

Reverse electrodialysis: evaluation of suitable electrode systems

J. Veerman · M. Saakes · S. J. Metz ·
G. J. Harmsen

Received: 15 September 2009 / Accepted: 27 March 2010 / Published online: 29 April 2010
© The Author(s) 2010. This article is published with open access at Springerlink.com

Abstract Reverse electrodialysis (RED) is a method for directly extracting electrical energy from salinity gradients, especially from sea and river water. For the commercial implementation of RED, the electrode system is a key component. In this paper, novel electrode systems for RED were compared with existing systems on safety, health, environment, technical feasibility and economics. Systems with inert DSA-type electrodes and a NaCl–HCl supporting electrolyte with the reversible $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple or the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ couple achieved the highest ranking. Improvements of the electrode system are also discussed like the use of special stable metal electrodes, graphite electrodes, other reversible redox couples, capacitive electrodes and electrolytes with carbon particles.

Keywords Reverse electrodialysis · Electrode reaction · Salinity gradient power · Electrodialysis · Stack design · Power production

Abbreviations

AEM	Anion exchange membrane
DC	Direct current
CEM	Cation exchange membrane
CDI	Capacitive deionization
DEA	Data envelopment analysis
DSA	Dimensionally stable anode
ED	Electrodialysis
EDR	Electrodialysis reversal
EMF	Electromotive force
ES	Electrode system
GS	Generating system
MMO	Mixed metal oxide
PRO	Pressure retarded osmosis
RED	Reverse electrodialysis
SHE	Standard hydrogen electrode
SHE	Safety, health and environment
SGP	Salinity gradient power

Definitions

Compartment	Space between the membranes
Cell	Combination of two membranes and two compartments
Generating system	A number of N cells without the electrode system
Electrode system	Anode, cathode, electrode rinse and outer membranes
Stack	A number of N cells with an electrode system

J. Veerman · M. Saakes · S. J. Metz (✉)
Wetsus, Centre of Excellence for Sustainable Water Technology,
P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands
e-mail: sybrand.metz@wetsus.nl

J. Veerman
e-mail: joost.veerman@wetsus.nl

J. Veerman
Department of Life Sciences and Technology, Noordelijke
Hogeschool Leeuwarden, Agora 1, 8934 CJ Leeuwarden,
The Netherlands

G. J. Harmsen
University of Groningen, Nijenborgh 4, 9747 AG Groningen,
The Netherlands

1 Introduction

Energy can be generated from the reversible mixing of salt solutions with different concentrations and is called salinity

gradient power (SGP). The energy that theoretically can be generated per m^3 river water is 1.7 MJ when mixed with the same volume sea water or even 2.5 MJ when mixed with a large surplus of sea water [1]. Post et al. proved experimentally that it is possible to convert 85% of this potential energy into useful electricity [2]. Wick and Schmitt [3] estimated the total global salinity power to be 2.6 TW, which is sufficient to supply the global electricity demand (2 TW) or 16% of the total present energy consumption [4].

There are two membrane technologies capable of converting this potential energy into electricity: reverse electrodialysis (RED) [5–7] and pressure retarded osmosis (PRO) [8, 9]. Both PRO and RED are sustainable technologies without CO_2 or other emissions. The only product is brackish water which is also formed when a river flows directly in the sea. Moreover, there is no thermal pollution: the conversion of entropy into electrical energy causes a slight decrease of the water temperature of about 0.1 K if all the potential energy is extracted [10]. Post et al. [11] showed that in the case of using seawater with river water, RED is a good choice. In 1954 Pattle already [5–7] showed the opportunities of this method.

A RED stack consists of a large number of cells. An example of a RED stack with only one cell is shown in Fig. 1. The cell consists (from left to right in the figure) of an anion exchange membrane (AEM), a sea water compartment, a cation exchange membrane (CEM) and a river water compartment. On the right side, the stack contains an extra AEM. The ions in the sea water diffuse through the membranes to the river water: the Na^+ ions through the CEM and the Cl^- ions through the AEM. The positive Na^+ movement to the right and the negative Cl^- movement to the left add together to a positive ionic current to the right. The electromotive force of such a cell is 175 mV if pure NaCl solutions are used of 1 and 30 g l^{-1} and ideal membranes are applied; practical cell voltages under conditions of maximal power generation are about 60 mV [1]. In practice, a large number of cells (N) is used, in the range from 50 in laboratory equipments to 1000 or more in commercial RED plants [1].

The N cells together are designed as ‘generating system’ (GS). At the electrodes, the ionic current is converted into an electron current. The electrode system (ES) consists at least of four parts: (i) electrodes, (ii) anolyte and catholyte, (iii) outer membranes, and (iv) technical equipment for recirculating the electrode rinse solution. Eventually the electrode rinse solution (pH etc.) is controlled by an additional system.

In principle, the recirculation system of the electrode rinse solution can cause short-circuiting of the RED stack. However, if the resistance of this recirculation system is much higher than the internal resistance of the stack, this

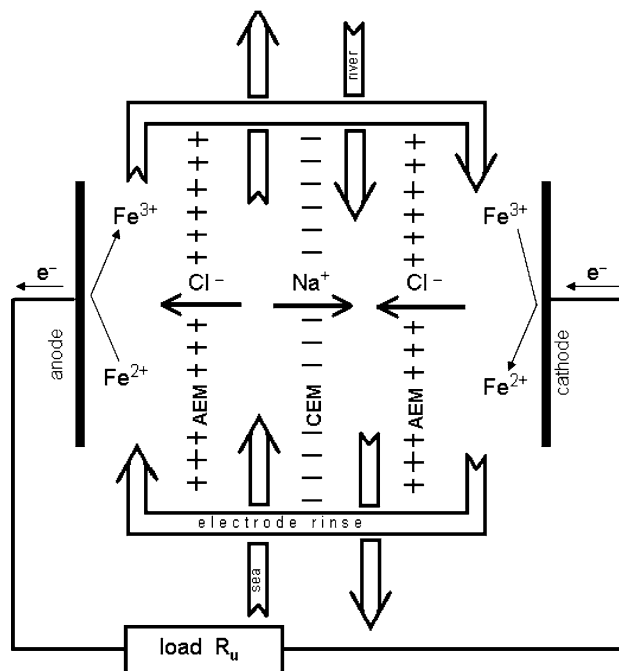


Fig. 1 A RED stack with only one cell

effect can be ignored. This can be done by applying relatively long tubes to the recirculating system.

The electrode system as shown in Fig. 1 is equipped with inert electrodes with a reversible redox couple containing $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions in a NaCl–HCl supporting electrolyte. The potential difference needed for reduction of Fe^{3+} to Fe^{2+} on the cathode is counterbalanced by the oxidation of Fe^{2+} to Fe^{3+} at the anode. Under zero current conditions, the total cell electromotive force (EMF) is obtained at the working electrodes. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is kept constant by recirculation the combined anolyte and catholyte through the electrode compartments. This type of redox system is called a homogeneous charge transfer reaction because all reactants are present in the same phase. In order to reduce the relative power loss of the electrode system, RED stacks should have a large number of cells.

In literature many electrode systems are described for RED. These systems are all used on laboratory scale and none of these systems has been evaluated for its practical applicability on a real scale. Many aspects of the electrode system are important for its operation: electrochemical reactions, energy consumption, transport through the membranes of the electrode system, reversibility etc. The objective of this paper is to compare these electrode systems for their suitability for RED. The evaluated systems include those already described in literature, but also contains electrode systems as used in supercapacitors, redox flow battery, electrodialysis and capacitive deionization, which might also be useful for RED.

