

# Electrochemical generators of pulsating or alternating current\*

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Received 7 October 1996; revised 25 October 1997

This paper concerns the design of three different electrochemical generators of nonsteady current: two generate a pulsating direct current, the third generates an irregular alternating current. The (Fe|NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub>|Pt) generator induces an alternating current in a secondary circuit connected to a transformer. The influence of electrode size and external resistance on current oscillation parameters and on power is shown. The shape of current oscillation in the generators (Fe|NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub>|Pt), (Zn|ZnSO<sub>4(aq.)</sub>||NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub>|Fe) and (Fe|NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub>|Fe) are also shown and the working of the three generators is explained.

Keywords: *electrochemical generators, pulsating current, alternating current*

## 1. Introduction

Electrochemical generators of current convert Gibbs free energy into electrical work almost in a steady mode and produce a steady direct current. Hence, the intensity cannot be changed in a transformer without using an alternator or another device able to transform the steady direct current into a pulsating one. The generators we have designed convert Gibbs free energy into electrical work in a pulsating mode, because the potential of one or both electrodes oscillates [1]. When only one electrode has an oscillating potential, a generator produces a current of constant direction and of oscillating intensity. When both electrodes have an oscillating potential in almost the same range, a generator produces an irregular alternating current.

Spontaneous oscillations in electrode potential can occur in the corrosion of some metals such as Cr in HCl and Fe in HNO<sub>3</sub> [2, 3] Co in chromium(vi)-oxide containing HCl [4] and Cu in sulphuric acid solutions of potassium dichromate [5–7]. We found [8] spontaneous oscillations in the potential of an iron electrode in bromate/sulphuric acid media in open circuit conditions. We explained these using the model of Franck and FitzHugh [9].

To obtain electrochemical generators of non-steady current, a Fe|NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub> half-cell was

connected with either a Pt|NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub> or a Zn|ZnSO<sub>4(aq.)</sub> or a Fe|NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub> electrode. This paper shows the effect of different external resistances and of the size of the two electrodes on the amplitude and frequency of current oscillations and on the power in a (Fe|NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub>|Pt) generator. The shape of the current oscillation in the couplings (Fe|NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub>|Pt), (Zn|ZnSO<sub>4(aq.)</sub>||NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub>|Fe) and (Fe|NaBrO<sub>3(aq.)</sub> + H<sub>2</sub>SO<sub>4(aq.)</sub>|Fe) is also shown.

## 2. Experimental details

The first generator (Fig. 1) consisted of a vessel containing a solution of sodium bromate and sulphuric acid in water with no stirring. Iron and platinum electrodes were placed in the solution. An insulating cover held the electrodes. A carbon tetrachloride layer at the bottom of the vessel is necessary to obtain regular oscillations. The platinum electrode may be replaced by a graphite electrode. The anode was an ARMCO iron sheet, width 10 mm, immersed to a depth of 18 mm. In order to study the influence of its size, the cathode consisted, in sequence, of a platinum wire of 1 mm diameter, a platinum sheet 2.7 cm wide, immersed to a depth of 1.7 cm, and a platinum dish, 6 cm in diameter and 2.5 cm high. The influence of the external resistance (10, 25, 50 Ω) on oscillatory pa-

\* Paper originally presented at the 4th European Symposium on Electrochemical Engineering, Prague, August, 1996.

rameters was studied using an nbn Elektronik resistance box. Also the use of a transformer allowed the induction, from the generator, of an alternating current in the secondary circuit, where the external resistance of the primary circuit was  $2\ \Omega$  and that of the secondary circuit  $355\ \Omega$ .

The second generator was made using the same vessel, solution and  $\text{CCl}_4$  layer as the iron electrode, which was connected by a  $\text{KNO}_3$  salt bridge to a zinc electrode in a  $0.1\ \text{M}$  zinc sulphate solution. The cathode consisted of an ARMCO iron sheet, width  $10\ \text{mm}$ , immersed to a depth of  $15\ \text{mm}$ . The anode was a Carlo Erba zinc cylinder (special high grade  $99.9985\%$ ) of  $7\ \text{mm}$  diameter, immersed to a depth of  $15\ \text{mm}$ . The external resistance was  $1100\ \Omega$ .

