



Where do ferrate ions form? A dual dynamic voltammetry study

Ábel Zsubrits^{a,b}, Miklós Kuti^{b,c}, Éva Fekete^b, Mária Ujvári^b, Győző G. Láng^{b,*}

^a Hevesy György Ph.D. School of Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary

^b Institute of Chemistry, Laboratory of Electrochemistry and Electroanalytical Chemistry, Eötvös Loránd University, Pázmány P. s. 1/A, H-1117 Budapest, Hungary

^c IMSYS Engineering Service Ltd., Mozaik s. 14/A, H-1033 Budapest, Hungary

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ABSTRACT

One of the most effective methods to produce ferrate ions (FeO_4^{2-}) is electrochemical synthesis. During the transpassive anodic dissolution of iron, the formation of ferrate ions and the evolution of oxygen occur simultaneously, and only the sum of the currents generated by the two processes can be observed in the voltammetric curves. Products of the above process have been investigated in 45 % (*m/m*) aqueous NaOH solutions by using the dual dynamic voltammetry (DDV) & rotating ring-disk electrode (RRDE) method (i.e., applying dynamic potential programs to the disk and the ring electrodes of the RRDE disk electrode and the RRDE ring electrode simultaneously) combined with spectrophotometric measurements. Fe disk/Pt ring and Pt disk/Pt ring RRDE tips were used in the voltammetric experiments. The electrode potential regions where ferrate ions and oxygen are forming could effectively be identified. The results imply that, under the applied experimental conditions, the oxygen evolved at the disk cannot be reduced at the ring. This can be explained by the fact that elemental oxygen practically does not dissolve in concentrated aqueous sodium hydroxide solutions due to the “salting-out effect”. By using the dual voltammetric method, it was also possible to determine the optimal potential range for the electrochemical production of ferrate ions in terms of charging efficiency. The latter quantity has an important impact on the economics of practical applications. The approach proposed in this study proved to be very promising for the simultaneous detection of different dissolution products.

1. Introduction

The use of ferrate salts is increasingly recommended for water treatment [1,2,3]. They have several advantages: at neutral and acidic pH they are stronger oxidants than chlorine and ozone, are better disinfectant than both ozone and chlorine, and there is no known resistant bacteria or virus to ferrate ion. In addition, ferrates are considered “green chemicals” since the reduction products of ferrate ions are non-toxic Fe(III) compounds (ferric oxide or hydroxide) that can be used as flocculants in the water treatment process.

One of the methods for the production of ferrate ions (FeO_4^{2-}) is the electrochemical (anodic) oxidation of metallic iron. This method does not require expensive reagents and can yield a very pure product. However, the information on the mechanism of the electrochemical ferrate synthesis is limited. One of the reasons for this is that the primary goal of most studies has been to determine the optimal conditions for ferrate production for a given experimental setup, so the results cannot be considered universal. Another reason is that due to the aggressive chemical properties of ferrate ions and the solutions used during their

production, specially designed vessels (cells) made of sufficiently resistant structural materials are necessary for the study of the electrochemical reaction. In particular, the choice and application of the appropriate reference electrode can cause problems that are difficult to avoid, therefore simple 2-electrode arrangements have been used in most experiments. The situation is further complicated by the fact that during the transpassive anodic dissolution of iron, the formation of ferrate ions and the evolution of oxygen occur simultaneously, and the sum of the currents generated by the two processes can be observed in the voltammetric curves. Thus, it is not even possible to unambiguously determine the negative limit of the electrode potential range in which the formation of ferrate ions occurs (see Fig. 1).

We expected that this problem can be solved by the combined application of a suitable generator-collector system such as the rotating ring-disk electrode (RRDE) [4,5] and the dual dynamic voltammetry (DDV) method [6,7,8]. One possible way to use dual voltammetry with an RRDE is to polarize the “disk electrode” at a sufficiently low and the “ring electrode” at a sufficiently high potential scan rate, and the potential and current data (cyclic voltammograms) registered on the ring

* Corresponding author.

