ was slightly lower than 1. When the anodic limit of the potential range was extended to 1.2 V, no presence of other peaks was otherwise observed. When the potential of the DSA electrodes was cycled for six hours in the presence of ferro/ferricyanide couple, the anodic peak did not change appreciably while a very slight decrease of the cathodic one was observed.

Thus, it is possible to conclude that the redox couple exhibits a stable cyclic voltammetric behavior at both graphite and DSA electrodes even if the formation of other products can arise, at least at graphite, if large anodic potentials are applied.

Since in RED applications NaCl may be used as supporting electrolyte, the cyclic voltammetric behavior of the couple was also studied in the presence of NaCl. After addition of NaCl (4 mol dm⁻³) to a water solution a drastic increase of the anodic current at potentials close to 1.2 and 1.05 V for graphite and DSA electrodes, respectively, and the appearance of a cathodic peak at about 0.8 - 1 V were observed. According to the literature, such behavior can be attributed to oxidation of Cl⁻ ions to active chlorine [23,24]. When the ferri-/ferrocyanide couple was added to the NaCl solution, the difference between the anodic and the cathodic peak currents due to the redox couple decreased, probably for the higher conductivity of the solution, while the peaks attributed to the chloride ions oxidation and hypochlorous acid reduction remained unaltered.

3.2.2 Long time electrolyses in an undivided cell.

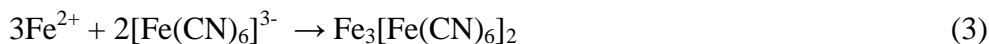
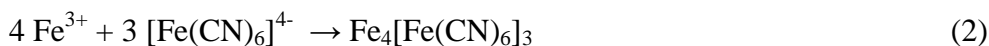
To test the long term stability of the redox couple, selected electrolyses were carried out for about 6 days in an undivided cell under dark and nitrogen atmosphere to avoid the O₂ promoted chemical oxidation of [Fe(CN)₆]⁴⁻ to [Fe(CN)₆]³⁻ and the sunlight activated cyanide liberation by equation (1) [25].



In aerated solution under dark, ferrocyanide was reported to be completely converted in ferricyanide in about 100 days at a pH of 7 [25] while in the presence of sunlight the ferrocyanide decomposes fastly with formation of cyanides. A solution of ferrocyanide 400 µg l⁻¹ was found to be almost totally converted in free cyanides in about 30 min at a pH of 12 [27]. Similar decomposition rates were reported also at a pH of 7 by Kuhn and Young [27] while Arellano and Martinez showed that the photolysis of aqueous ferricyanide decreases by lowering the pH [28]. On the other hand, in the absence of light and O₂, the couple is reported to be very stable if not too

acidic pH are involved and as an example iron cyanide complexes were estimated to have a half life of about 1000 years at a pH of 7.5 [29].

First electrolyses were performed at DSA electrodes under amperostatic alimentation with a current density of 9 mA cm^{-2} dissolving the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ couple in a water solution of Na_2SO_4 0.1 mol dm^{-3} . No appreciable variation of the concentration of the couple was observed for all the duration of the electrolysis (6 days) under the precision of the adopted analytical methodology (see Fig. 2 for the case of ferricyanide). On the other hand, a change of the color of the solution was observed from yellow to yellow-green and the anode presented a marked blue coloration at the end of the experiment compatible with the formation of HCF type compounds (Fig. 3). These species can be formed by reaction of ferrocyanide with Fe(III) (Eq. (2)) or ferricyanide with Fe(II) (Eq. (3)) [22].