The third generator was made like the first. Two ARMCO iron sheets, width  $10\ \text{mm}$ , immersed to a depth of  $10\ \text{mm}$ , were used as electrodes. The external resistance was  $50\ \Omega$ .

Generator voltages and currents were measured respectively by means of a high impedance electrometer (Keithley, model 610C) and a digital multimeter (Simpson, 360-2 Run II) connected with a two-channel potential recorder (Perkin Elmer, recorder 56).

The reagents sodium bromate, sulphuric acid and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  were from Carlo Erba R.P.E.

The standard test solution was an unstirred  $0.49\ \text{M}$   $\text{NaBrO}_3$  and  $0.54\ \text{M}$   $\text{H}_2\text{SO}_4$  solution. The zinc sulphate solution was  $0.1\ \text{M}$ .

### 3. Results

#### 3.1. $(\text{Fe}|\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Pt})$ generator

A pulsating conventional current (Fig. 2) circulated from the platinum to the iron electrode on closing the circuit, through a resistance. In addition, it induced an alternating current in a circuit connected with the secondary circuit of a transformer (Fig. 3).

The generator worked with current oscillations of stable amplitude for about  $4\ \text{h}$  until total iron sheet consumption. The regularity of the oscillations was increased by the presence of a carbon tetrachloride

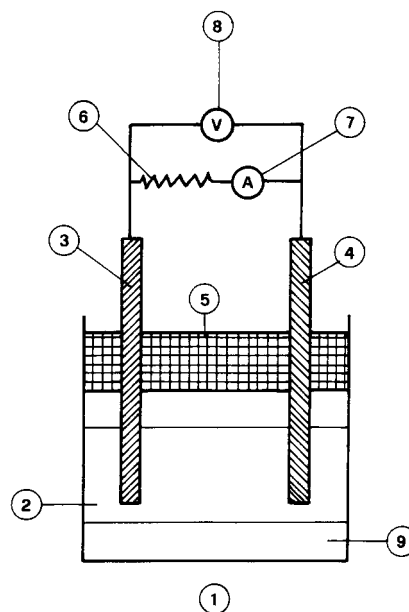


Fig. 1. Electrochemical pulsating current generator. Key: (1) vessel, (2) solution, (3) iron electrode, (4) platinum electrode, (5) cover, (6) resistance, (7) galvanometer, (8) voltmeter and (9) carbon tetrachloride layer.

layer, or by the addition of malonic acid or allyl alcohol, which gradually absorbed the bromine produced. Strong stirring influenced the potential oscillations [8] of an iron electrode in a bromate/sulphuric acid medium at open circuit conditions and prevented them from taking place at a  $0.5$  stirring rate (on an arbitrary proportional scale). Potential and current oscillations at closed circuit through a  $10\ \Omega$  resistance ceased at a stirring rate of  $5$  and again reappeared on decreasing the resistance to  $5\ \Omega$ .

Tables 1 and 2 show the values of the frequency and amplitude of the current oscillations. Table 3 shows the values of the maximum and minimum powers of the generator. All the tables show the values in relation to the platinum electrode surface with the external resistance as the parameter. The frequency increased with decrease in external resistance. It also increased with increase in the surface of the platinum electrode for resistances of  $50$  and  $25\ \Omega$ . For  $10\ \Omega$ , the system with the platinum wire did not

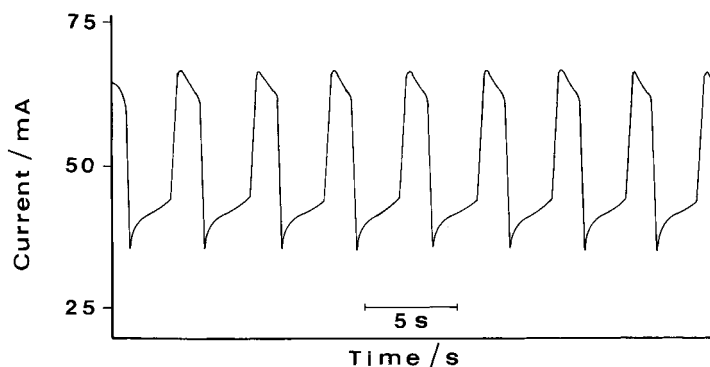


Fig. 2. Current against time behaviour for  $(\text{Fe}|\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Pt})$  generator in test with solution of composition:  $0.49\ \text{M}$  sodium bromate,  $0.54\ \text{M}$  sulphuric acid in water. Iron electrode: ARMCO iron sheet, width  $10\ \text{mm}$ , immersed to depth of  $18\ \text{mm}$ . Platinum electrode: sheet, width  $27\ \text{mm}$ , immersed to depth of  $17\ \text{mm}$ . External resistance  $10\ \Omega$ .