E-mail address: langgyg@chem.elte.hu (G.G. Láng).

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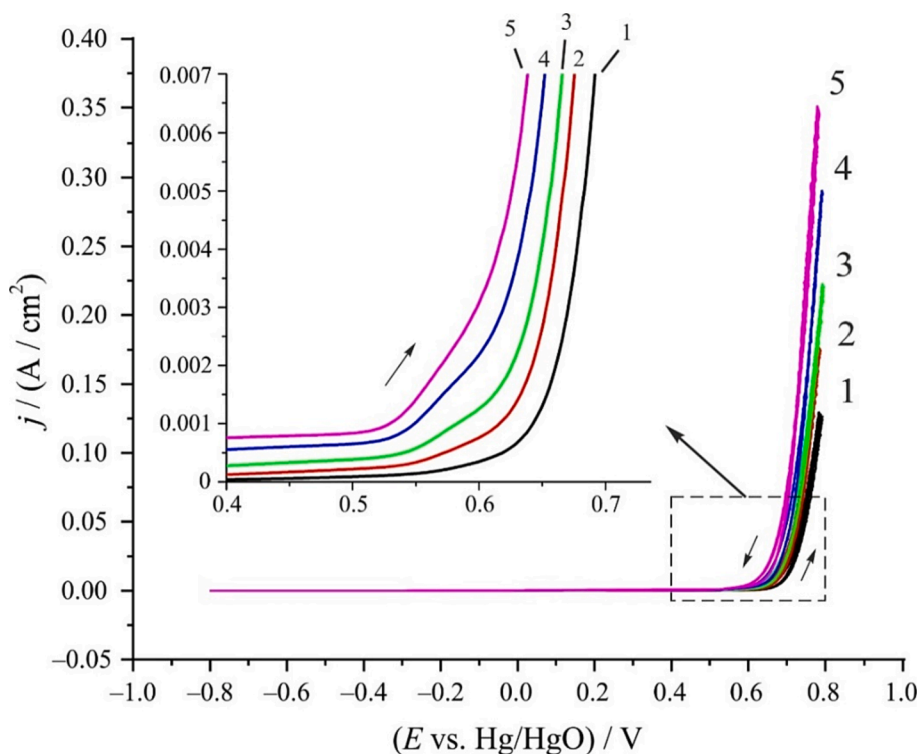


Fig. 1. Cyclic voltammograms of a pure iron disk in 45 % (m/m) aqueous NaOH solutions recorded between -0.8 V and 0.8 V vs. Hg/HgO (5 mol/dm³ KOH) at different temperatures: 15 °C (black, 1); 20 °C (red, 2); 25 °C (green, 3); 30 °C (blue, 4); and 35 °C (magenta, 5). Potential sweep rate: 10 mV/s, rotation rate of the disc: 1200 1/min. The inset shows the (enlarged) region of the positive-direction potential sweeps, where the formation of ferrate ions starts together with the evolution of oxygen.

