Electrochemical Synthesis of Ferrate (VI) by Regular Anodic Replacement

Hongyu Wang1,*, Yibing Liu1, Fancheng Zeng1, Shuang Song2*

1 School of civil Engineering and Architecture, Zhejiang University of Technology, Hangzhou 310014, China
2 College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310014, China
*E-mail: hywang@zjut.edu.cn, ss@zjut.edu.cn

Received: 1 July 2015 / Accepted: 20 July 2015 / Published: 26 August 2015

Ferrate (VI) is a green water treatment agent which possesses the function of oxidation, disinfection and coagulation. Electrochemical generation of ferrate (VI) by replacing anode regularly was studied in different models of a two-compartment batch electrochemical reactor at a laboratory scale. Different ways of replacing anode were compared and the resulting performance was discussed. Results show that replacing anode regularly can improve the ferrate (VI) generation obviously and replacing method 1 (replacing at 1h, 3h, 4h, 5h) is better than method 2 (replacing at 2h, 4h, 5h). Besides, the ratio of effective surface area of anode to the anolyte volume (S/V) was found interacted with current density (j) and had impact on the ferrate (VI) production in a same reactor. In the experiment, the resulting sodium ferrate (VI) can reach 0.39 M for the conditions found from this study: the electrolyte of 17 M NaOH, the thermostatic bath temperature of 13 °C, the reaction time of 3 h, the anodic replacement mode of method 1, the S/V value of 2.484 l/cm, the j of 33.8 mA/cm².

**Keywords:** Sodium ferrate (VI); anodic replacement; electrochemical synthesis; concentration; current efficiency

1. INTRODUCTION

As the formula FeO₄²⁻, ferrate (VI) is a powerful purifier reagent with the high oxidation potential of 2.2 ev in acidic solutions [1, 2]. As a result, ferrate (VI) can be used in a wide range of applications: the removal of water pollutants [3-6], the disintegration of sludge [7], the disinfection of water [8]. In addition, Fe (III) ions or ferric hydroxide as non-toxic by-products make ferrate (VI) an
environmentally friendly reagent [9] and the form of Fe (III) ions or ferric hydroxide during ferrate (VI) oxidation/disinfection also can contribute to the increase of flocculation process [10].

Thermal oxidation, wet oxidation by oxidising ferric salts in strong alkaline conditions and electrochemical method are the three main synthetic methods [1, 11]. The electrochemical synthesis is more promising than other methods, using an electron as a so-called clean chemical to get the high purity of the product [11, 12]. It needs not very high operating temperature and harmful chemicals, and thus can reduce energy consumption and the potential deleterious effects. In the previous studies, researchers used many methods to get a high ferrate (VI) concentration, such as the application of anode with different compositions [13-15], the exploration of auxiliary means [16, 17], the use of molten electrolyte [18, 19] and the pretreatment of electrode [20]. However, to the best of our knowledge, almost no research has been conducted to explore the effect of regular replacement of iron anode on the electro-generation of ferrate (VI).

The study focused on the electrochemical synthesis of ferrate (VI) by replacing iron anode regularly. Different ways of replacing anode were investigated. Meanwhile, a snowball effect related to ferric hydroxide was defined and the interaction of the ratio of effective surface area of anode to the electrolyte volume (S/V) and current density was also investigated to enhance the concentration of the resulting ferrate (VI).

2. EXPERIMENTAL AND METHODS

2.1. Materials and reagents

Iron mesh (99.9% in purity) was obtained from Hangzhou Longyun Metal Mesh Co. Ltd. Titanium plate was obtained from Ou Difu Material Co. Ltd. Sodium hydroxide (AR) were purchased from Hangzhou Xiaoshan Chemical Reagent Factory, which contained the following maximum impurity concentrations (in wt%): Cl\(^-\), 0.005; SO\(_4^{2-}\), 0.005; PO\(_4^{3-}\), 0.001; total nitrogen, 0.001; sodium carbonate, 0.015. Other chemicals and reagents used were obtained from Shanghai pharmaceuticals holding co. Ltd.

Before each run, iron and titanium electrodes were pre-treated via 5 steps, namely; pickling with hydrochloric acid, washing with sodium hydroxide, washing with water, drying, polishing into bright surface. After a period of use, the ion exchange membrane could be regenerated by pickling and washing with acid/base and water.