2 Electrode systems for RED

2.1 Classical systems

To be fair to the pioneers of RED, it should be mentioned that their electrode systems were designed for laboratory use and were *not* developed for real applications. However, we have used their systems in our comparison because their solutions vary so widely.

2.1.1 Overview

Table 1 shows the different published electrode systems for RED. These electrode systems can be classified into two groups: with or without opposite electrode reactions. First, for systems with opposite electrode reactions and a recirculating electrode rinse, there is no net chemical reaction. These systems have a zero equilibrium voltage. A RED system with such an electrode system can generate electrical energy with only a few cells because there is no energy consumption for a net chemical reaction. Another advantage is that there is no loss of chemicals (except for transport through the outer membranes) and no gas production. Pattle [6, 7] used copper gauze electrodes in a CuSO_4 solution. On the cathode the dissolved Cu^{2+} was reduced to metallic copper and at the anode the copper was oxidized to Cu^{2+} . With a typical RED current density of 5 mA cm^{-2} this effect on the thickness of electrodes is about 2 mm per week. Jagur-Grodzinski and Kramer [12] and Audinos [13, 14] used zinc electrodes with a ZnSO_4 electrode rinse solution. In another experiment Audinos used Ag/AgCl electrodes in a NaCl solution [13, 14].

In all these processes the electrodes play an active role in the redox process: one electrode is growing and the other is dissolving. In such systems the feed waters should be interchanged periodically to invert the direction of the electrical current and with that the electrode processes. This imposes limitations on the stack design: the stack should be equipped with identical sea and river water compartments. A less attractive solution is to mechanically perform the periodical interchange of anode and cathode.

This reversal can be avoided by taking a homogeneous redox couple with inert electrodes. This may be platinumized titanium for both electrodes, special coated titanium for specific anode and cathode and carbon or steel for the cathode. Jagur-Grodzinski and Kramer used platinumized carbon electrodes in their so called ‘REF system’, a combination of a RED system and the electrode system of a fuel cell. At the anode water is oxidized to O_2 and at the cathode oxygen from air is reduced to water. Because the electrode solution contained NaCl , it is also possible that Cl_2 is evolved at the anode. Veerman et al. used a system with FeCl_2 and FeCl_3 in a NaCl bulk as described in Sect.

2.2.1, the system $\text{K}_4\text{Fe}(\text{CN})_6$ with $\text{K}_3\text{Fe}(\text{CN})_6$ in a NaCl bulk [1, 15] and also a H_2/Cl_2 generating system with only NaCl [10].

Second, the alternative for the systems with opposite electrode reactions are the systems with gas generation. The disadvantage of these systems is the loss of energy due to these reactions; a significant number of cells should be used to overcome the cell equilibrium voltage before electricity production is possible. On laboratory scale the problem can be solved by using a small number of cells together with an external power supply. The virtual RED voltage (the voltage without the losses at the electrodes) is obtained from a pair of reference electrodes in the electrode compartments near to the outer membranes. Weinstein and Leitz [16], Wick [17], Loeb [18], Metha [19] and Suda et al. [20] reported such systems. At the cathode hydrogen is evolved and at the anode chlorine is evolved if a NaCl solution (or sea water) is used in the electrode compartments. A possible succeeding reaction is hypochlorite and chlorate formation [21]. Turek et al. avoided the formation of chlorine by using an electrode rinse solution with Na_2SO_4 [22, 23]. In this case oxygen is generated at the anode.

2.1.2 Membranes of the described electrode systems

The sequence of the membranes in a RED stack is always alternating, but for the outer membranes—confining the electrode system—there are some requirements. The systems described in literature are given in Table 1. Some authors (Weinstein and Leitz [16] and Suda et al. [20]) used seawater in the electrode compartments and applied two different outer membranes, ensuring in this way an alternating system of sea and river water compartments. However, the generated Cl_2 and ClO^- are discharged into the sea water which is unacceptable from the viewpoint of safety, health and environment (SHE). Also the formation of Cl_2 requires the application of chlorine resistant outer membranes.

Another possibility is to use a closed electrode system. Veerman et al. [15] used a closed electrode rinse containing NaCl with CEMs as outer membranes. In this case the negative ClO^- is confined together with the Cl_2 in the electrode rinse. Although there is no direct discharge of these products to sea water, the problem of disposing these chemicals is not solved. Pattle [7] used a CuSO_4 solution and in Table 1 it is seen that the Cu^{2+} -ions are maintained in the electrode compartments by the outer AEMs. Although an AEM (with positively fixed charges) is slightly permeable for monovalent (positive) co-ions, the bivalent positively charged Cu^{2+} -ions are strongly excluded and Cu^{2+} -loss is expected to be relatively low but not to be negligible in terms of SHE. The SO_4^{2-} in the electrode