Thus, a very small concentration of free Fe(III) was detected at the end of the experiment. In this perspective, it is important to observe that the limiting current density for the oxidation of ferrocyanide $i_{lim} = FD[\text{Ferrocyanide}]/\delta$ (where F is the Faraday constant, D and $[\text{Ferrocyanide}]$ the diffusion coefficient and the bulk concentration of Ferrocyanide, respectively, and δ the thickness of the stagnant layer) was just slightly lower than the applied current, thus giving rise to an high anodic potential of about 1.4 V vs. SCE. At these potentials, the anodic oxidation of water is likely to occur with the formation of protons (eq. (4)) and a strong local acidification of the solution in the porous structure of the anode, thus allowing the acid promoted decomposition of ferricyanide to free Fe(III) by the reaction reported in Eq. (5) that is expected to take place at very acidic pH [29].





If this tentative reconstruction would be correct, to avoid the formation of free iron and of HCF compounds on the anode surface, it would be necessary to work with a limiting current for the oxidation of ferrocyanide strongly higher than the applied current and as a consequence with higher [*Ferrocyanide*] or lower current densities. In this perspective, some long time electrolyses were carried out at different initial concentrations of the redox couple in the range 0.05 - 0.36 mol dm⁻³. At the end of the electrolysis performed at 0.1 mol dm⁻³, a change of the solution color from yellow to green, a blue colored anode and an increase of the anode potential up to about 1.3 V were still observed. On the other hand, at higher adopted concentration no effect of the time and of the passed charge on redox couple concentration and solution and anode color was observed also when the experiments were prolonged for 13 days. Furthermore, the anode potential did not change during the experiment remaining very close to 0.3 V vs. SCE and no presence of free Fe(II) and Fe(III) was detected.

To test the effect of the current density, two electrolyses were carried out with a concentration of the redox couple of 0.3 mol dm⁻³ and a current density of 9.5 and 39 mA cm⁻². At the highest adopted current density, the anode potential increased up to 1.4 V, the color of the solution changed and after 6 days the anode presented a marked blue color, thus confirming the necessity to work with both low current densities and high concentrations to avoid a degradation of the redox couple partners.

Since in RED applications NaCl is likely to be used as supporting electrolyte, some long time electrolyses were repeated in the presence of NaCl 0.1 mol dm⁻³ with a low current density of 10 mA cm⁻² and an high initial concentration of the redox couple of 0.36 mol dm⁻³, to avoid both the water and the chloride oxidation. After 7 days, the system did not show any appreciable modification with respect to initial conditions and formation of active chlorine was not detected.

Since graphite electrodes are less expensive with respect to metal oxides ones, some electrolyses were carried out for seven days by using graphite for both anode and cathode. Also in this case, when the experiment was performed with a current density of 10 mA cm^{-2} and an initial concentration of the redox couple of 0.36 mol dm^{-3} , no appreciable modification of the system was observed. On the other hand, when the same experiment was repeated with an initial concentration of 0.1 mol dm^{-3} , the graphite anode collapsed and showed a blue coloration, the presence of iron(III) was detected and the anode potential increased during the experiment up to about 1.6 V vs. SCE after few hours.

3.2.3 Electrolyses in three compartment cell.

According with above mentioned experiments, the redox couple ferro-/ferricyanide is expected to be very stable in oxygen free solutions under dark if proper current densities and iron ions concentrations are used. To evaluate the possible utilization of such a couple in RED processes, the transport of the couple partners through the outer membranes – confining the electrode system – was also studied. Thus, it should involve a periodic replacement of ferro- and/or ferricyanide and, more important, it would lead to a contamination of dilute and concentrated solutions that, in RED applications, are expected to be discharged in the natural sources where they are collected. Thus, the redox couple ferro-/ferricyanide is reported not to be toxic, but, in the presence of air and sunlight, it rapidly decompose to cyanides so that its presence in dilute and concentrated compartments has to be avoided. Please consider that usually no specific limitations are found for ferrocyanide and ferricyanide. On the other hand, the Italian limit for cyanide of 0.5 mg l^{-1} , was here considered prudentially assuming that ferro- and ferricyanide can be totally converted in free cyanides in the presence of sunlight after the discharge.

