Electrochemical Synthesis of Ferrate (VI): Factors Influencing Synthesis and Current Research Trends

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ARTICLE INFO	ABSTRACT
	Ferrate (VI) emerges as a multifaceted substance endowed with a substantial redox potential, showcasing considerable potential for utilization in realms such as battery materials and advancements in water treatment technologies. There are primarily three methods for preparing Ferrate (VI), including peroxide heating method, hypochlorite oxidation method and electrochemical synthesis method. This review centrally delves into the electrochemical synthesis of Ferrate (VI), given its mild reaction conditions, emerges as a highly potent means to synthesize Ferrate (VI) with substantial potential for industrial applications. The intricacies of influencing factors, including anode materials, electrolyte composition, electrolyte additives, reaction temperature, current density, membranes (ion-exchange membranes), and reactor types, are meticulously detailed, all of which exert a discernible influence on the synthesis process. A comprehensive exposition of the current research landscape and prevailing trends in the electrochemical synthesis of Ferrate (VI) is presented. However, the current discourse on the electrochemical synthesis of Ferrate (VI) remains insufficient. Addressing these issues not only demands the optimization of reaction conditions but also necessitates the exploration of novel methodologies. For instance, incorporating the contextual application of Ferrate (VI) and achieving in-situ synthesis for immediate utilization are pivotal directions for future research and development.

1. Introduction

Ferrate (FeO_4^{2-}) refers to oxygen-containing salts of iron in its highest oxidation state of +6. The oxidation state of iron can be changed by a discharge reaction involving the transfer of 3 electrons. High-valence iron salts exist in various forms, including K_2FeO_4, $BaFeO_4$ [1], Ag_2FeO_4 [2], Cs_2FeO_4, Li_2FeO_4, Rb_2FeO_4, $SrFeO_4$ [3] etc. This compound not only be used as electrode material in batteries, forming "super iron batteries" [4,5], but also as a class of high-performance green, strong oxidants. FeO_4^{2-} itself has a tetrahedral structure [6], with the iron atom at the center of the tetrahedron. Four

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oxygen atoms are located at the four corners of the tetrahedron. This enables high-valence iron salts to decompose in aqueous solutions, releasing oxygen, and the generated $Fe(OH)_3$ also has a coagulation effect. Therefore, high-valence iron salts have been extensively studied and applied as a new type of efficient and multifunctional water treatment agent. Possessing characteristics such as oxidation, adsorption, coagulation, and sterilization [7-9]. Furthermore, the application of high-valence iron salts is still expanding and being deeply researched [10-14].

The preparation methods of Ferrate (VI) mainly include three types: Peroxide heating method (Dry or melt method) [15,16], Hypochlorite oxidation method (Wet or chemical method) [17-20] and Electrochemical method [21-24].

The peroxide heating method (dry or melt method) involves the synthesis of ferrates through high-temperature solid-phase (or molten-phase) reactions, where compounds that can decompose into oxidizing substances under oxidative or high-temperature conditions, such as $NaNO_3$ and KNO_3 [25] and Na_2O_2 [26] etc, reacted with iron-containing compounds or iron itself in the presence of alkali. This method requires high reaction temperatures, resulting in lower product purity, necessitating subsequent purification. Also, it demands strict control over operating conditions due to its high-risk nature. The reaction process can be described as Eq. (1) and Eq. (2):

$$2FeSO_4 + 6Na_2O_2 \rightarrow 2Na_2FeO_4 + 2Na_2O + 2Na_2SO_4 + O_2 \tag{1}$$

$$Na_2FeO_4 + 2KOH \rightarrow K_2FeO_4 + 2NaOH \tag{2}$$

The hypochlorite oxidation method (wet or chemical method) involves reacting iron salts with sodium hypochlorite [7,27,28] or Cl_2 [2,29] in alkaline solutions to oxidize Fe (III) salts to Fe (VI) salts. Despite its seemingly simple nature, the operational procedure was intricate, requiring subsequent crystallization and purification. However, this approach involved the utilization of toxic chlorine, resulting in substantial environmental pollution. The reaction process can be depicted using the following reactions Eq. (3) and Eq. (4):

$$Cl_2 + 2KOH \rightarrow KClO + KCl + H_2O \tag{3}$$

$$2Fe(NO_3)_3 + 3KClO + 10KOH \rightarrow 2K_2FeO_4 + 3KCl + 6KNO_3 + 5H_2O \tag{4}$$