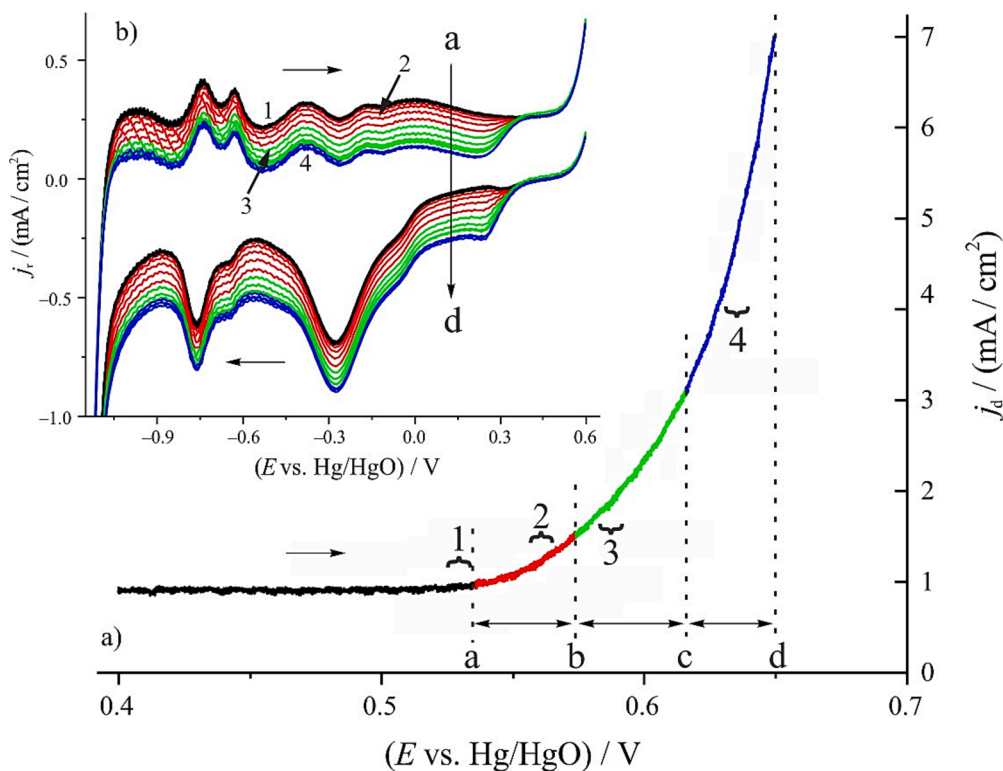


Fig. 2. Relevant parts of the voltammograms of the RRDE measurement with the Fe disk/Pt ring RRDE tip at $T = 30$ °C (E : electrode potential, j_d : disk current density, j_r : ring current density). Rotation rate 1200 rpm. Electrolyte solution: 45 m/m% aqueous NaOH solution. Iron disk: radius: $r = 0.5$ cm, geometric surface area: $A_d = 0.1964$ cm², sweep rate: $\nu = 0.5$ mV/s. Platinum ring: outer diameter: $d_o = 0.75$ cm, inner diameter: $d_i = 0.65$ cm, geometric surface area: $A_r = 0.1100$ cm², sweep rate: $\nu = 200$ mV/s. The ring CV-s marked with numbers (from 1 to 4) shown in the inset (b) were recorded in the potential ranges with the corresponding numbers of the disk voltammogram (a).

