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*M.M. Zipunnikov***FORMATION OF POTASSIUM FERRATE IN A MEMBRANE-LESS ELECTROLYSIS PROCESS OF WATER DECOMPOSITION****A.M. Pidhorny Institute of Mechanical Engineering Problems of the National Academy of Sciences of Ukraine, Kharkiv, Ukraine**

The aim of this work was to study the operating characteristics of the membrane-free electrolysis water decomposition for high-pressure hydrogen and oxygen production and ensure a maximum yield of the potassium ferrates as a target product without using expensive electrode metals. An electrode assembly consisting of two electrodes, steel 3 (passive, i.e. gas-releasing) electrode and porous Fe active (i.e. gas-oxidizing) electrode, was used. An aqueous solution of potassium hydroxide (25%) was used as an electrolyte. To assess the efficiency of the formation of potassium ferrates, the effects of the current density (in the range of 0.008 A/cm² to 0.03 A/cm²) and the number of the complete redox cycles on the density of the electrolyte were studied. It was determined that the density of an electrolyte increased from 1.23 g/ml to 1.26 g/ml after 10 complete cycles. This indicates an increase in the concentration of potassium ferrates in the course of the electrolysis process at the current density of 0.015 A/cm². A decrease in the current density below 0.01 A/cm² leads to a decrease in the rates of the gases release (both H₂ and O₂) and ferrate ions formation which is a critical condition for potassium ferrates formation taking into account their tendency for self-decomposition. The change of the Gibbs energy was determined taking into consideration the initial potential of hydrogen and oxygen evolution. Recommendations were given that concern the application of the developed method of ferric acid salts production to use them as an oxidizing agent in the process of waste-water treatment.

Keywords: hydrogen, oxygen, potassium ferrate, potassium hydroxide, electrolysis system.

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Introduction

Currently, the waste-water treatment shows a tendency to expand the technologies using potassium ferrates (PF) as an oxidizer in the chlorination processes [1–3]. Being strong oxidizing agents, ferrates readily oxidize organic pollutants and provide an antiseptic effect. At the same time, they, unlike chlorine, do not form the toxic products.

Therefore, ferrates are increasingly being used in water purification and water treatment. There are three main groups of methods for producing ferrates: chemical oxidation of iron (II) and (III) compounds in alkaline solutions; electrochemical oxidation of iron in alkaline solutions and high-temperature oxidation of iron, iron (II) and (III) compounds in the solid form [4–9].

A significant drawback of the high-temperature and electrochemical oxidation methods for producing ferrates is a high energy intensity of these processes.

Therefore, the problem of developing an electrochemical process for hydrogen and oxygen evolution from water while simultaneously producing PF for the above mentioned application is very topical. This method will give the possibility for producing potassium ferrate in a liquid form and with stable properties to result in reducing the cost of the electrolysis process. These PFs can be easily added to or injected into any solution or tank.

Earlier, a method of high pressure hydrogen and oxygen electrochemical generation in the membrane-less electrolyzer was developed using metals with variable valence [10–12]. According to this method, the process of water decomposition is cyclical, namely, the processes of hydrogen and oxygen evolution are alternating in time. The operating temperature range of the electrolysis process is from 280 K to 423 K and the pressure range is 0.1–70 MPa.

The aim of this work was to study the operating characteristics of the membrane-less electrolysis water decomposition for the production of high-pressure hydrogen and oxygen and ensure a maximum yield of the PF as a target product without using expensive electrode metals.

Experimental

Materials

When conducting the experimental study, we used an electrode assembly consisting of two electrodes: Steel 3 passive (gassing) and porous Fe active (gas-oxidizing) electrodes. An aqueous solution of KOH (25%) was used as electrolyte.

To assess the efficiency of the PFs formation, we investigated the effects of current density (in the range from 0.008 A/cm² to 0.03 A/cm²) and the number of the full redox cycles on the density of the electrolyte.