To evaluate the passage of species between electrode and lateral compartments, some amperostatic electrolyses were repeated in a three compartment cell equipped with Fumasep cationic membranes to avoid/minimize the passage of ferro- and ferricyanides. In the lateral

compartments, the anode and the cathode processes occurred in the presence of an initial concentration of 0.36 mol dm^{-3} of ferrocyanide and ferricyanide and of $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$. The central compartment was filled with various concentrations of NaCl (0, 0.5, 5 mol dm^{-3}). Very high concentrations of NaCl were also used due to the potential utilisation of very concentrated water solutions for reverse electrodialysis processes from salt ponds or desalination plants. The presence of a cationic membrane should minimize the passage of Cl^- ions and of the hypochlorite eventually formed at the anode. However, the presence of hypochlorite in the central compartments was also searched for.

After 1 h, a contact time drastically higher with respect to that expected in a stack for RED, no presence of ferrocyanide and ferricyanide in the central compartment was observed in all the experiments. Similar results were obtained also at longer times when experiments were performed with no NaCl in the central compartment. On the other hand, in the presence of NaCl, after 3 hours the presence of ferrocyanide was detected and increased with NaCl concentration (see Table 3), thus showing that the presence of chlorides affects the perm-selectivity of the membrane. In the experiment performed with a concentration of NaCl in the central compartment of 0.5 mol dm^{-3} , no presence of active chlorine in the central compartment was observed after 1h. On the other hand, when the concentration of NaCl was increased to 5 mol dm^{-3} , a concentration of active chlorine of about 3 mg l^{-1} was detected that is higher than the Italian limit value of 0.2 mg l^{-1} (Table 3).

Since the passage of species is likely to be dramatically affected by the nature of the membrane, some experiments were repeated with Fuji and Nafion membranes in the presence of 5 M NaCl in the central compartment. As shown in Table 3, the passage of the monitored species depends dramatically on the nature of the membrane.

Table 3. Electrolyses performed in three compartment cell in the presence of the system $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$.^a

Initial concentration	Membrane	Concentration of ferrocyanide in the central compartment (mg l^{-1})	Concentration of Active chlorine in the central
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of NaCl in the central compartment (mol dm ⁻³)		compartment (mg l ⁻¹)					
		1 h	3 h	20 h	1 h	3 h	20 h
0	Fumasep	-	-	-			
0.5		-	-	10	0.01	2	10
5		-	10	190	3	10	53
5	Nafion	-	5	21	-	-	-
5	Fuji	100	250		140	157	

^a Concentrations of ferrocyanide and of active chlorine detected in the central compartment of a three compartment cell vs. time using Fumasep, Nafion and Fuji cationic membranes and with different concentration of NaCl (0, 0.5 and 5 mol dm⁻³) in the central compartment. Electrolyses performed with DSA electrodes in a three compartment cell with the following configuration: 1) Anode compartment: water solution of Na₂SO₄ 0.1 mol dm⁻³ and [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ with an initial concentration 0.36 mol dm⁻³; 2) Central compartment: water solution of Na₂SO₄ 0.1 mol dm⁻³ or NaCl 0.5-5 mol dm⁻³; 3) Cathode compartment: water solution of Na₂SO₄ 0.1 mol dm⁻³ and [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ with an initial concentration 0.36 mol dm⁻³. The concentration of ferro- and ferricyanides was maintained between 0.2 and 0.4 mol dm⁻³ in the lateral compartments by stepwise additions.

In particular, very low concentrations of both active chlorine and hexacyanoferrate complexes were obtained with Nafion membranes. This is probably due to the fact that Nafion membranes were designed to work in the presence of high NaCl concentrations as they are used in the chlorine-alkali industry. These membranes present quite high cost. Hence, they are not suitable to be used in all the stack but their utilisation is suggested for the outer membranes confining with electrode compartments.