2.2. Electrochemical cells

Three different models had been developed for a two-compartment batch electrochemical reactor. Iron mesh was used as anode and titanium sheet as cathode. An ion exchange membrane (IONSEP-HC-06, HangZhou iontech Environmental Technology Co., Ltd., China) was used to separate the compartments. The reactor of model 1 was a Pyrex glass electrochemical reactor, comprised of two separate cylindrical half-cells. The diameters of anode and cathode chamber were 50
mm and 60 mm, respectively. The reactor of model 2 was made of organic glass and had two rectangular electrode chambers. The dimensions of anode and cathode chamber were 101 mm × 26 mm × 98 mm and 101 mm × 76 mm × 98 mm, respectively. The electrode gap of model 1 and model 2 were 36 mm and 22 mm, respectively. Model 3 had the same material and form as model 2 except that the anodic chamber size was 101 mm × 11 mm × 98 mm. The applied currents were controlled using a DC power supply (SK1760SL20A, Sanko Electric Appliance Co. LTD., Japan). A thermostatic bath (THD-2015, Ningbo Tianheng Instrument Factory, China) was used to control electrolysis cell temperature.

2.3. Analytical methods

The chromite method [21] was selected for analyzing the concentration of ferrate (VI). The total iron content was evaluated by measuring the absorbance at 510 nm of the Fe(II)-l, 10-phenanthroline complex [22].

The current efficiency (CE) was calculated based on the ratio of the experimentally produced ferrate (VI) to the theoretical amount of ferrate (VI) calculated by Faraday's law:

\[
\text{Current efficiency (CE)} = \left( \frac{\text{Ferrate}_{ep}}{\text{Ferrate}_{io}} \right) \times 100\% \quad (1)
\]

The Ferrate_{ep} is calculated by:

\[
\text{Ferrate}_{ep} = M \cdot c \quad (2)
\]

The Ferrate_{io} is calculated by:

\[
\text{Ferrate}_{io} = \frac{M \cdot I \cdot t}{z \cdot F} \quad (3)
\]

Where Ferrate_{io} is the amount of ferrate (VI) produced by Faraday's law (g), Ferrate_{ep} is the amount of ferrate (VI) obtained experimentally (g), c is the ferrate (VI) concentration (M) obtained, v is the anolyte volume (l), I is the applied current intensity (A), t is the time from beginning to each sample time (s), M is the molecular weight of Fe (56 g/mol), F is the Faraday constant (96,485 C/mol), z is the number of electrons involved in the reaction.

3. RESULTS AND DISCUSSION

Fig. 1 shows the variation of the ferrate (VI) concentration and CE with the time on regular anodic replacement and the conventional reaction. As it can be observed, a difference of ferrate (VI) concentration begins to appear from the anodic replacement at 2 h and the ferrate (VI) concentration of the anodic replacement increases by 32.75% within 2 h, indicating that regular replacement of the anode can significantly promote the ferrate (VI) concentration. An obvious rise of CE is also observed after the anodic replacement and it is the reason of the higher ferrate (VI) concentration. According to the literature [23], a passivating layer would form inevitably which prevents further ferrate (VI) generation. The replacement of iron anode can make electrolyte react with Fe continuously to lessen
the influence of anode passivation. Compared with the usage of anisomeric square pulse [24], ultrasonic [25] and sinusoidal alternating current [26], regular anodic replacement is also an effective method of getting a higher ferrate (VI) concentration.

![Graph showing ferrate (VI) concentration and current efficiency variation with time on regular anodic replacement and the conventional reaction.](image)

**Figure 1.** Variation of the ferrate (VI) concentration and current efficiency with time on regular anodic replacement and the conventional reaction, at the conditions: anolyte 172 ml, catholyte 300 ml, iron mesh electrode (effective area of 27.62 cm²), current of 4.2 A, electrolyte of 17 M NaOH, thermostatic bath temperature of 40 °C, model 1. The replacement of iron mesh on 2, 3, 4, 5 h and the conventional had no anodic replacement.