Electrochemical synthesis method refers to the process of using iron or inert electrodes as anodes to oxidize low-valence iron to Fe (VI) in concentrated alkaline solutions. There are two process routes in the electrolysis method: one involves the production of liquid high-valence iron salt products [21,22,30-34]; the other involves the direct electro-synthesis of solid Ferrate (VI) products in a molten alkaline system [35,36]. The reaction occurring at the anode was depicted as Eq. (5):

$$Fe + 8OH^- \rightarrow FeO_4^{2-} + 6e^- \tag{5}$$

The electrochemical approach effectively addresses the issue of low stability in K_2FeO_4 solution under alkaline conditions [37]. Perez-Sicairos [38] compared the effectiveness of electrochemically synthesized Ferrate (VI) with commercially available ones for wastewater treatment, indicating superior performance of the electrochemical method. This approach offered advantages such as mild preparation, simple operation, and rapid reactions. However, when maintaining higher current density and longer electrolysis times, challenges remain, including anode passivation, separation, and

purification of Ferrate (VI) [27], addressing issues related to product yield and purity.

To sum up, this overview discusses the influencing factors in the electrochemical synthesis of Ferrate (VI), encompassing anode materials, electrolyte composition, additives in electrolyte, reaction temperature, current density, membranes (ion-exchange membranes), and reactor types. These factors play a pivotal role in the electrochemical synthesis of Ferrate (VI), impacting the quality and yield of the resulting products.

2. Factors of Ferrate (VI) Electrochemical Synthesis
2.1 Anode Materials

In the context of electrochemical FeO_4^{2-} synthesis, the anode plays a pivotal role as both an electron acceptor and a source of iron ions. Concerning anode materials, a diverse range of iron-containing electrodes have been widely employed, subsequently giving rise to the application of carrier electrodes. These iron-containing electrodes encompass various forms of iron, including pure iron [39-41], iron alloys (such as carbon steel [40,41], silicon iron [39-41]), and iron compounds [42], contingent on their composition. Structural variations also encompass configurations like iron blocks [43,44], iron wire mesh [33,45], iron powder [46], and sponge iron [47]. Concurrently, as an emerging realm of study, carrier electrodes have found utility in the electrochemical synthesis of FeO_4^{2-}, employing direct electrolysis [48] or iron loading [23].

Attempts to employ pure iron as an electrode for Ferrate (VI) have been studied; however, pure iron electrodes are susceptible to surface passivation [49]. Hence, alloy materials are chosen as electrodes to overcome this issue. Denvir A *et al.,* [33] investigated the effect of carbon content in anode steel on the electrochemical production efficiency of FeO_4^{2-} and found that the current efficiency of FeO_4^{2-} formation significantly increases with higher carbon content in the alloy. An initial current efficiency exceeding 70% was achieved for an alloy with 0.90% carbon. The presence of carbide iron (Fe_3C) increases with higher carbon content in the anode material, leading to elevated surface porosity and defect density. M. Alsheyab [50] studied three types of steel with carbon contents of 0.10%, 0.11%, and 0.12%, revealing that the electrode with 0.11% carbon content exhibited the highest current efficiency. Research has also been conducted on silicon-containing iron materials as electrodes [22,51]. Shang [52] utilized silicon-rich material (FeSi) with 3.3% silicon as an electrode, achieving a FeO_4^{2-} yield of 236.87 mM and a current efficiency of 45.86% under conditions of 16M NaOH, 35°C, and 1-hour electrolysis. Z. Mácová [53] conducted studies on cast iron rich in carbon and steel rich in silicon, investigating their reaction in different electrolytes. The results indicated that the formation of FeO_4^{2-} on the electrode surface was influenced not only by the electrode surface properties but also by the anodic electrolyte. Both carbon-containing iron electrodes and silicon-rich steel electrodes exhibit similar depassivation effects, albeit the latter requiring lower electrolyte temperature than carbon iron. K. Bouzek, Rousar [54] studied the increase in the concentration of low-oxidation state iron species (FeO_2^-) in the solution as temperature rised during electrochemical synthesis experiments. For white cast iron, this concentration was nearly ten times higher than that reported for gray cast iron. L. Nikolić-Bujanović [32] compared the results of using pure iron, white cast iron (WCI), and gray cast iron (GCI) as electrodes, observing the lowest electrochemical activity for pure iron. The reaction products on WCI and GCI existed in the form of iron (II) iron (III) oxide-silicate hydroxides. K. BOUZEK [55] investigated the non-uniformity of the WCI electrode surface, attributing it to the presence of carbon in the form of graphite, while for GCI, the non-uniformity resulted from a significant amount of Fe_3C in the material structure. Hrnčiarikova [40] studied the passivation behavior of typical electrodes, including pure iron (Fe), silicon-rich steel (FeSi), and white cast iron (FeC). The cyclic voltammetry curves of all anode materials exhibited similar