3.3. The system Fe(III)-EDTA/Fe(II)-EDTA

3.3.1 Cyclic voltammetric investigations

The couple Fe(III)-EDTA/Fe(II)-EDTA is recognized as safe for the food uses [31]. The chemical stability of Fe(III)-EDTA was shown to be dependent on pH, exposure to light and temperature [32] while Fe(II)-EDTA is easily oxidized to Fe(III)-EDTA in the presence of air [33]. Under dark conditions, the stability of Fe(III)-EDTA decreased drastically with pH in the investigated range 7.75 – 9 [32]. The stability of this couple was investigated by Ibanez and co-authors by electroanalytical measurements in a wide range of pH at Pt electrodes [14]. Anodic and cathodic peaks were observed to be reproducible after several cycles at any pH between 3 and 7. Below a pH of 3, the complex appeared to decompose, whereas at pH higher than 7, the solution became cloudy. The CV of the couple was also reported to be stable for 20 weeks both at a pH of 5 and 7 [14]. According to the studies of Juzeliunas and Juttner [34], the electrochemical deposition of iron from both Fe(II)-EDTA and Fe(III)-EDTA takes place at potentials of water cathodic discharge at a platinum electrode. Also the anionic decomposition of EDTA was observed at $E > 0.6$ V at a pH of 3.3 by these authors.

The electroanalytical behavior of the couple Fe(III)-EDTA/Fe(II)-EDTA was here studied in water solutions of Na₂SO₄ 0.035 M at DSA and graphite electrodes at various scan rates (0.01 – 0.1 V/s) at a pH of 7 in the range -0.5 + 0.2 V vs. SCE. The cyclic voltammogram on a graphite electrode showed a symmetric wave for all the tested scan rates. The ΔE_p was about 120 mV at 10 mVs⁻¹, $i_{p,a}/i_{p,c}$ was about 0.95 and i_p changed linearly with the square root of the scan rate. When the electrode potential was cycled for six hours at the graphite electrodes in the presence of the couple, the cathodic peak current did not change while a very slight decrease of the anodic one was observed, thus suggesting a very slow degradation of Fe(II)-EDTA (Fig. 4).

When cyclic voltammograms of the couple Fe(III)-EDTA/Fe(II)-EDTA were repeated at DSA (Ti/IrO₂-RuO₂) electrodes, a lower ratio of $i_{p,a}/i_{p,c}$ of about 0.82 was measured. Furthermore, also in this case, when the electrode potential was cycled for 6 h, a very slight decrease of the anodic peak was observed while the cathodic one did not change with the time.

3.3.2 Long time electrolyses in an undivided cell.

Also in this case the long term stability of the redox couple was studied performing electrolyses for about 6 days in an undivided cell under dark in nitrogen purged solution to avoid the photo-reductive dissociation of Fe(III)-EDTA to free Fe(III) and the chemical oxidation of Fe(II)-EDTA to Fe(III)-EDTA [32,33]. First electrolyses were performed at graphite electrodes at a pH of about 7 in a water solution 0.1 M Na₂SO₄ and of the couple Fe(III)-EDTA/Fe(II)-EDTA (initial concentration about 80 mM) under amperostatic alimentation with a current density of 2 mA/cm². As shown in Fig. 5, a continuous decrease of the concentration of Fe(II)-EDTA was observed while the total concentration of soluble iron did not change appreciably. Thus, the iron(II) complex progressively decomposed with the formation of iron(III). The adopted analytical methodology did not allow us to discriminate between Fe(EDTA) and free iron. On the other hand, after two days, the solution changed its yellow color to a red one compatible with the presence of free iron(III) and contained some precipitates, thus suggesting the formation of iron oxyhydroxides. Also the anode was red colored. Furthermore, the anode potential increased during the experiment from 0.12 V to more than 1.5 V, where both the water cathode discharge but also the EDTA decomposition may take place [34]. On the other hand, when the experiment was repeated at the same conditions but monitoring the cathode potential, the latter did not change during the electrolysis, thus suggesting that the decomposition process did not involve significantly the Fe(III)-EDTA. Hence, it seems reasonable to propose, that only the anodic decomposition of Fe(II)-EDTA takes place with the formation of free Fe(II) that is anodically converted to free Fe(III) whose presence at a pH of 7 gives both the typical red coloration observed in the electrolysis and the formation of precipitates, as confirmed by independent tests realized with free Fe(II) and/or Fe(III) at a pH of 7.