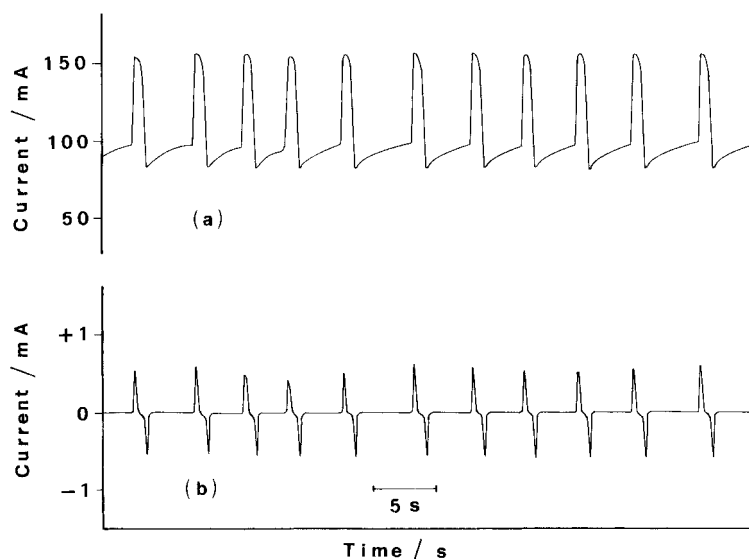


Fig. 3. Current against time behaviour in the primary electrochemical circuit, external resistance,  $R_1:2\Omega$  (a) and in the secondary electrical circuit, external resistance,  $R_2:355\Omega$  (b) connected by transformer for  $(\text{Fe}|\text{NaBrO}_3(\text{aq.}) + \text{H}_2\text{SO}_4(\text{aq.})|\text{Pt})$  generator in test with a solution of composition: 0.49 M sodium bromate, 0.54 M sulphuric acid in water. Iron electrode: ARMCO iron sheet, width 10 mm, immersed to depth of 18 mm. Platinum electrode: sheet of width 27 mm, immersed to depth of 17 mm.

oscillate and the frequency was the same for the sheet and the dish. The amplitude increased with decrease in external resistance for the sheet and the dish. For the wire the system showed the opposite behaviour. The amplitude increased with increase in the platinum surface. The maximum and minimum power of the generator increased with decrease in external resistance and with increase in the platinum electrode surface. Thus with a  $10\Omega$  external resistance and with a platinum dish electrode the maximum value of current oscillation amplitude (61.8 mA), frequency (0.11 Hz), maximum power (76 mW) and minimum power (6.25 mW) was obtained.

Oscillatory parameters did not seem to depend on the iron electrode size in any of the systems.

### 3.2. $(\text{Zn}|\text{ZnSO}_4(\text{aq.})||\text{NaBrO}_3(\text{aq.}) + \text{H}_2\text{SO}_4(\text{aq.})|\text{Fe})$ generator

A pulsating conventional current circulated from the iron to the zinc electrode in the external circuit through a resistance of  $1100\Omega$ . Figure 4 shows the very regular current oscillations. The oscillatory parameters of the generator were: frequency 0.024 Hz; amplitude 0.06 mA; maximum power 0.02 mW; minimum power 0.0062 mW. At resistances of less than  $1100\Omega$ , zinc and iron corrosion took place.

Table 1. Oscillation frequency in relation to the size of the platinum surface with external resistance as the parameter

Resistance/ $\Omega$	Frequency/ $s^{-1}$		
	Wire	Sheet	Dish
10	*	0.111	0.111
25	0.037	0.083	0.095
50	0.033	0.074	0.083

\* no oscillation.

Table 2. Oscillation amplitude in relation to the size of the platinum surface with external resistance as the parameter

Resistance/ $\Omega$	Amplitude/mA		
	Wire	Sheet	Dish
10	*	43.00	61.80
25	2.08	18.96	24.40
50	2.80	9.20	10.72

\* no oscillation.