Methods

When implementing the proposed cyclical technology, the reaction of water decomposition occurs continuously in the electrochemical cell with simultaneous hydrogen and oxygen evolution. At the first half cycle, hydrogen is generated on the passive electrode in a gaseous form and is fed to the high pressure line. At that time oxygen is chemically bound by the active electrode (forming a chemical compound).

During the subsequent half-cycle, the

electrochemical reduction of the active electrode with hydrogen is carried out that is accompanied by oxygen evolution at the passive electrode and its feeding into the external line. Cyclic generation of hydrogen and oxygen in time prevents the possibility of gas mixing and eliminates the need for using separation membranes in the electrolyzer inter-electrode space. The electrolyte density was measured by a hydrometer. The measurement of the evolved gases volume was performed by the volumetric method using U-shaped differential manometers of the oxygen and hydrogen highways. The used method is similar to that described elsewhere [10,11].

Results and discussion

The main data were obtained experimentally by studying the electrochemical activity of the Steel 3–Fe electrode twin. The data are given in Table 1 and in Fig. 1 and 2.

Based on the obtained results, it was determined that dark red ferric acid (H₂FeO₄) is formed near the iron anode (Steel 3) during the electrolysis process (Fig. 3) in the oxygen half-cycle and at voltage below (–1.2 V) when a porous iron electrode is oxidized by the following reactions:

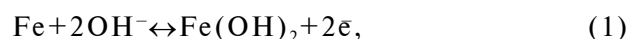


Table 1

The results of the electrochemical activity of the Steel 3–Fe electrode twin

Surface of the active electrode, cm ²	Current, A	Current density, A/cm ²	Amount of generated hydrogen, m ³ /h	Amount of generated oxygen, m ³ /h	Electricity consumption, kWh/m ³
31.5	0.5	0.015	0.26·10 ⁻³	0.13·10 ⁻³	4.07
	1.0	0.03	0.33·10 ⁻³	0.16·10 ⁻³	4.24

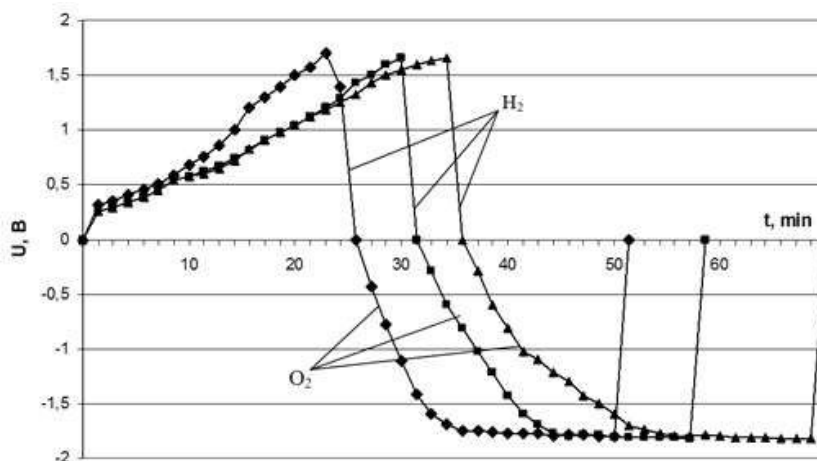


Fig. 1. Plots of electrode vs. time dependences of the full cycle of hydrogen and oxygen evolution when Steel 3–Fe electrode twin is used. Current density: ■ – 0.015 A/cm²; ◆ – 0.03 A/cm²; ▲ – 0.008 A/cm²