Table 1 Electrode systems described in literature

	anode	anolyte + bulk	repeating unit	catholyte + bulk	cathode	author	electrode reactions
described systems in literature							
1	Cu	CuSO ₄	\ddagger <u>S</u> \equiv <u>R</u> \ddagger ← → ← Cl ⁻ Na ⁺ Cl ⁻	CuSO ₄	Cu	<i>Pattle [5,6,7]</i>	cath.: Cu ²⁺ + 2e → Cu anode: Cu → Cu ²⁺ + 2e net: nil
2	metal	sea	\ddagger <u>S</u> \equiv <u>R</u> \ddagger ← → ← Na ⁺ Cl ⁻	sea	metal	<i>Weinstein/Leitz [16]</i>	cath.: 2 H ₂ O + 2e → H ₂ + 2OH ⁻ anode: 2 Cl ⁻ → Cl ₂ + 2e net: 2H ₂ O + 2 Cl ⁻ → H ₂ + 2OH ⁻ + Cl ₂
3	Ag/AgCl	NaCl	\ddagger <u>S</u> \equiv <u>R</u> \ddagger ← → ← Cl ⁻ Na ⁺ Cl ⁻	NaCl	Ag/AgCl	<i>Audinos [13,14]</i>	cath.: AgCl + e → Ag + Cl ⁻ anode: Ag + Cl ⁻ → AgCl + e net: nil
4	Zn	ZnCl ₂	\ddagger <u>S</u> \equiv <u>R</u> \ddagger ← → ← Cl ⁻ Na ⁺ Cl ⁻	ZnCl ₂	Zn	<i>Jagur-Grodzinski/Kramer [12]</i>	cath.: Zn ²⁺ + 2e → Zn anode: Zn → Zn ²⁺ + 2e net: nil
5	C/Pt	NaCl	\equiv R \ddagger <u>S</u> \equiv R \ddagger → ← → ← Na ⁺ Cl ⁻ Na ⁺ Cl ⁻	NaCl	C/Pt air	<i>Jagur-Grodzinski/Kramer [12]</i>	cath.: ½ O ₂ + 2H ⁺ + 2e → H ₂ O anode: H ₂ O → ½ O ₂ + 2H ⁺ + 2e and 2Cl ⁻ → Cl ₂ + 2e separated anolyte and catholyte
6	Ti/Pt	Na ₂ SO ₄	\equiv <u>R</u> \ddagger <u>S</u> \equiv → ← → Na ⁺ Cl ⁻ Na ⁺	Na ₂ SO ₄	Ti/Pt	<i>Turek [22, 23]</i>	cath.: 2H ₂ O + 2e → H ₂ + 2OH ⁻ anode: H ₂ O → ½ O ₂ + 2 H ⁺ + 2e net: H ₂ O + → 2 H ₂ + ½ O ₂
7	C	sea	\ddagger <u>S</u> \equiv <u>R</u> \ddagger ← → ← Na ⁺ Cl ⁻	sea	C	<i>Suda [20]</i>	cath.: 2 H ₂ O + 2e → H ₂ + 2OH ⁻ anode: 2Cl ⁻ → Cl ₂ + 2e net: 2H ₂ O + 2 Cl ⁻ → H ₂ + 2OH ⁻ + Cl ₂
used systems by author							
8	Ti/RuR	Fe ²⁺ /Fe ³⁺ NaCl / HCl	\ddagger <u>S</u> \equiv <u>R</u> \ddagger ← → ← Cl ⁻ Na ⁺ Cl ⁻	Fe ²⁺ /Fe ³⁺ NaCl / HCl	Ti/RuR	<i>Veerman et al. [this paper]</i>	cath.: Fe ³⁺ + e → Fe ²⁺ anode: Fe ²⁺ → Fe ³⁺ + e net: nil
9	Ti/RuR	Fe(CN) ₆ ³⁻ / Fe(CN) ₆ ⁴⁻ NaCl	\equiv <u>R</u> \ddagger <u>S</u> \equiv → ← → Na ⁺ Cl ⁻ Na ⁺	Fe(CN) ₆ ³⁻ / Fe(CN) ₆ ⁴⁻ NaCl	Ti/RuR	<i>Veerman et al. [1,15]</i>	cath.: Fe(CN) ₆ ³⁻ + e → Fe(CN) ₆ ⁴⁻ anode: Fe(CN) ₆ ⁴⁻ → Fe(CN) ₆ ³⁻ + e net: nil
10	Ti/RuR	NaCl	\equiv <u>R</u> \ddagger <u>S</u> \equiv → ← → Na ⁺ Cl ⁻ Na ⁺	NaCl Fe(CN) ₆ ⁴⁻ NaCl	Ti/RuR	<i>Veerman et al. [10]</i>	cath.: 2 H ₂ O + 2e → H ₂ + 2OH ⁻ anode: 2Cl ⁻ → Cl ₂ + 2e net: 2H ₂ O + 2 Cl ⁻ → H ₂ + 2OH ⁻ + Cl ₂
suggested systems							
11	graphite	Fe ²⁺ /Fe ³⁺ NaCl / HCl	\ddagger <u>S</u> \equiv <u>R</u> \ddagger ← → ← Cl ⁻ Na ⁺ Cl ⁻	Fe ²⁺ /Fe ³⁺ NaCl / HCl	graphite	<i>Veerman et al. [this paper]</i>	cath.: Fe ³⁺ + e → Fe ²⁺ anode: Fe ²⁺ → Fe ³⁺ + e net: nil
12	graphite	Fe(CN) ₆ ³⁻ / Fe(CN) ₆ ⁴⁻ NaCl	\equiv <u>R</u> \ddagger <u>S</u> \equiv → ← → Na ⁺ Cl ⁻ Na ⁺	Fe(CN) ₆ ³⁻ / Fe(CN) ₆ ⁴⁻ NaCl	graphite	<i>Veerman et al. [this paper]</i>	cath.: Fe(CN) ₆ ³⁻ + e → Fe(CN) ₆ ⁴⁻ anode: Fe(CN) ₆ ⁴⁻ → Fe(CN) ₆ ³⁻ + e net: nil

| is the anode, | cathode, \equiv cation exchange membrane and \ddagger anion exchange membrane. The repeating unit is underlined. S stands for sea water and R for river water. Direction of the ions through the membranes is designated by arrows

system will be exchanged rapidly for Cl^- from the sea water. This exchange has no effect on the functioning of the system as long as the Cu^{2+} ions stay in the electrode compartments.

Jagur-Grodzinski and Kramer [12] also used active metal electrodes (zinc) but their design was improved by taking Cl^- as anion. Turek and Bandura [22] described a system with a Na_2SO_4 electrode rinse in combination with anion exchange outer membranes, evolving H_2 at the cathode and in first instance O_2 at the anode. In such systems the SO_4^{2-} can be exchanged for Cl^- . This can cause generation of Cl_2 because after some time there is enough Cl^- in the electrode rinse solution ($>5 \text{ g l}^{-1}$) to generate Cl_2 .

We conclude: if there is a closed electrode rinse loop, it is possible to contain only one type of ion (anion or cation) in the combined electrode compartments. In this case, the outer membranes should be of the same kind (both AEM or both CEM) and the ionic charge transport between the water compartments to the electrode rinse solution is done respectively by Cl^- or by Na^+ .

2.2 Self-developed systems

In our laboratory, we used three different electrode rinse solutions, always with the same DSA (dimensionally stable anode) type electrodes: titanium mesh electrodes, coated with Ru–Ir mixed metal oxides. These electrodes are suitable as anode as well as cathode and therefore current reversal is allowed. The first electrode rinse solution was unpractical for laboratory use; the other two are described in the different articles on RED performance [1, 10, 15].

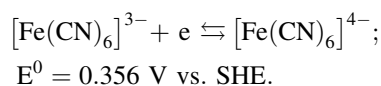
2.2.1 $\text{Fe}^{2+}/\text{Fe}^{3+}$ in NaCl-HCl

In order to avoid the large overvoltages of gas generating systems, we first used the system $\text{Fe}^{2+}/\text{Fe}^{3+}$ in a NaCl bulk together with the mentioned inert electrodes. For an electrode rinse containing FeCl_2 (0.05 mol l^{-1}), FeCl_3 (0.05 mol l^{-1}) and NaCl (0.5 mol l^{-1}), the resulting pH was 2.4. The disadvantage of this system is that O_2 oxidizes Fe^{2+} to Fe^{3+} and H^+ diffuses through the outer membranes, both causing an increase of the pH. After prolonged use, the electrode rinse solution obtained a red brownish color which can be explained by the formation of iron(III) oxyhydroxides. Oxidation can be prevented by means of an airtight system and the formation of insoluble salts can be avoided by controlling the pH to a low value (<2.3) by the addition of HCl . However, buffering with HCl is difficult because anion exchange membranes are somewhat permeable for H^+ and a constant supply of HCl is necessary. In this way the pH of the effluent decreases that which is unacceptable from an environmental viewpoint. A possible solution is the use of an external

electrodialysis system with bipolar membranes, generating NaOH as well as HCl . The NaOH can be directed to the output stream and the HCl to the electrolyte. This process is pH neutral and there are no environmental implications. An internal electrodialysis system with bipolar membranes (built in the RED stack) for the same purpose is patented by Hamelers et al. [24].

2.2.2 $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in NaCl

For the development and testing of RED systems in the laboratory the $\text{Fe}^{2+}/\text{Fe}^{3+}$ appeared to be rather unpractical. Therefore, we changed to a quite stable system: the iron hexacyanoferrate system:



This system is described in former articles [1, 15]. Again, the inert electrodes were used as described in Sect. 2.2. To prevent loss of the iron complex we used CEMs as outer membranes. As long as the electrolyte is not in contact with the AEMs, there are no problems to be expected. However, in case of internal leakages, hexanoferrate ions may poison the AEMs in the stack by irreversible binding, eventually resulting in a decreased performance [25].

2.2.3 NaCl

To prevent the poisoning of the membranes, we changed to a pure NaCl solution in the electrode compartments. With this system, we characterized some membrane pairs for the use in RED stacks [10]. By applying CEMs as outer membranes, the generated Cl_2 and OCl^- was kept within the electrode system.