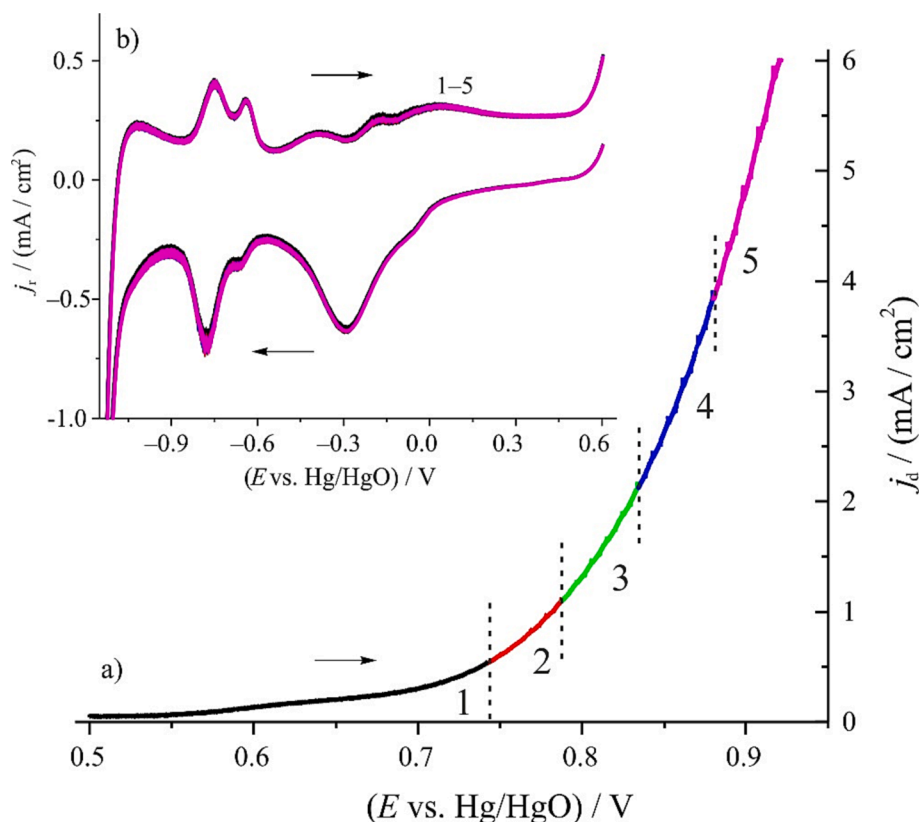


Fig. 3. Relevant parts of the voltammograms of the RRDE measurement with the Pt disk/Pt ring RRDE tip. Experimental conditions and notations are the same as those given in Fig. 2. The ring CV-s marked with numbers (from 1 to 5) shown in the inset (b) were recorded in the potential ranges marked with the corresponding numbers of the disk voltammogram (a).

may reveal the electroactive intermediates or products that are formed in the electrode process(es) taking place on the disk. The method proposed in this study can be used both to identify the potential region where the ferrate ions are formed and to estimate the relative rates of the reaction at different potentials.

2. Experimental

All experiments were carried out in a special electrochemical cell made of polypropylene. The classical voltammetric experiments were carried out in a standard three-electrode arrangement using a Metrohm Autolab PGSTAT 302 N electrochemical workstation. The working electrodes were made of high purity (99.98%) iron (Alfa Aesar). A Hg/HgO electrode (Mercury Oxide Reference Electrode 5088 Koslow Scientific Company USA.), filled with 5 mol/dm³ KOH solution at 25 °C (the potential of the electrode reaction $E_r = +0.085$ V vs. SHE) was used in all electrochemical experiments. The counter electrode was a cylindrically bent high-purity iron plate that fitted precisely into the double-walled polypropylene cell container. 45 m/m% aqueous NaOH (Sigma-Aldrich, reagent grade) solutions were used as the electrolyte solution for the experiments. The temperature (T) of the electrolyte was (30.0 ± 0.2) °C (set by a LAUDA RE 106 Refrigerating Circulator Chiller and measured by an electronic thermometer). In the dual dynamic voltammetric studies we used a specially modified AFRDE 5 Pine bipotentiostat [9] and a four-electrode cell arrangement, consisting of one reference electrode, a counter electrode and two working electrodes, i.e., the disk (made of high purity iron (Alfa Aesar, 99.98%) or high-purity platinum (PINE)) and the ring (made of high-purity platinum) of an RRDE tip rotated at 1200 rpm using a PINE AFMSRCE rotator. The scan rate of the electrode potential was 200 mV/s for the disk electrode and 0.5 mV/s for the ring electrode. The disk and ring were polished using 1 μm and 0.1 μm diamond suspension, rinsed in high purity water and dried before

each experiment. The added sodium-ferrate solutions were prepared from a stock solution produced electrochemically in a specially designed electrochemical synthesis cell [10,11,12], and their concentrations were determined using a Shimadzu UV Mini-1240 spectrophotometer. To determine the effective current of ferrate formation and current efficiency, the average ring current was calculated in the ring potential range $E_r = 0.05$ V – 0.15 V vs. Hg/HgO (5 mol/dm³ KOH). The effective current of ferrate formation at the disk in the potential range $E_d = 0.4$ V – 0.8 V vs. Hg/HgO was determined using this value, the ring current corresponding to the disk potential $E_d = 0.4$ V vs. Hg/HgO, and the collection efficiency of the RRDE ($N = 0.2555$).