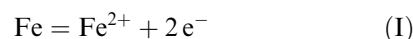
### 3.3. $(\text{Fe}|\text{NaBrO}_3(\text{aq.}) + \text{H}_2\text{SO}_4(\text{aq.})|\text{Fe})$ generator

When the electrical circuit was closed, an irregular alternating current (Fig. 5) occurred.

## 4. Discussion

### 4.1. Mechanism of the oscillations

One anodic process



and two cathodic processes, a bromate reduction

Table 3. Maxima and minima of power in relation to the size of the platinum surface with external resistance as the parameter

Resistance/ $\Omega$	Power/mW					
	Wire		Sheet		Dish	
	$P_{\text{max}}$	$P_{\text{min}}$	$P_{\text{max}}$	$P_{\text{min}}$	$P_{\text{max}}$	$P_{\text{min}}$
10	*0.040	*0.040	36.000	2.900	76.000	6.250
25	0.320	0.064	21.000	2.500	38.000	5.200
50	0.720	0.070	12.000	2.200	20.000	4.400

\* no oscillation.

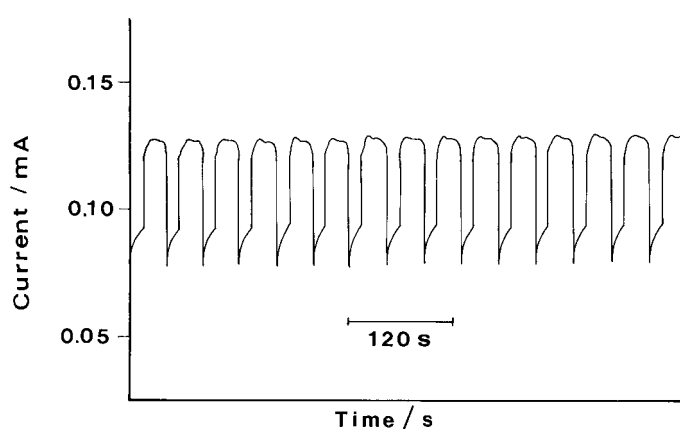
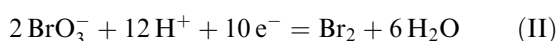
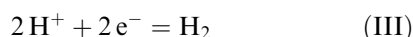


Fig. 4. Current against time behaviour for  $(\text{Zn}|\text{ZnSO}_{4(\text{aq.})}|\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Fe})$  generator in test with iron electrode (ARMCO iron sheet, width 10 mm, immersed to depth of 15 mm) placed in solution of composition: 0.49 M sodium bromate, 0.54 M sulphuric acid in water; and zinc electrode (cylinder 7 mm diameter, immersed to depth of 15 mm) placed in 0.1 M zinc sulphate solution in water. External resistance 1100  $\Omega$ .



and a cation hydrogen ion reduction



take place on the iron electrode surface. The potential is thus due to the mixed potential of the three reactions. When Reaction I prevails over Reactions II and III, the iron electrode behaves anodically; when reactions (II) and (III) prevail over reaction (I), the iron electrode behaves cathodically.

According to the Franck and FitzHugh model [9], oscillations in iron electrode corrosion are due to the alternate active and passive behaviour [8] of the iron electrode. Reactions II and III consume  $\text{H}^+$  ions, increasing the local pH at the electrode/solution interface,  $\text{H}^+$  transport from the bulk of the solution decreases the pH. When  $\text{H}^+$  consumption exceeds its rate of supply, the increase in pH causes precipitation of a passivating film [8–11], while Reactions II and III slow down. When the supply of  $\text{H}^+$  ions from the bulk solution exceeds  $\text{H}^+$  consumption, the local pH at the interface decreases and dissolution of the passivating film [8–10] takes place. Reactions II and III again accelerate and  $\text{H}^+$  consumption prevails; the phenomenon is then repeated.