2.3 Proposal for a novel system: $\text{Fe}^{2+}/\text{Fe}^{3+}$ in NaCl-HCl with graphite electrodes

The formerly used DSA type electrodes (as described in Sect. 2.2) are designed for gas generation with low overvoltages. However, in our electrode systems with a reversible redox couple (the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system and the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ system) gas evolution is undesirable.

Therefore, we suggest the use of graphite electrodes in these systems. Graphite electrodes have been extensively studied for use in redox flow batteries. One of these energy storage systems—the Fe/Cr system—uses the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple in the positive half-cell at low pH. It appears that this system is well reversible in electrochemical sense [26]. Graphite felt is tested until current densities of 700 mA cm^{-2} [27] whereas the optimal current density at

RED is much lower; Veerman et al. reported 4 mA cm^{-2} for their experiments whereas an improvement with a factor 5 is expected in the future with high performance membranes and spacers [1].

Advantages of carbon electrodes to Ti/Ru/Ir electrodes are:

- No use of exhaustible precious metals.
- High overpotentials for gas formation.

There is no risk of evolution of dangerous and aggressive gasses (H_2 , O_2 and Cl_2). Even with a reversible redox couple this may be the case if the flow of the electrode rinse solution is obstructed locally.

A disadvantage of graphite may be the lower mechanical stability with respect to DSA-type electrodes during longer operation times and the need for a proper current collecting system. Therefore, graphite electrodes may be advantageous for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system as well as for the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ system. We added such systems to Table 3 (column 11 and 12). The rather good end scores encourages further research on these systems.

2.4 Symmetry in RED stacks

If the sea and river water inlets of a RED stack are interchanged, the polarity of the generated voltage is reversed. Consequently, the performance of the RED stack is unaltered if the generating system (GS) and the electrode system (ES) are both symmetrical. It is evident that the symmetrical properties of GS and ES are related.

2.4.1 Reversal of the electrical current

For some electrode systems periodical reversal is obligatory as for systems with participating (one dissolving and one growing) electrodes. These electrode systems are designated as ‘obligatory reversal’ or ES_1 . Other systems consist of ‘universal’ electrodes where reversal is possible but not obligatory and are called ‘facultative reversal’ or ES_2 . A third case consists of the specific electrodes that are only suitable as cathode or as anode and in which reversal of the electrical current is not possible. These are denoted as *forbidden interchange* or ES_3 .

2.4.2 Interchange of the feed water in RED stacks

Just as with the electrode system, we distinguish for the generating system between three types:

GS₁: obligatory interchange

In RED, growth of microorganisms in the stacks may be a serious problem. One approach to prevent this, is the periodical interchange of the river and sea water inputs. A comparable method is used for normal electro dialysis for

desalination purposes and is called ‘electrodialysis reversal’ (EDR) [28, 29]. From experiments in the future, it may be proven that such a procedure is necessary and we denote this system as ‘obligatory interchange’ or as GS_1 .

GS₂: facultative interchange

If it should be proved that feed water interchange is not beneficial for prevention of microbial growth or for breaking down polarization layers, then this interchange is not obligatory. If, besides that, the GS is symmetrical (with identical sea and river water compartments), the interchange of sea and river water is also not forbidden. In this case we have a ‘facultative interchange’ system or GS_2 .

GS₃: forbidden interchange

Bottlenecks in stack design for RED are the hydrodynamical fluid resistance in all compartments and electrical resistance in river water compartments [1]. Optimization can lead to an asymmetric stack: sea water compartments may be thicker than river water compartments to reduce hydrostatic resistance without affecting electrical resistance substantially; also length and width can differ. In such a stack interchanging sea and river water is possible for cleaning purposes but during this interchange the power production is low. We call this a ‘forbidden interchange’ system GS_3 ; although the adjective forbidden should not to be interpreted strictly.

2.5 Voltage losses in electrode systems

Electrode systems introduce a voltage loss in the RED system due to an overpotential, concentration polarization, an ohmic potential and a Nernst potential in each electrode compartment. In RED, current densities are relatively low (in our own experiments about 4 mA cm^{-2} [1]) and the losses due to concentration polarization and the ohmic potential are minimal. This is a general property of all studied electrode systems for RED. Further, with respect to voltage losses, these systems can be divided in low, high and medium loss electrode systems.

Low loss In systems with opposite electrode reactions and a recirculating electrode rinse, there is no net chemical reaction and the Nernst voltages on both electrodes cancel each other. In most of these systems no gas reactions are involved and the overpotentials are low. The total voltage loss in the whole electrode system is about 0.1 V; which is comparable to the generated voltage of 1-2 cells.

High loss Electrode systems with gas evolution have higher voltage losses. For the electrolyses of water, the needed voltage based on the Nernst equation is 1.23 V, and the overpotentials are 0.03 V for H_2 and 0.52 V for O_2 evolution at a current density of 10 mA cm^{-2} [30], together 1.78 V. Because the typical cell voltage is about 60 mV under power generating circumstances, a number of 30 cells is used to overcome the voltage loss of this electrode system.

Medium loss A special case is the so called ‘REF system’ of Jagur-Grodzinski and Kramer [12] (system 5 in Table 1). At the anode O₂ is evolved and at the cathode O₂ is consumed, so there is no net generation of O₂. Because there are separated anode and cathode compartments, the net reactions is: H₂O → H⁺ + OH⁻. This water dissociation in ions consumes about 15 kJ mol⁻¹ [31], much lower than the 286 kJ mol⁻¹ as necessary for splitting of water in H₂ and O₂ [32]. Therefore, this system is classified in the category ‘medium loss’.

It should be noted that electrode losses are only important in stacks with a small number of cells as in laboratory equipments. In a stack with 1000 cells the loss of a high loss system is only 3%. High loss systems are assessed with minus 1 point with respect to low loss systems (Sect. 3.2.1.5 and Appendix A₅).

3 Criteria for electrode systems

3.1 Method of assessment

In the assessment of electrode systems, all relevant aspects concerning safety, health, environment (SHE), technical feasibility and economics are taken into account. In total 13 of these aspects were considered. A judgment in a scale from 0 (unacceptable) to 5 (good) is given. Because a commercial RED power plant was never built so far, there is no experience with the different systems under real economical power producing circumstances. Nine different electrode systems for RED are described in literature. To rank the quality of different systems, there are a large number of methods. Data envelopment analysis (DEA) is a powerful method, especially because the different weight factors are determined by the method itself. However, the consequence is that the method is only applicable if the number of systems is larger than the number of the aspects [33, 34] and that is not the case in our current topic.

Often a much more simple system is used: the end result is calculated as the arithmetic mean of the different marks. However, to prevent compensation of bad marks by other good aspects, we achieved the total rating by calculating the geometric mean *A* of all (*n*) parts *A_i*. Each aspect *A_i* is judged with a mark in the range from 0 (unacceptable) to 5 (good).

$$A = \left(\prod_{i=1}^n A_i \right)^{\frac{1}{n}} \tag{1}$$

In fact, the geometric mean is closely related to the logarithmic mean with the difference that the first method can cope with zeros and the second method cannot. The advantages of this way of ranking are: (i) unacceptable

systems are mentioned (judged as 0 on a single criterion) but always remain at the lowest level of the ranking, (ii) there is no need for ambiguous weight factors (iii) very different variables can be used for different items; even nominal and ordinal data can used together (iv) masking bad properties by averaging with good properties hardly occurs.

For most items, the generating system (*N* cells of the stack) is independent of the electrode system: each generating system can be combined with each electrode system. An important exception to this rule is the aspect of feed water interchange as discussed in Sect. 3.2.1.1. This aspect requires a separate ranking system for stacks with obligatory, facultative and forbidden river and sea water interchange.