3. Results and discussion

Fig. 2 shows the results of a dual dynamic voltammetry experiment with an RRDE, i.e., a very slow polarization of the disk electrode is coupled with the “fast” polarization of the ring electrode. In the main figure (a) the relevant part of the voltammogram recorded at the iron disk at 30 °C between –0.8 and 0.8 V vs. Hg/HgO at a potential sweep rate of 0.5 mV/s (“slow polarization”) is shown. Cyclic voltammograms recorded at a sweep rate of 200 mV/s (“fast polarization”) at the platinum ring electrode during the slow polarization of the disk electrode are presented in the inset (b). The current densities at the disk and at the ring are denoted by j_d and j_r , respectively. As it can be seen in the figure, as long as only a small anodic current (resulting mainly from the anodic dissolution of iron in the form of Fe(III)) flows on the disk (up to about $E \approx 0.5$ V vs. Hg/HgO, i.e. in the potential range more negative than the potential corresponding to point a in Fig. 2a), the shapes of the CV-s recorded at the ring (Fig. 2b) practically do not depend on the potential of the disk. When the potential of the disk electrode changes further in the positive direction (a → c in Fig. 2a), i.e., at more positive potentials than the “onset of product formation”, a rapid increase of the

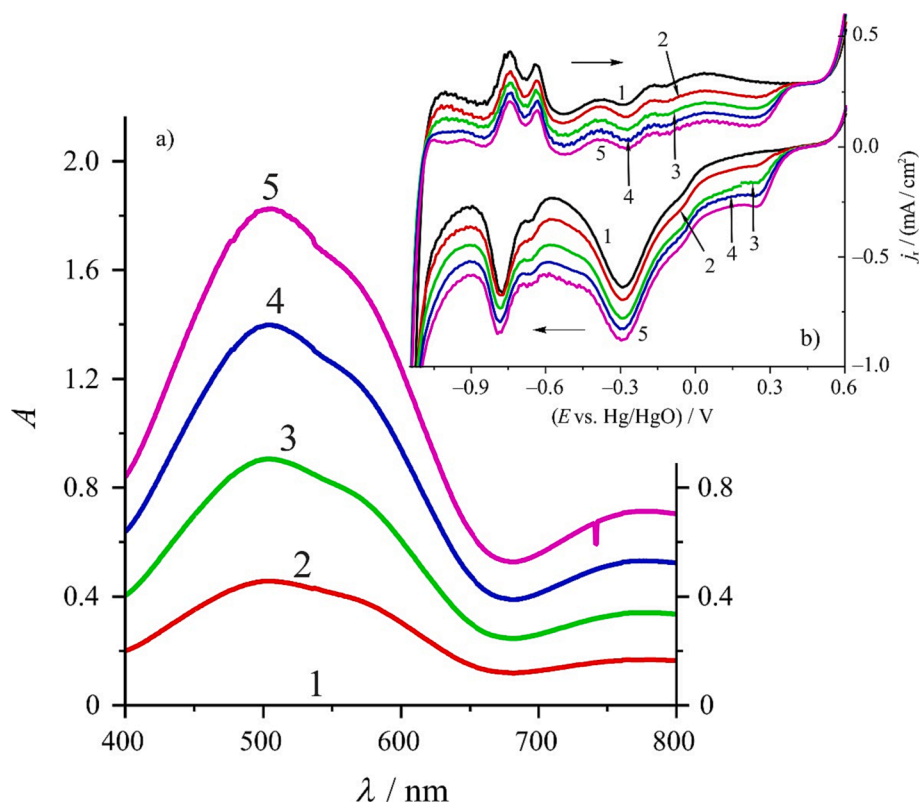


Fig. 4. A) vis spectra of 45 m/m% aqueous NaOH solution, and VIS spectra of the resulting solutions after adding sodium ferrate to the solution in four steps at 30 °C. The concentration of the FeO_4^{2-} ions: (1) $0 \text{ mol}\cdot\text{dm}^{-3}$, (2) $3.95\cdot 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, (3) $7.84\cdot 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, (4) $1.21\cdot 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, (5) $1.28\cdot 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, respectively. λ is the wavelength of light. b) The voltammograms recorded at the platinum ring of the RRDE in the above solutions. Experimental conditions were the same as those given in Fig. 2.

anodic current can be observed, which indicates the start of ferrate ion formation and/or oxygen evolution. Parallel to this, at ring potentials of about $E_r < 0.4 \text{ V}$ the ring CV currents shift in the negative direction (a \rightarrow c in Fig. 2b), indicating that electroactive species are being reduced at the ring. At $E_r < 0.30 \text{ V}$ the shift in current density is almost the same at all potentials. At even more positive disk potentials (e.g., c \rightarrow d in Fig. 2a), while the anodic current on the disk increases practically exponentially, the currents measured on the ring change only to a lesser extent (c \rightarrow d in Fig. 2b).