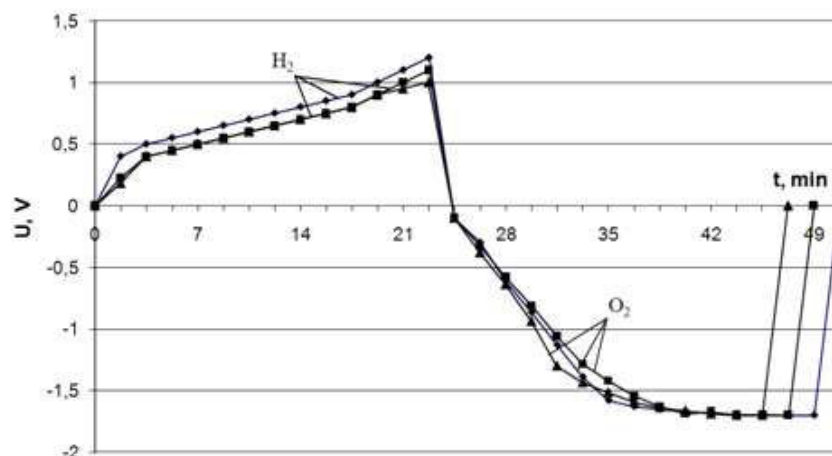


Fig. 2. Plots of voltage vs. time for complete cycles of hydrogen and oxygen evolution during the electrolysis when the Steel 3–Fe (sponge) electrode twin is used. Current density 0.015 A/cm²

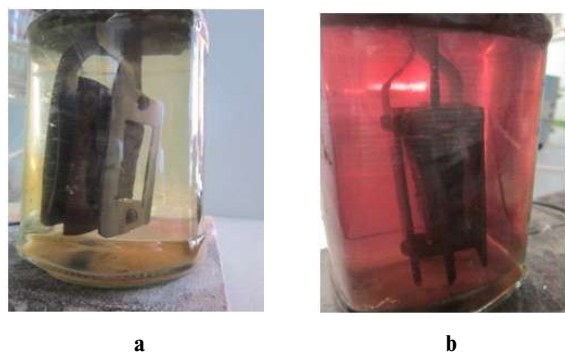


Fig. 3. Photos of the Steel 3–Fe electrolysis cell in a glass reactor: a – before the beginning of the redox cycle; b – at the end of the redox cycle

This effect is associated with the process of ion transfer between the passive and active electrodes during the corresponding half-cycles.

The dark red solution of the ferric acid salt gradually decomposes with oxygen evolution by the reaction:



The salt of ferric acid is one of the most powerful oxidizing agents with respect to organic compounds. It can oxidize even water. It was experimentally determined that a gradual increase in the oxygen evolution half-cycle time is observed with each subsequent electrochemical cycle of gas evolution. This is due to the deposition of the formed salts on the electrodes surfaces by the following reaction:



namely, with each subsequent cycle of hydrogen (oxygen) evolution the PF density and oxygen evolution half-cycle duration are gradually increase due to the additional energy consumption in the formation of iron salts and gaseous oxygen (Fig. 2).

After 10 complete redox cycles, the electrolyte density was increased from 1.23 g/ml to 1.26 g/ml. In this case, 2.6 liters of hydrogen were generated which corresponded to a flow rate of $2.18 \cdot 10^{-3}$ liters of water per 500 ml of the stock electrolyte (KOH solution). The dependence of the electrolyte density on the number of H₂ (O₂) evolution cycles at the current densities of 0.015 A/cm² and 0.03 A/cm² is showed in Fig. 4.

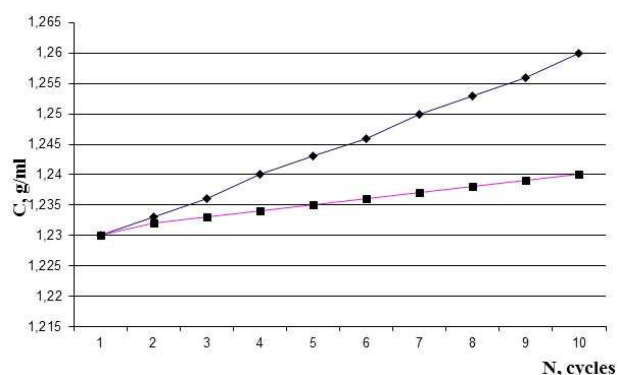


Fig. 4. Dependence of the electrolyte density on the amount of the performed cycles at the current density: \blacklozenge – 0.015 A/cm²; \blacksquare – 0.03 A/cm²

With an increase in the current density to 0.03 A/cm², the amount of the generated H₂ (O₂) increases by ~20% (Table 1, Fig. 5), a slight increase in the electrolyte density is observed (up to 1.24 g/ml).