characteristics, with lag phenomena observed in the displacement potential region. This outcome may be attributed, in part, to the weakening of the desalination inhibitory effect at high potentials and, on the other hand, to mechanical damage to the anode surface caused by the abundant generation of oxygen.

Regarding electrode surface area, iron plates are commonly chosen, and there was also research using iron wires as electrodes [56]. Simultaneously, researchers have also made efforts in expanding the structural aspect of the electrode surface area [57]. Utilizing sponge iron as the anode, compared to gray cast iron anodes, has led to higher Ferrate (VI) yield [47]. De Koninck [46] employed pressed iron powder as an anode for electrochemical synthesis of high-valence iron salt. The porous structure of the iron powder electrode favors iron dissolution, resulting in higher concentrations and yields of electrochemically generated FeO_4^{2-} compared to iron plate electrodes. However, the electrochemical activity thickness of the iron powder electrode is only about 1% of the actual iron powder thickness. Activated electrodes are also a method to enhance anode material efficiency. Pre-treatment of stainless steel electrodes, such as acetone degreasing, silicon carbide polishing, and deionized water rinsing in ultrasonic baths [58], as well as pre-treatment using HCl, can effectively improve their efficiency [59]. The reactions occurring on iron-based electrodes were depicted by Eq. (6) and Eq. (7) [60,61]:

$$Fe + 8OH^- \rightarrow FeO_4^{2-} + 4H_2O + 6e^- \qquad E^0 = -0.8V \text{ vs. SHE} \qquad (6)$$

$$Fe^{3+} + 4H_2O \rightarrow FeO_4^{2-} + 8H^+ + 3e^- \qquad E^0 = -2.2V \text{ vs. SHE} \qquad (7)$$
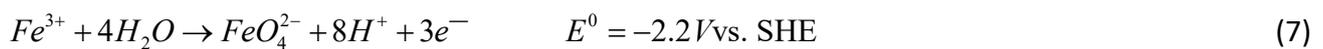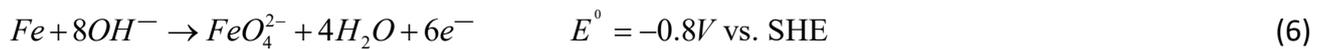
Utilizing carrier electrodes for the electrochemical synthesis of FeO_4^{2-} has opened up a brand-new pathway. These carriers include Pt [53], Au [62], high oxidation potential electrodes (such as SnO_2-Sb_2O_3/Ti [63]), boron-doped diamond (BDD) [64-65], or carbon electrodes [66]. Inorganic carrier electrodes effectively overcome the drawbacks of electrode material reduction and the tendency of iron electrodes to passivate, while also being reusable. Several researchers [31,67] confirmed through cyclic voltammetry that the surface of BDD electrodes can directly generate iron salts through oxidation. This method can directly act on solutions containing iron ions (Fe^{2+}, Fe^{3+}), synthesizing FeO_4^{2-} directly under the influence of an electric field, and the principle of oxidative synthesis on BDD electrodes was proposed as mentioned (Eq. 8 and Eq. 9) [68]. Similar studies have also been conducted.