3.2 Assessed aspects

In this paragraph, different aspects are summarized. Applied criteria are included in the appendix. Aspects are classified in three groups: (i) technical feasibility (5 aspects), (ii) safety, health and environment (SHE; 5 aspects) and (iii) economics (3 aspects). A larger number of aspects in a group make this group more important in the end score. Sometimes the classification is rather arbitrary.

3.2.1 Technical feasibility

3.2.1.1 Reversal of the electrical current/interchange of the feed water Discussed in Sect. 2.4 are three types of electrode systems and three types of generating systems. Interchange of the feed water of a GS has consequences for the electrode system: by the reversal of the direction of the electrical current the anode becomes cathode and vice versa. Table 2 shows the scores of the different combinations. All combinations are permitted except GS₃-ES₁.

The combination GS₁-ES₃ is not strictly forbidden because the following reason. Most modern electrodes are designed specifically as cathode or as anode. Cathodes can be made of different materials like stainless steel and graphite; however, the requirements for anodes are much higher than for cathodes. Special mixed metal oxide electrodes based on thin layers of precious metals on titanium can act both as anode and as cathode but their lifetime is

Table 2 Marking the different combinations of generating systems with electrode systems

	Reversal of the electrical current		
	ES ₁ : obligatory	ES ₂ : facultative	ES ₃ : forbidden
Interchange of the water inlets			
GS ₁ : obligatory	4	5	1
GS ₂ : facultative	5	5	5
GS ₃ : forbidden	0	5	5

severely lowered if current reversal is applied [35, 36]. In some patents for electrodialysis (ED), systems are described with composite electrodes [37–39]. These electrodes consist of an alternate array of strips of anode and cathode material. The power supply can be connected to the proper array on each side, dependent on the electrical current direction. In this way each used electrode material, as used in normal ED, can also be used also in the EDR mode, an ED method where the current is reversed periodically to prevent scaling on the membranes. Composite electrodes can be used in principle also for RED to cope with current reversal due to interchange of sea water and river water. Therefore, this ‘forbidden’ combination GS₁–ES₃ is judged with 1 point.

The combination GS₁–ES₁ is not definitely ideal because the GS and the ES may demand different switch frequencies and therefore, only 4 points are noted.

3.2.1.2 Stability of anolyte/catholyte Most anolytes/catholytes as listed in Table 1, contain only stable inorganic ions. The exception is the electrolyte with the hexacyanoferrate redox system. The complex ions in this solution are able to decompose and to form stable insoluble complexes with many multivalent metal ions with the risk of poisoning the membranes.

3.2.1.3 Gas formation at the electrodes Gas formation (Cl₂ and O₂ at the anode and H₂ at the cathode) can cause problems at the electrodes (electrical obstruction) and Cl₂ is highly corrosive. Besides this, Cl₂ formation has a negative environmental value (again called in aspect B₃) and H₂ is an explosion hazard (again called in aspect B₁).

3.2.1.4 Participating electrodes Participating electrodes are already counted at the reversal item. However, dissolving and plating (growing) should be reversible many thousand times. For example, it is known that Zn in this way is a difficult metal and special provisions should be taken with the electrode rinse.

3.2.1.5 Electrical properties of the electrode system

Voltage loss

As stated in Sect. 2.5, electrode systems can cause low, medium or high losses. If at both electrodes opposite electrochemical reactions occur in the same electrolyte, the voltage loss is low; otherwise this loss is high. For a large stack, this voltage loss is a minor problem.

Resistance of the electrode system

Electrodes are normally made from good conducting materials. An exception is the Ag/AgCl electrode with a thick AgCl layer where the Ag⁺ has to diffuse from the solution to the Ag surface. This system was described by Audinos [16, 17] and included as system nr. 3 in Table 1.

3.2.2 Safety, health and environment

3.2.2.1 Safety H₂ is explosive and especially dangerous in closed spaces as sea containers or units for underwater operation.

3.2.2.2 Health Toxicity is judged in case of skin and eye contact, swallowing and inhalation. Especially organic redox couples like hydroquinone/1,4-benzoquinone can be a risk if in contact with the skin. The same holds true for acidified solutions of the couple Fe²⁺/Fe³⁺. Nearly all electrolytes are toxic if swallowed except NaCl solutions. The most probable danger of inhalation is Cl₂; HCN can be evolved under extreme conditions (low pH, UV-light) from the [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ couple.

3.2.2.3 Environment: normal exhaust of Cl₂, ClO⁻ and ClO₃⁻

If sea water or NaCl is used in the electrode system without a reversible redox couple, Cl₂ can be evolved at the anode and H₂ at the cathode. If anolyte and catholyte are combined, ClO⁻ is formed and there is the possibility of formation of ClO₃⁻ [21]. Sometimes these products are useful (e.g. as biocide) but mostly they are unwanted. To prevent contamination of the outlet streams with ClO⁻ and ClO₃⁻, the outer membranes should be of the CEM type. However, due to the non ideal behavior of these membranes, there is also a small transport of these anions into the effluent. If other ‘safe’ salts (Na₂SO₄, NaNO₃ etc.) are used in the electrode rinse solution, there is still the danger of Cl₂ evolution because Cl⁻ can diffuse from the sea water compartment to the electrode compartment through the CEM.

Even in the presence of a redox couple, Cl₂ formation is not excluded totally if Cl⁻ is present in the electrode rinse solution because the redox couple can be exhausted locally due to obstructions in the flow path in the electrode compartment.

If seawater is used as electrolyte, there is the possibility of a closed electrode rinse loop or an open single pass system. The last system is unacceptable from environmental viewpoint due to the discharge of Cl₂.

3.2.2.4 Environment: normal exhaust other chemicals

In principle, ions can be blocked by a proper choice of the outer membranes although blocking of co-ions is not 100%. Especially protons can easily pass the most types of AEMs. Technically, the problems of transport from unwanted species from the electrode compartments to the sea or river water compartments and vice versa can be solved by using double outer membranes. Between these outer membranes a guard electrolyte is recirculated. Disadvantageous is the need of conditioning this guard electrolyte.

3.2.2.5 Environment: accidentally exhaust Loss of anolyte/catholyte may occur by accident: rupture of the outer membranes, human errors and defects in the electrode rinse pumping system are possible causes. The effects of outer membrane damaging can be decreased by using double outer membranes as described above under B_4 . Defects in the electrode rinse system can be controlled by leakage tanks. Moreover, a RED installation is built modular and in event of an accident only a small part of the electrolyte is drained.

3.2.3 Economics

3.2.3.1 Special provisions for the anolyte/catholyte

The most frequent measures to be taken are:

a pH control

At low pH, H^+ can diffuse easily through AEMs to the output stream and new H^+ should be added to the electrolyte. This can be achieved by adding HCl; an environmentally better way is the use an external electro dialysis system with bipolar membranes generating NaOH and HCl. The NaOH can be directed in the output stream and the HCl to the electrolyte. This process is pH neutral.

b Redox control

In redox systems as Fe^{2+}/Fe^{3+} , the optimal Fe^{2+}/Fe^{3+} ratio is about unity. However, by oxidation by air this ratio may be affected. An airtight system should be used and/or a reduction system should be incorporated.

c Concentration control

In fact, each anolyte/catholyte should be controlled, especially electrolytes containing monovalents ions like NO_3^- which can be exchanged rapidly with Cl^- from the sea water.