To find operative conditions at which the decomposition of Fe(II)-EDTA does not occur, several electrolyses were carried out by changing current density (from 1.2 to 10 mA/cm²), initial redox couple concentration (from 50 to 100 mM, the latter being the solubility limit). Unfortunately, under all the investigated conditions a clear reduction of the concentration of the redox couple was

always detected after three days. To have more information on the process, few experiments were repeated with a very high oxygen overpotential anode such as Boron doped diamond (BDD). In the case of BDD the anode potential reached values of about 1.4 V, too low for the oxygen evolution reaction on BDD, thus suggesting that the decomposition of Fe(EDTA) takes place.

3.3. The system FeCl₃/FeCl₂

3.3.1 Cyclic voltammetric investigations

Fe(III)/Fe(II) couple is usually used at pH < 3 to prevent the precipitation of ferric oxyhydroxides. The utilisation of an airtight system is also required for RED applications [4] to avoid the oxidation of Fe²⁺ to Fe³⁺ by means of oxygen. The electroanalytical behavior of the couple FeCl₃/FeCl₂ 20 mM was first studied in water solutions of Na₂SO₄ 0.035 M at graphite electrodes at various scan rates (0.01 - 1 V/s) at a pH of 2 in the range 0 - 1 V vs SCE. The ΔE_p was about 190 mV at 10 mV/s⁻¹, $i_{p,a}/i_{p,c}$ was close to 1 for all the tested scan rates and i_p changed linearly with the square root of the scan rate. Similar cyclic voltammograms were recorded also at pH 3 and 5.

When the couple was cycled for six hours at the graphite electrodes at pH 2 or 3, a slight increase of the current of the peaks associated to the Fe(II)/Fe(III) couple was observed, probably arising from an enhancement of the active electrode area (Fig. 6a for experiments performed at a pH of 3). When experiments were repeated at the same conditions but at a less acidic pH of 5, a slow but continuous decrease of both anodic and cathodic peaks was observed while the solution became slightly turbid, thus confirming that the couple is not stable at not very acidic pH (Fig. 6b).

3.3.2 Electrolyses

Also in this case we studied the behavior of the redox couple in long time electrolyses that were carried out for about 5 days in an undivided cell under nitrogen atmosphere to avoid the chemical oxidation of Fe(II) to Fe(III) and at an initial pH of 2 to avoid the precipitation of ferric

oxyhydroxides. Experiments were performed at graphite electrodes in a water solution of NaCl 0.5 M and of the couple Fe(III)/Fe(II) 0.3 M under amperostatic alimentation with a current density of 10 mA/cm². No appreciable variation of the concentration of the couple (Fig. 7) and of the color of the solution and of the electrodes was observed during all the experiment. The pH slowly decreased during the experiment from 2 to 1.7 while the cell voltage and the electrode potentials did not show relevant changes.

In order to decrease the overvoltages and consequently the cell voltage, some experiments were repeated in an undivided cell equipped with Pt electrodes. Indeed, the cell potential was reduced from 0.4 -0.5 V observed for graphite electrodes to about 0.15 V in the case of Pt based electrodes. However, at the end of the experiment after 3 days, some parts of the cathode showed a change of the color due to the deposition of metallic iron. On the contrary, when the experiment was repeated at graphite electrodes for 10 days, no appreciable variation of the concentration of the couple and of working and cell potentials were still observed while the electrodes did not show appreciable modifications.