#### 4.2. Three-electrode representation of the $(\text{Fe}|\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Pt})$ generator

On closing the external circuit both the cathodic Reactions II and III occur on the inert platinum electrode. The iron sacrificial electrode behaves as an anode, on which Reactions I, II and III occur. Reaction I prevails, however, as the direction of the conventional current in the external circuit indicates. The generator can be represented by the three-electrode system in Fig. 6.  $C_{\text{Pt}}$  is the platinum cathode,  $C_{\text{Fe}}$  is the iron cathodic zone on which reactions II and III take place, and  $A_{\text{Fe}}$  is the iron anodic zone on which Reaction I takes place. Macroscopically  $C_{\text{Fe}}$  and  $A_{\text{Fe}}$  are the same iron electrode, but single adjacent atoms act respectively as the cathode or the anode, as stated by the mixed potential theory.  $I$  is both the platinum cathodic current, due to the occurrence of Reactions II and III on the platinum electrode and the current in the external circuit;  $I_1$  is the iron cathodic current due to the occurrence of Reactions II and III on the iron electrode and  $I_2$  is the iron anodic current due to the occurrence of Reaction I on the iron electrode. The pulsating increase in the internal resistance of the generator due to the passivating film leads to the generation of a pulsating

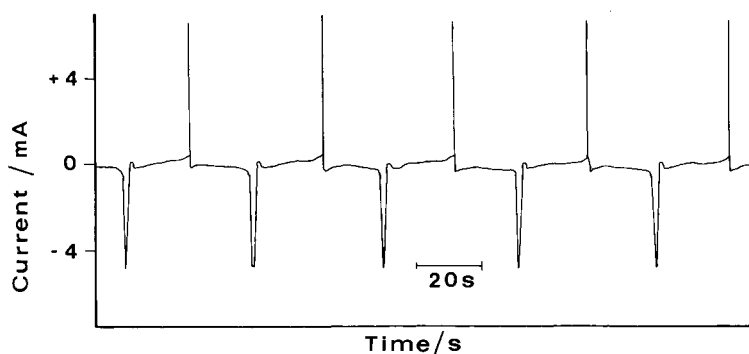


Fig. 5. Current against time behaviour for  $(\text{Fe}|\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Fe})$  generator in test with two iron electrodes (ARMCO iron sheets, width 10 mm, immersed to depth of 10 mm) placed in same solution of composition: 0.49 M sodium bromate, 0.54 M sulphuric acid in water. External resistance 50  $\Omega$ .

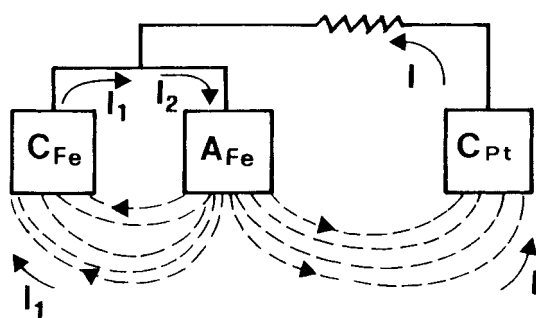


Fig. 6. Three-electrode representation of  $(\text{Fe}|\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Pt})$  generator.  $\text{C}_{\text{Fe}}$ , iron cathodic zone;  $\text{A}_{\text{Fe}}$ , iron anodic zone;  $\text{C}_{\text{Pt}}$ , platinum cathode;  $I_1$ , iron cathodic current;  $I_2$ , iron anodic current;  $I$ , platinum cathodic current and current in external circuit.

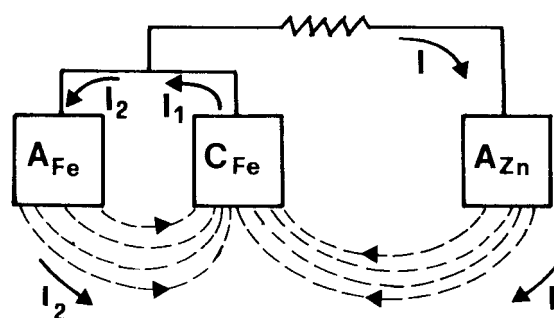


Fig. 7. Three-electrode representation of  $(\text{Zn}|\text{ZnSO}_{4(\text{aq.})}||\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Fe})$  generator.  $\text{A}_{\text{Fe}}$ , iron anodic zone;  $\text{C}_{\text{Fe}}$ , iron cathodic zone;  $\text{A}_{\text{Zn}}$ , zinc anode;  $I_1$ , iron cathodic current;  $I_2$ , iron anodic current;  $I$ , zinc anodic current and current in external circuit.