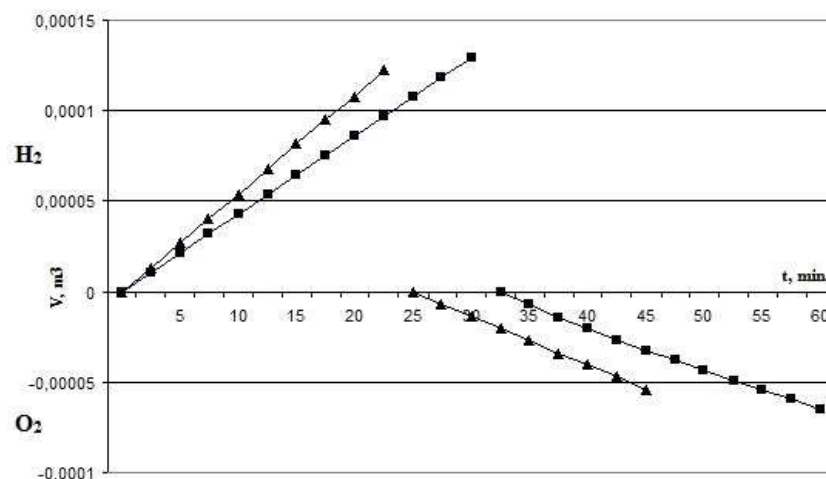
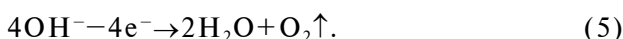


Fig. 5 Dynamics of the complete cycle of hydrogen and oxygen evolution during electrolysis when the Steel - Fe electrode twin is used at current density: ■ – $I = 0.015 \text{ A/cm}^2$; ▲ – $I = 0.03 \text{ A/cm}^2$

Upon completion of 10 complete gases evolution cycles, the rate of oxygen evolution increases in accordance with the following reaction:



This results in a decrease in generation of the ferrate ions at the anode.

Conducting the process at lower current densities ($<0.01 \text{ A/cm}^2$) is not economically feasible. This is due to the fact that a lower current density leads to a decrease in the rate of the gases evolution (H_2 and O_2) and formation of ferrate ions. That is critical condition taking into account the tendency of the resulting PF to self-decomposition.

In the gas evolution process, the initial potentials of hydrogen and oxygen evolution were 0.35 V and -1.22 V , respectively. After 10 complete cycles of gases evolution, the initial gas evolution potentials reached the maximum values: 0.41 V for H_2 and (-1.4 V) for O_2 . Then the potentials were constant in the next half cycles (Table 2). This indicates the maximum possible density of the formed PF in the electrolyte solution under given parameters.

Deposition of the PFs on the electrodes surfaces

leads to an increase in overvoltage at the corresponding half-cycles and to an increase in the energy consumption per unit of the gas generated volume. There is a need to provide multi-stage washing of the resulting PF precipitate as well as the following recrystallization, extracting in the inorganic and organic solvents and subsequent drying to use it as a commercial product [13].

The changes of the Gibbs free energy were calculated (Eq. (6)) to confirm thermodynamic probability of H_2 and O_2 evolution reactions in the initial period [14].

$$\Delta G = -zF\varphi, \quad (6)$$

where z is the number of the electrons participating in the process; F is the Faraday constant; φ is the electrode potential in the initial period of H_2 (O_2) evolution.

The obtained results are listed in Table 2.