The way of regular anodic replacement was first studied using method 1 (replacement of iron mesh on the 1, 3, 4, 5, 6 h) and method 2 (replacement of iron mesh on the 2, 4, 5 h) for comparison. Fig. 2 shows the variation of the ferrate (VI) concentration with time on method 1, method 2 and the control group. It can be observed that method 1 has the best performance; the optimal ferrate (VI) concentration was the highest (0.24 M) and the decay time was the latest (5 h). The control group was by far less efficient than the other two methods, only 0.12 M ferrate (VI) concentration was produced with a relatively early decay time of 2 h. The results mean that the replacement of anode regularly can dramatically improve the ferrate (VI) concentration by electrochemical synthesis and the way of replacement has an important influence on the yield.
Figure 2. Variation of the ferrate (VI) concentration with time on method 1, method 2 and the control group, at the conditions: anolyte 250 ml, catholyte 618 ml, 4 iron mesh electrodes (single effective area of 62.1 cm²), current of 8.4 A, electrolyte of 17 M NaOH, thermostatic bath temperature of 25 °C, model 2. Method 1 had anodic replacement on 1, 3, 4, 5 h, method 2 had on 2, 4 h and the control group had no anodic replacement.

Fig. 3 shows the variation of the current efficiency with time on the above three ways. It can be seen that method 1 has the best performance of CE in the whole process, contributing to the highest concentration. The better results of method 1 and method 2 than the control group during a same time period suggest that anodic replacement can accelerate the rate of ferrate (VI) generation. The CE of all groups drops from an initial value of 40.01% at 1 h to 10.61-17.5% during a 4-6 h electrolysis, which is consistent with the results of ferrate (VI) concentration time curves in Fig. 2. and other literatures [27, 28]. Generally, the decomposition rate and amount of ferrate(VI) [29] or the reduction of electrolyte would increase with the time prolonged during a continuous electro-synthesis of ferrate(VI), and CE is expected to decrease. Reasons for the above phenomena that results varied with the ways of anodic replacement were analyzed and the snowball effect which was related to ferric hydroxide was defined. Known from the literatures [28, 30-33], ferric hydroxide can catalyze the self-decomposition of ferrate (VI). Accompanied by the generation, ferrate (VI) ions undergo the spontaneous decomposition proceeding with the Eq. (4).

$$2\text{FeO}_4^{2-} + 5\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 \downarrow + 4\text{OH}^- + (3/2)\text{O}_2 \uparrow \quad (4)$$

Ferric hydroxide is produced and then catalyze the decomposition of ferrate (VI), making the more generation of ferric hydroxide to promote the more catalytic decomposition of ferrate (VI), just liking a snowball effect and having a growing influence on the yield of ferrate (VI). Thus the
continuous catalytic decomposition of ferrate (VI) caused by ferric hydroxide was defined as the snowball effect. Without taking into account other factors, when the decomposition quantity of ferrate (VI) caused by ferric hydroxide is equal to the amount generated, the concentration of ferrate (VI) reaches the maximum value, and if continue it declines.

![Graph](image)

**Figure 3.** Variation of the current efficiency with time on method 1, method 2 and the control group, at the conditions: anolyte 250 ml, catholyte 618 ml, 4 iron mesh electrodes (single effective area of 62.1 cm²), current of 8.4 A, electrolyte of 17 M NaOH, thermostatic bath temperature of 25 °C, model 2. Method 1 had anodic replacement on 1, 3, 4, 5 h, method 2 had on 2, 4 h and the control group had no anodic replacement.

The performance of all methods also can be analyzed by the snowball effect in Fig. 2. Conditions are most suitable for generating ferrate (VI) during the initial period, leading a massive production of ferrate (VI) along with the formation of ferric hydroxide. Meanwhile the passive layer grows gradually to prevent the generation of ferrate (VI) and the irreversible oxygen evolution reaction (OER) (Eq. (5)) would become dominant under the same current, consuming more hydroxyl ions and electricity to decrease the current efficiency.

\[
4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 4\text{e}^- + \text{O}_2 \uparrow \tag{5}
\]

The serious OER may promote the decomposition of ferrate (VI) by the overflow and rupture of oxygen bubbles. The earlier anodic replacement makes the cumulative amount of ferric hydroxide in method 1 is less than that in method 2. According to the snowball effect, more ferric hydroxide formation would catalytically result in more decomposition of ferrate (VI) and then a lower concentration. Another possible reason also needs to be pointed out that the longer dominant OER means the less ferrate (VI) generation occurs in the same period. On the premise of other equal conditions, the maximum rate of ferrate (VI) generation is considered to be consistent. Therefore the gap of ferrate (VI) concentration is always there, as shown in Figure 2. Besides, the more hydroxyl ions consume by the OER also should be considered.