Direct oxidation at the electrode surface:

$$BDD(Fe^{2+}) + 4H_2O \rightarrow FeO_4^{2-} + 8H^+ + 4e^- \qquad (8)$$

Oxidation by surface OH· radicals at the electrode:

$$BDD(4 \bullet OH) + Fe^{2+} \rightarrow FeO_4^{2-} + 4H^+ \qquad (9)$$

A. Sánchez-Carretero [69] used hematite suspension as a raw material to compare the electrochemical synthesis of FeO_4^{2-} using iron hydroxide and iron powder, similar to a study by Cañizares [64]. The generation of FeO_4^{2-} at the electrode was constrained by the initial material transfer [70,71]. The use of ultrasonic diffusion of precursor substances enhanced mass transfer and promoted the continuous supply of the source iron [23]. The use of ultrasound facilitated the diffusion

and transfer of iron powder material loaded onto inorganic electrode surfaces. Wang [72] studied the combined use of BDD electrodes and Fe(III) for electrochemical selective oxidation and degradation of organic compounds (EOCs), demonstrating that the generation of Fe(IV) and Fe(V) has little impact on the degradation of organic substances. Fe(VI) generation only happened after the complete degradation of organic substances, as shown in Figure 1.
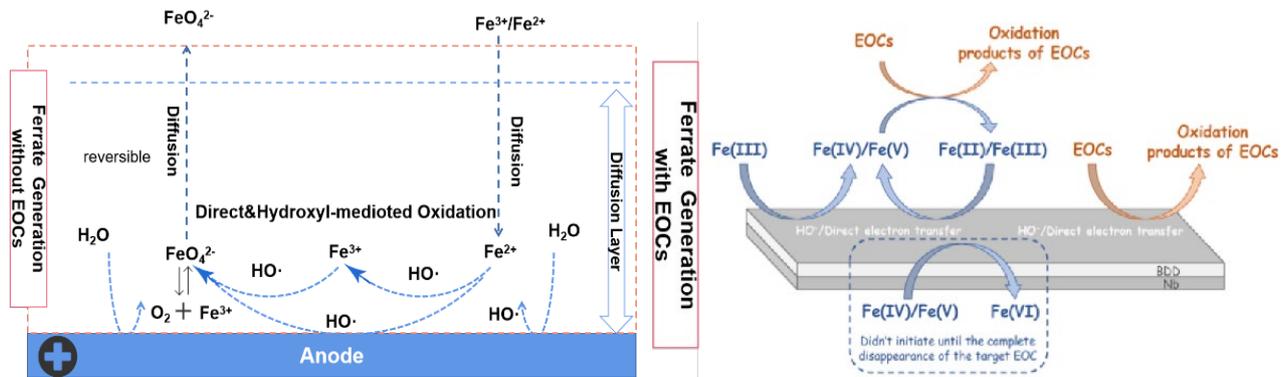
Fig. 1. Principle of FeO_4^{2-} generation on inorganic electrode surfaces

Zhang [63] utilized SnO_2-Sb_2O_3/Ti electrodes to study the existence of $Fe(OH)_3$ and FeO_2^- acidic ion forms of $Fe(OH)_3$ in higher concentrations of NaOH solution, and proposed the reaction mechanism under this condition (Eq. (10)-(12)). McBeath [73] conducted comparative experiments on BDD, NAT/Ni-Sb-SnO_2, and AT/Sb-SnO_2 electrodes, confirming that BDD electrodes are the only materials among these three that facilitate direct electron transfer for oxidation. They also suggested that the NAT electrode operates based on an ozone-mediated mechanism for the electrochemical synthesis of Fe(VI).

$$OH^- + Fe(OH)_3 \rightarrow FeO_2^- + 2H_2O \tag{10}$$

$$FeO_2^- + 4OH^- - 2e \rightarrow FeO_4^{3-} + 2H_2O \tag{11}$$

$$3FeO_4^{3-} + 2H_2O \rightarrow 2FeO_4^{2-} + FeO_2^- + 4OH^- \tag{12}$$
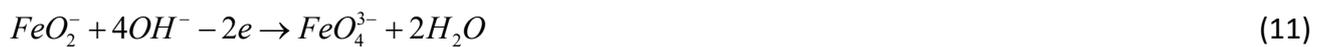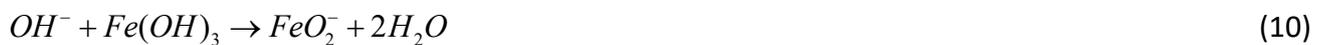
Zeng [66] employed carbon-coated iron as the anode and combined it with a dual-cathode/single-anode electrolytic device to synthesize ferrates. This approach effectively mitigated anode passivation, resulting in an initial electrolysis efficiency eight times higher than when using iron sheets as the anode.