The negative values of the Gibbs free energy indicate a high thermodynamic probability of H_2 (O_2) evolution at the initial period of gas formation. An increase in the initial potential of gas evolution leads to an increase in the time of the beginning of the gas

Table 2

Data on electrochemical activity of the Steel 3-Fe (sponge) electrode twin

Active electrode surface, cm^2	Current, A	Current density, A/cm^2	Gassing beginning voltage, V		Change of Gibbs standard energy, $-\Delta G$, J/kg		Electric power consumption, kWh/m^3
			H_2	O_2	H_2	O_2	
31.5	0.5	0.015	0.35	-1.22	$2.23 \cdot 10^7$	$8.123 \cdot 10^7$	4.07
			0.41	-1.4	$2.611 \cdot 10^7$	$10.537 \cdot 10^7$	4.3

formation process and a corresponding increase in the energy consumption per 1 m³ of hydrogen produced in the industrial conditions.

Conclusions

1. Generation of hydrogen and oxygen in a membrane-less electrolysis system using the Steel 3-Fe electrodes twins is accompanied by the PF formation upon reaching the -1.2 V potential in the oxygen evolution half-cycle which results in an additional energy consumption for 1 m³ hydrogen generation.

2. Maximum concentration of the formed PF is reached under the maximum initial potentials of hydrogen and oxygen evolution (0.41 V and -1.4 V, respectively), an increase in the KOH aqueous solution density being observed (up to 1.26 g/ml).

3. Conducting the process at a low current densities (<0.01 A/cm²) is not economically feasible. This is due to the fact that a lower current density causes a decrease in the rate of the gases evolution (H₂ and O₂) and formation of ferrate ions. That is a critical condition taking into account the tendency of the resulting PF to self-decomposition.

4. Analysis of the values of the Gibbs free energy change calculated taking into account the electrode potential in the initial period of gases evolution under corresponding half-cycles showed a high probability of the H₂ (O₂) evolution reactions.

A high oxidation level of iron (+6) allows using the PF powder after selection and technological treatment for cleaning the domestic and industrial waste-water from mobile heavy metal ions as well as for microbiological purification from the bacteria and viruses. It was stated that liquid potassium ferrates having stable properties can be produced as an additional commercial product in the process of hydrogen and oxygen generation by controlling the gases evolution parameters. This is a positive economic effect of the considered electrolysis process.

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УТВОРЕННЯ ФЕРРАТУ КАЛІЮ В БЕЗМЕМБРАННОМУ ЕЛЕКТРОЛІЗНОМУ ПРОЦЕСІ РОЗКЛАДАННЯ ВОДИ

М.М. Зіпунніков

Метою даної роботи було встановлення режимних характеристик, що забезпечують максимальний вихід калій феррату як цільового продукту без використання вартісних електродних металів в умовах безмембранної електролізної технології розкладання води і одержання водню і кисню з високим тиском. При здійсненні експериментальних досліджень застосовувалась електродна збірка, що складається з пасивного (газовидільного) електрода – Сталь 3 і активного (газоокислюваного) електрода – пористого Fe. Як електроліт використовувався 25%-ний водний розчин калій гідроксиду. Для оцінювання ефективності утворення калій феррату було досліджено вплив густини струму в інтервалі від 0,008 А/см² до 0,03 А/см² і кількості повних окисно-відновних циклів на густину використовуваного електроліту. Встановлено, що після 10-ти повних циклів густина електроліту підвищилась від 1,23 г/мл до 1,26 г/мл, це свідчить про підвищення концентрації утвореного калій феррату в електролізному процесі при густині струму 0,015 А/см². Зниження густини струму нижче 0,01 А/см² призводить до зменшення швидкості утворення газів (H₂, O₂) і феррат-іонів, що є критичним з огляду на схильність до саморозкладання утворюваного калій феррату. Визначено значення зміни енергії Гіббса з урахуванням початкового потенціалу газовиділення водню і кисню. Запропоновані рекомендації щодо застосування даного способу для одержання солей ферратної кислоти з метою їх використання в якості окислювача при обробленні води і водних відходів.

Ключові слова: водень, кисень, калій феррат, калій гідроксид, електролізна система.

FORMATION OF POTASSIUM FERRATE IN A MEMBRANE-LESS ELECTROLYSIS PROCESS OF WATER DECOMPOSITION

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