Fig. 4 shows the variation of the concentration of ferrate (VI) and total iron, the ratio of ferrate (VI) to total iron with time on method 1. The overall reaction is showed as follow:
Fe + 2H_2O + 2OH^- → FeO_4^{2-} + 3H_2↑ \hspace{1cm} (6)

Taken together with Eq. (4) and Eq. (6), the possible direct formation of ferric hydroxide in the electrolysis is ignored, that is to say, all ferric hydroxide generated is assumed to come from the decomposition of ferrate (VI). As it can be observed, the total iron concentration increases homogeneously but the ratio of ferrate (VI) decreases in a gathering pace, which shows a serious decomposition of ferrate (VI) happens. Accompanied by the more generation of ferric hydroxide, the catalytic effect on the degradation of ferrate (VI) would be much stronger, just like the snowball effect. It is important to remark that the catalytic effect is not the only factor affecting the ferrate (VI) concentration, others are the rising concentration of ferrate (VI) generated [30, 34] and the consumption of hydroxyl ions. The decline of ferrate (VI) concentration (when the ratio is less than 67%) suggests the decomposition of ferrate (VI) begins to be superior to the formation during the same period. In a past research, He et al. [35] removed the ferric hydroxide generated in midway of the preparation and obtained a concentration of 0.83 M. Jeżowska-Trzebiatowska and co-workers observed that the reaction order of the ferrate (VI) decomposition was halved, after precipitation of some ferric hydroxide from solution [31].

![Figure 4](image_url)

**Figure 4.** Variation of the concentration of ferrate (VI) and total iron, the ratio of ferrate (VI) to total iron with time on method 1, at the conditions: anolyte 250 ml, catholyte 618 ml, 4 iron mesh electrodes (single effective area of 62.1 cm²), current of 8.4 A, electrolyte of 17 M NaOH, thermostatic bath temperature of 25 °C, model 2, the anodic replacement on 1, 3, 4, 5 h.

The snowball effect correlates with other optimized experimental conditions in this experiment. Fig. 5 shows the variation of the concentration of ferrate (VI) and the CE in the first two hours with the different thermostatic bath temperatures on model 2. It can be observed that the temperature of 25 °C has the best performance of ferrate (VI) concentration at the second hour, although it is worst at the first hour. On the whole, the optimal temperature of the first hour is in the range of 30 °C to 35 °C, which is close to the literature [14, 36, 37]. By contrast, the performance of the second hour decreases with the increase of temperature. The abrupt change of the CE in the second hour is the main reason. The high temperature can promote the generation and the decomposition of ferrate (VI)
simultaneously. With the more ferrate (VI) generation of the first hour in a high temperature (30 °C ~35 °C), more ferric hydroxide is produced which accelerates the decomposition of ferrate (VI). The maximum ferrate (VI) concentration would reach when the rate of decomposition is equal to that of formation. When continuing to the temperature of 40 °C, the snowball effect would exacerbate the decomposition and lead to a low concentration. In the electrochemical synthesis, the reduction of ferrate (VI) decomposition can improve the ferrate (VI) production and eliminate the energy waste. Thus a relatively low temperature is suggested in long process of preparation for high ferrate (VI) concentration. In view of the high local heat surrounding in the anodes when high current passes through, especially in long process of preparation with a relatively high temperature, the low current (or low current density) is also recommended for the high ferrate (VI) yield as the previous work disclosed; e.g., He et al. [29] obtained at $j=4.3 \text{ mA/cm}^2$ and Jiang et al. [38] at $j=3.6 \text{ mA/cm}^2$.