To sum up, changing the composition of electrode materials and increasing their surface area can both enhance the efficiency of FeO_4^{2-} generation. Inexpensive and highly oxidative electrodes have significant research potential. However, the current reaction mechanisms involve both free radical and ozone oxidation synthesis pathways. If the pollutants are directly degraded through online electrolysis, the generation of FeO_4^{2-} occurs after the complete degradation of pollutants.

2.2 Electrolyte Composition

The electrochemical synthesis of ferrates is typically carried out under strong alkaline conditions, with the main electrolyte solution being NaOH. However, other alkaline hydroxides like KOH, LiOH, CsOH, BaOH, and their combinations can also be used. Mohammad Alsheyab [74] conducted an

analysis of different concentrations (10M-20M) of NaOH with the goal of achieving the highest current efficiency and lowest energy consumption. The results showed that NaOH at a concentration of 16M exhibited the best performance, with a current efficiency of up to 46% and energy consumption reduced to 5.8 kWh/kg. 20M NaOH also demonstrated high performance, while the least efficient was 10M NaOH with a current efficiency of only 17%, consuming more than twice the energy of other concentrations. In the electro-synthesis of FeO_4^{2-}, its yield increased with increasing NaOH concentration, but at higher concentrations, the current efficiency slightly decreased due to the influence of water presence and iron dissolution [21,75,76]. However, excessively high NaOH concentrations can lead to electrode passivation [77]. Subsequent studies indicated that using KOH or KOH-NaOH electrolyte solutions yielded better results than using NaOH alone [21]. Additionally, the use of KOH-NaOH electrolyte not only prevented anode passivation but also inhibits the decomposition of FeO_4^{2-} in water [16,35]. Nevertheless, the solubility of solid K_2FeO_4 in alkaline solution is significantly lower than that of Na_2FeO_4. The higher the concentration of potassium ions in the electrolyte, the more K_2FeO_4 adhered to the anode, hindering the oxidation of iron atoms [45]. A comparison between the electrochemical synthesis of ferrates in a NaOH-KOH eutectic melt environment and a highly alkaline NaOH-KOH mixed aqueous solution was conducted. Using cyclic voltammetry, significant deviations were observed in cathodic potentials during reverse point scans, confirming distinct differences in the surface film properties formed in the reverse potential region under the two environments [78].

Expanding the pH Range of Electrochemical Synthesis of FeO_4^{2-}, Lee [65] studied the direct electrochemical preparation of FeO_4^{2-} on BDD electrodes under acidic conditions. It was found that the generated FeO_4^{2-} rapidly oxidizes with water to produce Fe^{3+} and oxygen. McBeath [79] researched the synthesis of ferrates under neutral conditions for pesticide degradation. When combined with low concentrations of Fe^{2+}, the decomposition rate of ferrates followed a second-order reaction. In contrast, Cataldo-Hernández [80] solely used FeO_4^{2-} for impurity treatment in drinking water. In a broader pH range of 5 to 13, the degradation of ferrates more closely resembled a first-order reaction. Rush [81] and others presented the forms of ferrates under different pH conditions and their conversion formulas as Eq. (13)-(15). The decomposition of ferrates in acidic and alkaline solutions Eq. (16) and Eq. (17) [74]:

$$H_3FeO_4^+ \longleftrightarrow H^+ H_2FeO_4 \qquad \mathrm{p}K_1 = 1.6 \quad pH = 0 \quad to \quad 5 \tag{13}$$

$$H_2FeO_4 \longleftrightarrow H^+ HFeO_4^- \qquad \mathrm{p}K_1 = 3.5 \quad pH = 3 \quad to \quad 8 \tag{14}$$

$$HFeO_4^- \longleftrightarrow H^+ HFeO_4^{2-} \qquad \mathrm{p}K_1 = 7.3 \quad pH = 7 \quad to \quad 10 \tag{15}$$