3.2.3.2 Price of the electrodes Inert electrodes can be made of massive platinum, sometimes with added ruthenium or iridium for mechanical strength. Such electrodes are used in laboratories as measuring electrode or as working electrode in different analytical processes. These electrodes are very expensive and efforts have been made to platinize other metals or carbon in such a way that the inert properties of platinum are combined with the economics of other metals. This resulted in platinum coated titanium with 20–50 g platinum per square meter. These electrodes are rather expensive and not catalytic enough for gas evolving processes. The next step was the invention of the so called ‘dimensional stable electrode’ (DSA) for the chlor-alkali membrane process [40].

Modern stable electrodes consist of a metal support (mostly titanium) with a mixed metal oxide (MMO) layer [41]. The MMO consist of two components: one is a catalytic and conducting (e.g. RuO_2 , IrO_2 , $PtO_{0.12}$), the other is inert and nonconducting (e.g. TiO_2). The catalytic part of

the electrode cover is developed for special electrochemical purposes like Cl_2 or O_2 evolution. On these electrodes the amount of precious metal is only 10–12 $g\ m^{-2}$. Moreover the price of iridium and especially of ruthenium is much lower than of platinum. This may result in acceptable prizes.

A further reduction of electrode price can be achieved by using partial electrodes: electrodes with a reduced surface by a proper dimensioning of a stretched metal process. In RED, partial electrodes can be used because the current density in the RED process is much lower than in other electrochemical processes for which these electrodes are developed.

Graphite electrodes are rather inexpensive. However, at larger surfaces, current collection may be a problem and results in a higher price.

3.2.3.3 Lifetime of the electrodes Marks for the aspects of price (C_2) and lifetime (C_3) are generally opposite. In our used criteria (Appendix) all DSA type electrodes get the same judgment (mark = 5). The actual lifetime of these electrodes is dependent on current direction (anodic or cathodic use), electrolyte and current density. Fields of application of electrodes with long erasing time are water desalination with electro dialysis (ED) and the chlor-alkali process. In normal ED for desalination, a 5-year life of a platinum plated electrode is normal. Anode life was generally less than cathode life [42]. In fact all modern electrodes are MMO covered on titanium (DSA type). For chlorine evolving DSAs, as used in the chlor-alkali industry, typical current densities are more then 300 $mA\ cm^{-2}$ in the membrane cell process [43]. In this case the lifetime of DSAs is guaranteed to be up to 10 years [44]. In contrast, optimal current densities in our RED process were 4 $mA\ cm^{-2}$ or possibly 20 $mA\ cm^{-2}$ in the future with improved systems [1]. Therefore, life time of chlorine evolving DSAs may be expected to be much more than 10 years for RED. For oxygen evolution, Chen and Chen [45] predicted for their $Ti/RuO_2-Sb_2O_5-SnO_2$ electrode a life time of 8.3 years at a current density of 20 $mA\ cm^{-2}$ and even 27 years at 10 $mA\ cm^{-2}$. These lifetimes are also an indication for use in RED electrode systems. The foregoing refers to unidirectional use of the electrodes. Current reversal (as in EDR) generally decreases electrode lifetime substantially [42, 46].

4 Discussion

4.1 Described electrode systems

Described electrode systems in literature for RED are not yet suitable for use in economical operated RED systems.

A RED system should fulfill the requirements on safety, health, environment, technical feasibility and economics. In Table 3 the formulated criteria are applied to the different described electrode systems from Table 1 (for GS_1 in bold, for GS_2 regular and for GS_3 in italics). The row ‘reversal to the electrical current’ (A_1) is split up in three parts for the combination of the different generating systems with the electrode system in question. The same goes for the rows with the end-scores and ranks.

Table 3 shows that from the described used systems (column 1–10), the iron system with Ti/Ru, Ir electrodes (column 8) is the best system in combination with each of the three generating systems.

The hexacyanoferrate system with the same electrodes (column 9) may be useful in laboratory equipment. The table also indicates that by application of graphite electrodes the score of these systems is approached (column 11 and 12).

4.2 Proposal for improved electrode systems

Possible improvements are:

a Use of graphite electrodes

As indicated in Sects. 2.3 and 4.1, the use of graphite electrodes in combination with homogeneous redox system like Fe^{2+}/Fe^{3+} has good prospects.

b Improved electrodes of the DSA type

– *Longer lifetime*

For their experiments Veerman et al. [1, 11, 15] used titanium mesh end electrodes, coated with Ru–Ir mixed metal oxides. These electrodes are reversible (i.e. current reversal is possible) and therefore usable for all types of stacks. Lifetime of these electrodes is more than 10 years under the applied current density (4 mA cm^{-2}). An improvement of the lifetime with a factor 5 can be achieved with special Ir–MMO (mixed metal oxide) coated titanium anodes and Ru–MMO coated cathodes; another option is to use the extra stability of these electrodes for reducing the cost of these electrodes by decreasing the surface of the electrodes (the so called partial electrodes). A limitation of this system is that frequent current reversal during longer times is not possible with these electrodes.

– *High overvoltages for Cl_2/O_2 evolution*

The success of DSA type electrodes is due to a combination of high mechanical and electrochemical stability with good catalytic properties and low overvoltages for special electrode reactions. Especially such anodes are developed for Cl_2 and O_2 generation. However, in a RED process with a homogeneous redox couple (e.g. the Fe^{2+}/Fe^{3+} or the system $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$), these reactions are unwanted. Therefore, high overvoltages for gas

evolution are favorable to the process. It requires some extra development to realize this with DSA type electrodes.

– *Specific composite electrodes for RED*

For use in normal electro dialysis some systems with composite electrodes are patented [37–39]. These systems allow current reversal with electrodes which are specifically usable as cathode or anode. In each current direction only one part of each electrode is used. Eventually the unused part can be protected with a low potential difference between this part and the adjacent part in operation.

c New homogeneous redox couple

Homogeneous redox systems (e.g. the system $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$) do not cause net chemical reactions and therefore the power losses are low. Most organic homogeneous redox couples involve protons in their reactions and special measures should be taken to control the pH. However, there are many iron complexes and possibly candidates are available that satisfy all mentioned criteria. The use of graphite electrodes may be considered again in this case.

d Capacitive electrodes

The last decades, special high ion absorbing carbon has been developed for use in super capacitors [47–50] and in capacitive deionization (CDI) [51, 52]. If this material is used as electrode in a RED stack, during a certain time an internal ionic current can persist. The electrodes behave as a capacitor and during that time there is also an external electrical current. After some time, the process should be inverted by changing the sea water and the river water feed. It is obvious that the changing time is related to the residence time in the system. Assuming that time to be 1 min, then a half period (the time between two feed interchanges) should be at least about 60 min. Current RED stacks operate at maximum power output with a current density of about 4 mA cm^{-2} or $144,000 \text{ C m}^{-2} \text{ h}^{-1}$. The cathode should adsorb then $144,000/F = 1.5 \text{ mol Na}^+$ and on the anode the same amount of Cl^- (F is the Faraday constant; $1 F = 96,485 \text{ C mol}^{-1}$).

Typical specific capacitances are reported of 100–200 $F \text{ g}^{-1}$ carbon in aqueous solution [47–50]. Using the highest value of 200 F g^{-1} , for an uploading to 1 V, there is 200 F g^{-1} carbon needed. For a 1-h operation, the electrodes should consist of $720 \text{ g carbon per m}^2$. This seems a realistic value for further development of such a system.

In principle, the method is very clean and sustainable. Carbon aerogel electrodes may have lifetimes of more than 10 years [53]. A restriction of this system is the obligatory interchange. For optimal performance, the connected load should be adapted continuously during one cycle. This is possible with modern DC–DC converters. For normal electro dialysis, such a system is patented by Wei et al. [54].