**Figure 5.** Variation of the concentration of ferrate (VI) and the current efficiency in the first two hours with different thermostatic bath temperatures in model 2, at the conditions: anolyte 250 ml, catholyte 618 ml, 4 iron mesh electrodes (single effective area of 62.1 cm$^2$), current of 8.4 A, electrolyte of 17 M NaOH.

Both the reaction surface area of anode ($s$) and the volume of electrolyte in anode chamber ($v$) determine the concentration of ferrate (VI). According to the literature [29], $S/V$ was associated with the ferrate (VI) concentration during electrolysis closely. In this work, the interaction of $S/V$ and current density ($j$) on ferrate (VI) concentration was found in the same reactor. Fig. 6 shows the variation of the ferrate (VI) concentration of one hour with the $S/V$ and $j$ in model 2. As it can be observed, the optimal point was at $j=33.8 \text{ mA/cm}^2$, $S/V=0.99 \text{l/cm}$ and the ferrate (VI) concentration is not always increased with the $S/V$. It could be explained that an increase in $s$ would cause a decrease in $j$ inevitably in the same reactor. The point comes when the increase of ferrate (VI) concentration with $S/V$ is equal to the negative effect on ferrate (VI) concentration of the decrease in $j$. It should be noted that the $j$ (33.8 mA/cm$^2$) of the optimal point in Fig. 6 is not in contradiction with the above suggested $j$. For short electrolysis of ferrate (VI) preparation ($\leq 1 \text{ h}$ in this work), the formation of ferric
hydroxide is so limited that it would not have a decisive effect on ferrate (VI) concentration when a relatively high $j$ is applied.

**Figure 6.** Variation of the ferrate (VI) concentration with the $S/V$ and current density ($j$) in model 2, at the conditions: anolyte 250 ml, catholyte 618 ml, iron mesh electrode (effective area of 62.1 cm$^2$), current of 8.4 A, electrolyte of 17 M NaOH, thermostatic bath temperature of 35 °C, the reaction time of 1 h.

**Figure 7.** Variation of the ferrate (VI) concentration with time in model 3, at the conditions: anolyte 100 ml, catholyte 500 ml, 4 iron mesh electrodes (single effective area of 62.1 cm$^2$), current of 8.4 A, thermostatic bath temperature of 13 °C, electrolyte of 17 M NaOH, the anodic replacement on 1, 3, 4 h.
Besides, if the $S/V$ value increases with a constant $j$ by adding the current, more energy would consume. However, the increase of $S/V$ by reducing the $v$ with a constant $j$ usually means a new reactor is needed. In this work, model 3 which had a smaller anodic chamber than model 2 was used for the generation of ferrate (VI). Fig. 7 shows the variation of the ferrate (VI) concentration with time in model 3 at the $S/V$ of 2.484 1/cm, the thermostatic bath temperature of 13 °C and the method 1 of anodic replacement. As it can be observed, a ferrate (VI) concentration of 0.39 M is obtained at 3 h. The result indicates that the ferrate (VI) concentration can be further improved when the regular anodic replacement and other factors are considered synthetically.

4. CONCLUSIONS

In this study, the beneficial effect of the regular anodic replacement on the improvement of ferrate (VI) production by electrochemical synthesis has been demonstrated. The method 1 of anodic replacement achieved the best ferrate(VI) production performance for below operating conditions:

- the electrolyte of 17 M NaOH with 100 ml of anolyte and 500 ml of catholyte, the anode of 4 iron meshes (the effective area of 62.1 cm$^2$), the thermostatic bath temperature of 13 °C, the $j$ of 33.8 mA/cm$^2$, the $S/V$ of 2.484 1/cm (reduce the $v$ by using model 3). Result showed the optimal ferrate (VI) concentration of 0.39 M was obtained for 3 hours.

The snowball effect (the continuous catalytic effect of ferric hydroxide) was considered to be the main reason for the degradation of ferrate (VI) in the production process. The effect of $S/V$ and current density ($j$) on the resulting ferrate (VI) concentration was found. It should be noted that various factors can have an important impact on the ferrate (VI) generation. Thus, it might be interesting to use porous electrodes [14] and an electrochemical cell with two cathode chambers [29] to obtain a higher ferrate (VI) concentration.

ACKNOWLEDGMENTS
The study was supported by Natural Science Foundation of China (NO.21376219).

References


© 2015 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).