To estimate the mass transfer across adopted membranes, some amperostatic electrolyses were repeated in a three compartment cell equipped with anionic membranes to avoid/minimize the passage of Fe(II) and Fe(III) to the central compartment. In the end compartments, the anode and the cathode processes occurred in the presence of an initial concentration of Fe(II) and Fe(III) both 0.3 M, in an aqueous solution with HCl (pH=2). The central compartment was filled with a 0.5 M NaCl solution. The presence of the anionic membrane should minimize the passage of hypochlorous acid potentially formed at the anode. As shown in Fig. 8a, a very slow decrease of the pH was observed in the central compartment while no appreciable drift of the pH was observed in the anode and cathode compartments after 3 hours. The dilute and concentrated solutions are expected to present a short residence time in the stack of few seconds. Hence, according to above mentioned results, the pH of these solutions is expected not to change significantly so that a basification of discharged dilute and concentrated solutions is not necessary. On the other hand, the electrode rinse

solution is going to be continuously re-circulated in the stack so that the slow passage of protons to the central compartments will lead inevitably to a continuous increase of the pH. Hence, a periodic acidification of the electrolytic solution is probably required to avoid the precipitation of iron oxyhydroxides. As shown in Figs 8b and 8c, the passage in the central compartment of the redox couple and of the active chlorine depended drastically on the nature of the adopted anionic membrane. No passage of both species was, in particular, observed with Selemion membranes, thus showing that the Fe(III)/Fe(II) couple can be potentially used for RED and ED applications in the presence of suitable anionic membranes. To evaluate in a more detailed way the decrease of the pH in the electrode compartments, one experiment was carried out in a two compartment cell (first compartment equipped with cathode, anode and reference and a water solution of NaCl 0.1 M, FeCl₂ and FeCl₃ 0.3 M at a pH of 2; second compartment with a water solution of NaCl 0.1 M) separated by a Selemion membrane with a current density of 10 mA/cm² for 10 days. Quite interestingly, the electrode potentials and the concentrations of iron species did not change appreciably during the experiment while the pH of the electrode compartment did not show an appreciable increase during the whole experiment. It follows that the periodical acidification of the electrodes compartments should take place with a quite low frequency to maintain the pH of the electrode compartment between 2 and 3. Furthermore, the possible utilisation of a buffer media could minimize the need of acidification.

4. Conclusions

The possible utilisation of three iron redox couples (namely, FeCl₃/FeCl₂, hexacyanoferrate(III)/hexacyanoferrate(II) and Fe(III)-EDTA/Fe(II)-EDTA) for RED and ED applications was assessed by electroanalytical investigations and electrolyses performed in one and three compartment cells. The system Fe(III)-EDTA/Fe(II)-EDTA was studied in a large range of operative conditions by changing current density (from 1.2 to 10 mAcm⁻²), initial cumulative concentration of the redox couple (from 50 to 100 mM), electrodes (compact graphite and BDD).

Unfortunately, under all the adopted conditions the system was not stable enough after three days. In spite of the fact that the hexacyanoferrate(III)/hexacyanoferrate(II) couple is widely used for electrochemical characterizations, no data are available in literature regarding its stability under operative conditions of interest for RED applications. We have shown that this couple can be used for these applications in the absence of light and oxygen by working with high redox couple concentrations and low current densities both at compact graphite and DSA electrodes. The utilization of Nafion cationic outer membranes – confining the electrode system – allowed to confine the redox couple in the electrode compartments. The last result is quite relevant to avoid a contamination of the discharged dilute and concentrated solutions by the hexacyanoferrate(III)/hexacyanoferrate(II) couple that can decompose under sunlight and oxygen with the formation of free cyanides. The system $\text{FeCl}_3/\text{FeCl}_2$ was shown to be stable at acidic pH for long times at compact graphite electrodes. The utilization of Selemion anionic outer membranes allowed to confine the redox couple in the electrode compartments and to obtain very slow passages of protons to the side compartment, thus avoiding basification post treatments of the discharged dilute and concentrated solutions flowing in the stack.