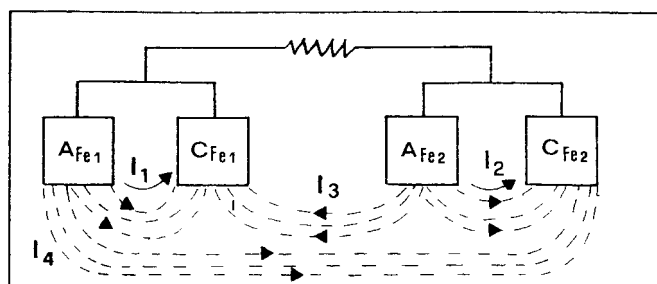
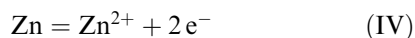


Fig. 8. Four-electrode representation of  $(\text{Fe}|\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Fe})$  generator.  $\text{A}_{\text{Fe}1}$ , anodic zone of first iron electrode;  $\text{C}_{\text{Fe}1}$ , cathodic zone of first iron electrode;  $\text{A}_{\text{Fe}2}$ , anodic zone of second iron electrode;  $\text{C}_{\text{Fe}2}$ , cathodic zone of second iron electrode;  $I_1$  cathodic and corrosion anodic current on first iron electrode;  $I_2$  cathodic and corrosion anodic current on second iron electrode;  $I_3$  and  $I_4$  cathodic and anodic currents that run by turns between the two electrodes in external circuit and inside solution.

current,  $I$ , in the external circuit. The generator also works if the anodic and cathodic solutions are separated and connected by a salt bridge.

#### 4.3. Three-electrode representation of the $(\text{Zn}|\text{ZnSO}_{4(\text{aq.})}||\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Fe})$ generator

On closing the external circuit zinc anodic dissolution (IV) takes place



and the conventional current in the external circuit goes from the iron electrode to the zinc electrode. The iron electrode behaves overall as a cathode, because Reactions II and III prevail over Reaction (I). The generator can be represented as the three-electrode system of Fig. 7.  $\text{A}_{\text{Zn}}$  is the zinc anode,  $\text{A}_{\text{Fe}}$  the iron anodic zone,  $\text{C}_{\text{Fe}}$  the iron cathodic zone,  $I_1$  the iron cathodic current,  $I_2$  the iron anodic current, and  $I$  both the zinc anodic current due to the occurrence of Reaction IV and the current in the external circuit.

#### 4.4. Four-electrode representation of the $(\text{Fe}|\text{NaBrO}_{3(\text{aq.})} + \text{H}_2\text{SO}_{4(\text{aq.})}|\text{Fe})$ generator

The anodic Reaction I and both the cathodic Reactions II and III occur at the same time at the surfaces of two iron electrodes immersed either in the same

solution or in two separate solutions of the same composition, connected by a salt bridge. As the potentials of both the electrodes oscillate in the same range, each of them can, by turns, play the overall roles of cathode or anode with respect to the other and an alternating current is generated.

The generator can be represented as the four-electrode system of Fig. 8. A conventional current  $I_1$  passes inside the first iron electrode from  $\text{C}_{\text{Fe}1}$  (cathodic zone) to  $\text{A}_{\text{Fe}1}$  (anodic zone) and inside the solution from  $\text{A}_{\text{Fe}1}$  to  $\text{C}_{\text{Fe}1}$ . A conventional current  $I_2$  passes inside the second iron electrode from  $\text{C}_{\text{Fe}2}$  (cathodic zone) to  $\text{A}_{\text{Fe}2}$  (anodic zone) and inside the solution from  $\text{A}_{\text{Fe}2}$  to  $\text{C}_{\text{Fe}2}$ .  $I_3$  and  $I_4$  are the conventional currents that run by turns between the two electrodes in the external circuit, respectively  $I_3$  from  $\text{C}_{\text{Fe}1}$  to  $\text{A}_{\text{Fe}2}$  and  $I_4$  from  $\text{C}_{\text{Fe}2}$  to  $\text{A}_{\text{Fe}1}$ , and inside the solution, respectively  $I_3$  from  $\text{A}_{\text{Fe}2}$  to  $\text{C}_{\text{Fe}1}$  and  $I_4$  from  $\text{A}_{\text{Fe}1}$  to  $\text{C}_{\text{Fe}2}$ . The alternation between them leads to an irregular alternating current.

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