Table 3 Ranking the systems described in literature for practical use

	Described systems in literature												Used systems by author						Suggested systems				
	1	2	3	4	5	6	7	8	9	10	11	12	8	9	10	11	12	8	9	10	11	12	
Anolyte/catholyte:	Pattle	Weinstein	Audinos	Jagur-G	Jagur-G	Turek	Suda	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman	Veerman
Bulk	CuSO ₄	NaCl	NaCl	ZnCl ₂	NaCl	Na ₂ SO ₄	NaCl	NaCl-HCl	HCF ^b	NaCl	NaCl-HCl	NaCl	NaCl-HCl	HCF ^b	NaCl	NaCl-HCl	NaCl	NaCl-HCl	HCF ^b	NaCl	NaCl-HCl	NaCl	
Cathode:	Cu	Ti/Pt ^a	Ag/AgCl	Zn	C/Pt/O ₂	Ti/Pt	C	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Pt	C	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	
Anode:	Cu	Ti/Pt ^a	Ag/AgCl	Zn	C/Pt	Ti/Pt	C	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Pt	C	C	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	Ti/Ru, Ir	
Type:	ES1	ES2	ES1	ES1	ES3	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	ES2	
Technical feasibility	GS ₁	A ₁ Reversal of the el. current	4	5	4	4	4	5	5	1	5	5	5	5	5	5	5	5	5	5	5	5	
	GS ₂	A ₁ Reversal of the el. current	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
	GS ₃	A ₁ Reversal of the el. current	0	5	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
	All	A ₂ Stability of anolyte/catholyte	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
	All	A ₃ Gas formation	5	2	5	5	5	4	4	4	4	2	5	5	2	5	5	5	5	5	5	5	
	All	A ₄ Participating electrodes	4	5	3	2	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
	All	A ₅ Electrical properties	5	4	4	5	3	3	4	4	4	4	5	5	4	5	5	5	5	5	5	5	
Safety, health and environment (SHE)	All	B ₁ Hydrogen formation	5	3	5	5	5	5	5	5	3	3	3	5	5	3	5	5	5	5	5	5	
	All	B ₂ Toxicity	4	3	5	4	4	3	3	5	5	3	4	4	4	3	4	4	4	4	4	4	
	All	B ₃ Normal exhaust of Cl ₂ etc.	5	0	5	5	5	4	4	4	4	0	5	5	5	5	5	5	5	5	5	5	
	All	B ₄ Normal exhaust other chem.	4	5	4	4	4	5	5	5	5	5	4	4	4	5	4	4	4	4	4	4	
	All	B ₅ Accidentally exhaust	3	5	5	4	4	5	5	5	5	5	4	4	3	5	4	4	4	4	4	4	
Economics	All	C ₁ Special provisions	4	3	4	4	4	2	4	2	4	3	3	4	4	3	3	4	4	4	4	4	
	All	C ₂ Price of the electrodes	5	1	2	5	5	1	1	1	1	5	4	4	4	4	3	4	4	4	3	3	
	All	C ₃ Life time of the electrodes	2	4	2	2	2	4	4	4	4	2	5	5	5	5	3	5	5	5	3	3	
	GS ₁	Score	4.1	0.0	3.9	4.0	4.0	3.2	3.9	3.2	3.9	0.0	4.5	4.3	3.5	4.2	4.2	4.3	3.5	4.2	4.2	4.1	
		Rank	4	11	7	6	6	10	7	10	7	11	1	2	9	3	3	2	9	3	3	5	
	GS ₂	Score	4.2	0.0	4.0	4.1	4.1	3.6	3.9	3.6	3.9	0.0	4.5	4.3	3.5	4.2	4.2	4.3	3.5	4.2	4.2	4.1	
		Rank	4	11	7	6	6	9	8	9	8	11	1	2	10	3	3	2	10	3	3	5	
	GS ₃	Score	0.0	0.0	0.0	0.0	0.0	3.6	3.9	3.6	3.9	0.0	4.5	4.3	3.5	4.2	4.2	4.3	3.5	4.2	4.2	4.1	
		Rank	8	8	8	8	8	6	5	6	5	8	1	2	7	3	3	2	7	3	3	4	

The marks in the rows A1 are dependent on the generating system (GS₁, GS₂ or GS₃). The same holds for the score/rank rows at the bottom

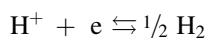
^a Ti/Pt assumed

^b HCF hexacyanoferrate = Fe(CN)₆³⁻/Fe(CN)₆⁴⁻

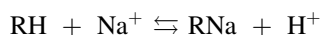
Brogioli succeeded in the *reversal of the capacitive deionization* (CD) technique [55]. The capacitor is formed by two activated carbon electrodes, immersed in the feed solution, alternately salt and fresh water. When filled with salt water, it is charged, and with fresh water it is discharged. Charging and discharging are promoted by the diffusion of ions and consequently there is a net energy gain.

e Systems with an electrode rinse solution containing carbon particles and/or ion exchange resin particles

These systems are described by Kedem et al. for use in normal electrodialysis and patented [56, 57]. The electrode rinse solution contains about 1% active carbon and 1% cation exchange resin in a NaCl solution of about 2%. The authors suggest that this system is based on the reversible system

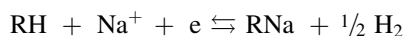


The H_2 gas, as evolved at the cathode is adsorbed by the carbon and transported to the anode where the reverse reaction proceeds. The involved H^+ is transported by the ion exchange resin:



where RH is the resin in the acid form and RNa the resin in the salt form.

The net reaction at the cathode and at the anode is therefore:



5 Conclusions

In this work, self-developed electrode systems and electrode systems described in literature are compared on safety, health, environment, technical feasibility and economics. A robust system of judging the different systems is presented. Applying this system to the described and used systems, a ranking was made of the different electrode systems. It is shown that the applicability of an electrode system is related to the generating system. Three types of generating systems can be distinguished: systems with (i) obligatory, (ii) facultative and (iii) forbidden interchange of the feed water inlets. The highest rankings for all the three generating systems are found for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple in a NaCl–HCl supporting electrolyte with bidirectional Ru/Ir covered titanium electrodes.

This system is not ideal and may be improved for application in commercial operating, large scale RED. There are five interesting topics: (i) improved stable metal electrodes (with longer lifetime, suitable for current reversal and high overpotential for gas evolution), (ii) a new homogeneous redox couple (e.g. an iron complex),

(iii) a system with capacitive electrodes, (iv) a system with an electrolyte, containing carbon particles and/or ion exchange resin particles, and (v) the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple in combination with graphite electrodes. The last improvement seems to be the most realistic alternative; however, duration test should be performed under real RED conditions to prove that it has sufficient mechanical and electrochemical stability.

Acknowledgement This work was performed in the TTIW-cooperation framework of Wetsus, centre of excellence for sustainable water technology (www.wetusus.nl). Wetsus is funded by the Dutch Ministry of Economic Affairs, the European Union Regional Development Fund, the province of Fryslân, the city of Leeuwarden and the EZ/Kompas program of the “Samenwerkingsverband Noord-Nederland”. The first author would like to thank the Noordelijke Hogeschool Leeuwarden who facilitated this research by detaching him to Wetsus and the participants of the theme “Energy” for their fruitful discussions and their financial support.

Open Access This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

Appendix

Applied criteria.

The used marks are: good = 5; reasonable = 4; acceptable = 3; poor = 2; bad = 1 and unacceptable = 0. In some cases minus signs are used. These mean that their value should be subtracted from the maximal score of 5.