Acknowledgments

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FIGURE CAPTIONS

Figure 1. Cyclic voltammograms of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ performed at graphite in water solution of $0.035 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ under dark and nitrogen atmosphere. Fig. 1a reports the cyclic voltammograms with potential limits: -0.1 to 0.4 V/SCE at various concentrations (2 (---), 5 (-), 10 (··) 20 (--) 30 (-) mM) with scan rate of 0.1 V s^{-1} . Fig. 1b reports the cyclic voltammogram for a 10 mM ferro-/ferricyanide solution for a scan extended to $-1.3 - 1.1 \text{ V/SCE}$, (scan rate 0.1 V s^{-1}). Cyclic voltammogram snapshots taken at 1 h intervals during continuous potential cycling in 10 mM ferro-/ferricyanide solution with a scan rate of 0.1 Vs^{-1} are also reported in Figs. 1b. $T = 25 \text{ }^\circ\text{C}$. $V = 50 \text{ ml}$.

Figure 2. Concentration profiles of $[\text{Fe}(\text{CN})_6]^{3-}$ with the charge passed for long-time electrolyses performed with different initial concentrations of the couple (50 (Δ), 100 (\times), 300 (\square), 360 (\bullet) mM) at DSA electrodes in undivided cell with water solution of Na_2SO_4 0.1 mol dm^{-3} under amperostatic alimentation with a current density of 9 mA cm^{-2} under dark and nitrogen atmosphere.

Figure 3. Photo of the DSA anode used for 6 days in the electrolysis of water solution of Na_2SO_4 0.1 mol dm^{-3} and of the couple $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ 50 mM in undivided cell under amperostatic alimentation with a current density of 9 mA cm^{-2} . Experiment was carried out under dark and nitrogen atmosphere.

Figure 4. Cyclic voltammograms of Fe(III)-EDTA/Fe(II)-EDTA performed at graphite in a water solution $0.035 \text{ mM Na}_2\text{SO}_4$ 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 with a scan rate of 0.1 V s^{-1} . $T = 25 \text{ }^\circ\text{C}$. $V = 50 \text{ ml}$.

Figure 5. Concentration profiles of Fe(II)-EDTA (■) and total iron (○) with the charge passed for long-time electrolysis performed with an initial concentrations of the couple of about 80 mM at compact graphite electrodes in undivided cell with water solution Na_2SO_4 0.1 mol dm^{-3} under amperostatic alimentation with a current density of 2 mA cm^{-2} under dark and nitrogen atmosphere.

Figure 6. Cyclic voltammogram snapshots of $\text{FeCl}_3/\text{FeCl}_2$ performed at graphite in a water solution of Na_2SO_4 taken at 1 h intervals during potential cycling with a scan rate of 0.1 V s^{-1} at a pH of 3 (Fig. 6a) and 5 (Fig. 6b) under nitrogen atmosphere. $T = 25 \text{ }^\circ\text{C}$. $V = 50 \text{ ml}$. Concentration of the couple $\sim 20 \text{ mM}$.

Figure 7. Concentration profiles of Fe(II) (■) and Fe(III) (○) with the time passed for long-time electrolysis performed with an initial concentrations of the couple $\text{FeCl}_3/\text{FeCl}_2$ of about 300 mM and an initial pH of 2 at compact graphite electrodes in undivided cell with water solution of NaCl 0.5 mol dm^{-3} under amperostatic alimentation with a current density of 10 mA/cm^2 under nitrogen atmosphere.

Figure 8. Electrolyses performed with DSA electrodes with the redox couple $\text{FeCl}_3/\text{FeCl}_2$ 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: water solution of the redox couple (0.3 mol dm^{-3}), NaCl and HCl (initial pH = 2); 2) Central compartment: water solution of 0.5 mol dm^{-3} NaCl . Fig. 8a reports the plot pH vs. time passed in the lateral and central compartments while the concentrations of Fe(tot) and active chlorine detected in the central compartment are reported in Fig.s 8b and 8c, respectively. The concentration of Fe(II) and Fe(III) was maintained between 0.2 and 0.4 mol dm^{-3} by stepwise additions. Dashed line represents the Italian law limit for iron.