Due to the composition of the system, the electroactive substance that can be reduced at the ring can be either oxygen or the product of iron dissolution (mainly ferrate ions), or both. The fact that the reduction of the electroactive substance formed on the disk begins at $E_r \approx 0.4 \text{ V}$, and that the significant increase in the disk current with a positive change in the disk potential is not followed by the increase in the ring current, indicates that the reduction of oxygen on the ring takes place to a limited extent at most.

To determine the species that is responsible for the reduction current at the Pt ring, and to verify the above assumption dual dynamic voltammetric RRDE measurements were carried out by using a disk on which oxygen can evolve, but ferrate ions cannot form. The following procedure was followed: In the RRDE tip, we replaced the iron disk with a platinum disk of the same size. All other features of the experimental setup remained unchanged, including the potential limits and scan rates selected for the voltammetric measurements with the iron disk/platinum ring RRDE. In this system, the formation of ferrate ions is obviously not possible, the current flowing through the Pt disk can only be the result of oxygen evolution. So, what we experience on the Pt ring can only be linked to the reduction of the evolving oxygen. The results obtained with the Pt/Pt RRDE tip are shown in Fig. 3.

From the voltammetric curves presented in Fig. 3 it is clearly visible,

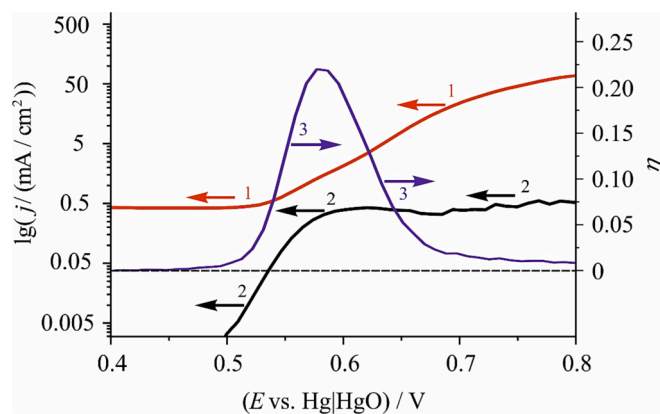


Fig. 5. The logarithm of the total disk current density (1), the logarithm of the effective current density of the ferrate ion formation at the disk (2), and the current efficiency (3) determined at $T = 30 \text{ °C}$.

that despite the high anodic current that can be measured on the disk in a wide potential range, the shape of the cyclic voltammograms recorded on the ring is practically independent of the disk potential. This implies that the O_2 formed at the disk cannot be reduced at the ring. This phenomenon can probably be explained by the fact that elemental oxygen practically does not dissolve in concentrated aqueous sodium hydroxide solutions (according to the relevant literature [13,14], c_{O_2} clearly decreases strongly with an increase in the NaOH concentration due to the “salting-out effect”). Hence, the cathodic (reduction) ring current observed in the case of the iron disk electrode (Fig. 2) can only be attributed to the reduction of ferrate ions.