A Technical feasibility

A₁ Reversal of the electrical current

score: Already given in Table 2

A₂ Stability of the anolyte/catholyte

Score	
No instable ions	5
$[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$	4

A₃ Gas formation at the electrodes

Score	
No gas	5
O_2 formation	–1
Cl_2 formation	–2
H_2 formation	–1

A₄ Participating electrodes

Score	
No participating electrodes	5
Participating without problems (Cu)	4

Appendix continued

Participating with minor problems (Ag/AgCl)	3
Participating with more severe problems (Zn)	2
Participating with severe problems	0

A₅ Electrical properties of the electrode system

Score	
No problems	5
Net chemical reaction	-1
High overvoltage	-1
Slow redox couple	-1
High electrode resistance	-1

*B Safety, health and environment**B₁ Hydrogen formation at the cathode*

Score	
No gas formation	5
H ₂ formation	3

B₂ Toxicity

Score	
No danger	5
Skin danger	-1
Swallowing danger	-1
Inhalation danger	-2

B₃ Environment: normal exhaust of Cl₂, ClO⁻ and ClO₃⁻

Score	
No Cl ₂ generation	5
Minor Cl ₂ production in closed circuit	4
Major Cl ₂ production in closed circuit	1
Minor Cl ₂ production in open system	1
Major Cl ₂ production in open system	0

B₄ Environment: normal exhaust other chemicals

Score	
No emission	5
Low emission	4
Above emission norm	0

B₅ Environment: accidentally exhaust

Score	
Na ⁺ , Cl ⁻ , HCO ₃ ⁻ , Mg ²⁺ , Ca ²⁺	5
Zn ²⁺ , Fe ²⁺ , Fe ³⁺	4
[Fe(CN) ₆] ⁴⁻ , [Fe(CN) ₆] ³⁻ , Cu ²⁺	3

Appendix continued

Quinone, pyrocatechol, hydroquinone etc.	2
--	---

*C Economics**C₁ Special provisions for the anolyte/catholyte*

Score	
No provisions	5
pH control	-1
Concentration control	-1
Air supply	-1
Cl ₂ , ClO ⁻ and ClO ₃ ⁻ discharge	-2

C₂ Price of the electrodes

Score	
Ti, C, Zn, Cu	5
DSA type	4
Graphite	3
Ag	2
Platinized Ti or C	1

C₃ Lifetime of the electrodes

Score	
DSA type	5
Platinized Ti or C	4
Graphite	3
Participating electrodes, carbon	2

References

1. Veerman J, Metz SJ, Saakes M, Harmsen GJ (2009) J Membr Sci 327:136
2. Post JW, Hamelers HVM, Buisman CJN (2008) Environ Sci Technol 42:5785
3. Wick GL, Schmitt WR (1977) Mar Technol Soc J 11:16
4. Energy information administration; www.eia.doe.gov
5. Pattle RE (1954) Nature 174:660
6. Pattle RE (1955) Chem Proc Eng 35:351
7. Pattle RE (1955) Patent GB 731.729
8. Loeb S (1975) Science 189:654
9. Loeb S (1976) J Membr Sci 1:49
10. Veerman J, de Jong RM, Saakes M, Metz SJ, Harmsen GJ (2009) J Membr Sci 343:7
11. Post JW, Veerman J, Hamelers HVM, Euverink GJW, Metz SJ, Nymeyer K, Buisman CJN (2007) J Membr Sci 288:218
12. Jagur-Grodzinski J, Kramer R (1986) Ind Eng Chem Process Des Dev 25:443
13. Audinos R (1983) J Power Sources 10:203 (In French)
14. Audinos R (1992) Ind J Chem 31A:348
15. Veerman J, Post JW, Metz SJ, Saakes M, Harmsen GJ (2008) J Membr Sci 310:418
16. Weinstein JN, Leitz FB (1976) Science 191:557

17. Wick GL (1978) *Energy* 3:95
18. Loeb S (1979) Patent US 4,171,409
19. Metha GD (1982) *J Membr Sci* 11:107
20. Suda F, Matsuo T, Ushioda D (2007) *Energy* 32:165
21. Czarnetzki LR, Janssen LJJ (1992) *J Appl Electrochem* 22:315
22. Turek M, Bandura B (2007) *Desalination* 205:67
23. Turek M, Bandura B, Dydo P (2008) *Desalination* 221:462
24. Hamelers HVM, Post JW, Metz SJ (2007) Patent WO 2007/094659 A1
25. Lacey RE (1980) *Ocean Eng* 7:1
26. Lopez-Atalaya M, Codina G, Perez JR, Vazquez JL, Aldaz A (1992) *J Power Sources* 39:147
27. Pupkevich V, Glibin V, Karamanev D (2007) *Electrochem Commun* 9:1924
28. Katz WE (1979) *Desalination* 28:31
29. Grebenyuk VD, Grebenyuk OV (2002) *Russ J Electrochem* 38:906
30. International Critical Tables (1929) 6:339
31. Nagasubramanian K, Chlanda FP, Liu Kang-Jen (1977) *J Membr Sci* 2:109
32. Lide DR (ed) (2004) *Handbook of chemistry and physics*, vol 5, 85th edn. CRC press, Boca Raton, pp 18
33. Charnes A, Cooper WW, Rhodes E (1978) *Eur J Oper Res* 2:429
34. Adler N, Friedman L, Sinuany-Stern Z (2002) *Eur J Oper Res* 140:249
35. Qu J-X, Liu S-M (1983) *Desalination* 46:233
36. Kuhn AT, Mortimer CJ (1972) *J Appl Electrochem* 2:283
37. Chen W K-W (1965) Patent US 3,192,148
38. Mihara K, Kato M, (1969) Patent US 3,453,201
39. Jain SM (1984) Patent US 4,461,693
40. Beer HB, US Appl. 549 194 (1966), US 3632498 (1972) and US 3711 385 (1973)
41. Comninellis CH, Vercesi GP (1991) *J Appl Electrochem* 21:335
42. Price K (ed) (2003) *Desalination handbook for planners*, 3rd edn. RosTek Associations, Tampa, Florida
43. O'Brien TF, Bommaraju TV, Hine F (2005) *Handbook of chlor-alkali technology*, vol 1. Springer, Berlin, p 33
44. Trasatti S (2000) *Electrochim Acta* 45:2377
45. Chen X, Chen G (2005) *Electrochim Acta* 50:4155
46. Kraft A (2008) *Platinum Metals Rev* 52:177
47. Lota G, Centeno TA, Frackowiak E, Stoeckli F (2008) *Electrochim Acta* 53:2210
48. Frackowiak E, Béguin F (2001) *Carbon* 39:937
49. Gamby J, Taberna PL, Simon P, Fauvarque JF, Chesneau M (2001) *J Power Sources* 101:109
50. Kim C, Choi YO, Lee WJ, Yang KS (2004) *Electrochim Acta* 50:883
51. Farmer JC, Fix DV, Mack GV, Pekala RW, Poco JF (1996) *J Electrochem Soc* 143:159
52. Zou L, Li L, Song H, Morris G (2008) *Water Res* 42:2340
53. Welgemoed TJ, Schutte CF (2005) *Desalination* 183:327
54. Wei C, Yu D, Wei C, Xiong R, Cao L (2008) Patent WO 2008/030646 A2
55. Brogioli D (2009) *Phys Rev Lett* 103:058501-1
56. Kedem O, Tanny G, Maoz Y (1978) *Desalination* 24:313
57. Kedem O, Robinson T (1978) Patent US 4,226,688