In order to prove that the ferrate ions are indeed reduced on the

platinum ring, the following experiments were performed: By immersing the RRDE tip in 45 m/m% aqueous NaOH solutions containing ferrate ions at different concentrations, cyclic voltammograms were recorded at the Pt ring in the same potential range and at the same potential sweep rate as in the previous experiments. The concentration of ferrate ions in the solutions was determined by spectrophotometry (Fig. 4a) using the molar absorption coefficient $\epsilon(\lambda = 508\text{--}510\text{ nm}) = 1150\text{ M}^{-1}\cdot\text{cm}^{-1}$ [15,16]. It is clearly visible that the shapes of the cyclic voltammograms in Fig. 4b are very similar to those recorded at the Pt ring during the DDV measurements (Fig. 2b). This and the gradual negative shift of the CV-s (i.e., the CV currents) strongly indicate that the electroactive species being reduced on the ring in the DDV experiments is the ferrate ion.

The capabilities of the dual dynamic voltammetric method can be well illustrated with the help of Fig. 5, which shows the effective current density of the ferrate ions formed at the disk and the potential dependence of the current efficiency (η) [17]. From the point of view of economics of practical applications (e.g., in electrolysis equipment), knowledge of the latter quantity is of fundamental importance. Based on Fig. 5, it can be concluded that the electrode potential range between 0.58 V and 0.60 V vs. Hg/HgO seems optimal for the electrochemical production of ferrate ions from the point of view of current (charge) efficiency. This is also confirmed by the examination of the effective current of the formation of ferrate ions, since its value increases only slightly (if at all) even if the electrode potential of the disk is further changed in the positive direction.

4. Conclusions

The experimental results confirmed the expectations that dual dynamic voltammetry can be a good choice for studying the mechanisms of the production of ferrate ions. Although during the transpassive anodic dissolution of iron, the formation of ferrate ions and the evolution of oxygen occur simultaneously, and only the sum of the currents generated by the two processes can be observed in the voltammetric curves, by using Fe disk/Pt ring and Pt disk/Pt ring RRDE tips it was possible to determine the negative limit of the electrode potential range where ferrate ions are forming in 45 % (m/m) aqueous NaOH solution at $T = 30\text{ }^\circ\text{C}$: “the onset potential for ferrate ion formation” is $E \approx 0.5\text{ V}$ vs. Hg/HgO (5 mol/dm³ KOH). Of course, this value can be obtained in the same way as described in this study at other temperatures and in other electrolyte solutions. According to the voltammetric results the oxygen formed at the disk cannot be detected (reduced) at the ring. This phenomenon may be explained by the “salting-out effect” (namely the oxygen molecules are driven to the gas phase due to the high concentration of NaOH in the solution). Even though this goes beyond the scope of the present short communication, it is important to note that the method also provides an opportunity to determine the ratio of the amounts of the two products (ferrate ions and oxygen), as well as to select the most optimal temperature for the operation of a reactor designed for the electrochemical production of ferrate ions. According to the results, in terms of charging efficiency, the optimal range of the electrode potential for the electrochemical production of ferrate ions is between 0.58 V and 0.60 V vs. Hg/HgO.

CRedit authorship contribution statement

Ábel Zsubrits: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. **Miklós Kuti:** Investigation, Resources, Funding acquisition. **Éva Fekete:** Investigation, Resources. **Mária Ujvári:** Investigation, Resources, Project administration. **Győző G. Láng:** Conceptualization, Methodology, Validation, Supervision, Formal analysis, Writing – original draft, Visualization, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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