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \qquad E^0 = +2.20V \tag{16}$$

$$FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \qquad E^0 = +0.72V \tag{17}$$
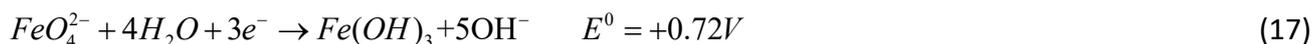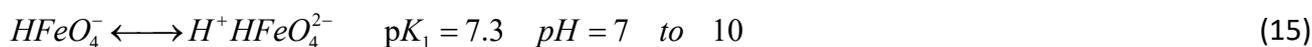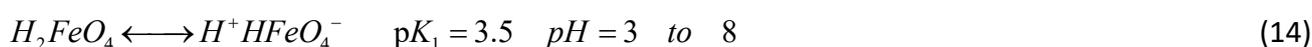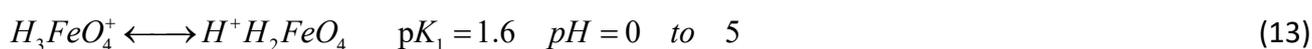
The electrolyte's primary characteristic is pH. Under acidic and neutral electrolyte conditions, FeO_4^{2-} rapidly oxidizes with water to produce Fe^{3+} and oxygen, which can be directly employed for pollutant degradation. It has been observed that the degradation of FeO_4^{2-} occurs at a first-order rate. To synthesize FeO_4^{2-}, the electrolyte is typically maintained under strongly alkaline conditions. A mixed electrolyte (NaOH-KOH) exhibits advantages in the synthesis reaction. However, excessively high NaOH concentrations may result in electrode passivation, and the presence of K_2FeO_4 adhered

to the anode could impede the ongoing oxidation of iron atoms.

2.3 Additives in Electrolyte

Generally, alkaline substances are used as electrolytes to achieve the electrochemical synthesis of ferrates. It has been demonstrated that successful electrochemical synthesis of ferrates can be achieved under highly alkaline conditions. However, to further explore the impact of other elements in the electrolyte on electrochemical synthesis, in studies involving iron-containing electrodes, Bi Dongqin [82] added additives in a mass ratio of 0.02% to the anode electrolyte. Except for NaBr and NaCl, the addition of several other additives improved the current efficiency. Their effects ranked from smallest to largest as follows: NaCl < NaBr < no addition < Na_2MoO_4 < NaF < Na_2WO_4 < Na_2SiO_3 < Na_3PO_4 < KIO_4. The authors believed that the adsorption of negatively charged ions around Fe^{3+} reduces the catalytic decomposition of Fe^{3+} to FeO_4^{2-}. You Xuena [83] observed an increase in current efficiency when adding substances such as KI, $CuCl_2$, $KClO_3$, $KBrO_3$, KIO_3, and Na_2SiO_3 to the electrolytic system.

In studies involving inert electrodes, M. Villanueva [84] examined the effect of in-situ synthesis of FeO_4^{2-} using BDD electrodes with different Fe^{2+} ion concentrations (from $FeSO_4$) on pollutant degradation. The results indicated that the best pollutant removal rate was achieved under conditions of 1mM $FeSO_4$. A comparison of the effects of adding $Fe(NO_3)_3$, $FeSO_4$, $FeCl_3$, and $FeCl_2$ revealed that $FeCl_3$ and $FeCl_2$ exhibited higher ferrate yields. Chloride ions triggered OH radical oxidation, while sulfate radical and hydroxyl radical engaged in intense kinetic competition. In an alkaline environment, sulfate radicals promoted the generation of hydroxyl radicals. However, in an acidic environment, the abundance of sulfate radicals in solution resulted in faster reactions with electrophilic groups than with electron-donating groups, leading to a decrease in the oxidation rate of sulfate radicals on the BDD electrode due to the presence of ferrate. Nitrate ions did not react with hydroxyl radicals and exhibited passivity during the electro-oxidation process. Additionally, diffusion rate was one of the main factors influencing BDD electrode efficiency [85]. Similar results have also been observed by other researchers [60]. The use of $FeCl_3$ instead of Fe_2O_3 and Fe(OOH) as iron sources showed higher synthetic efficiency due to the strong oxidative capability of halides under electrolytic conditions, enabling assisted chlorine oxidation reactions [86]. In a molten NaOH-KOH system, the addition of Fe_2O_3 (0.5wt.%) may lead to the formation of FeO_2^{2-} or hydroxide layers on the anode surface [87]. Mauricio Chiliquinga [88] introduced $FeSO_4$ into $HClO_4$ and Na_2SO_4 media, producing FeO_4^{2-} in situ on the BDD electrode surface. Comparing the effects of $HClO_4$ and Na_2SO_4 media on the degradation of organic pollutants, it was found that the use of sulfate media resulted in a faster pollutant degradation rate due to the generation of persulfate ions during electrolysis. Villanueva-Rodríguez [89] observed that an excess of Fe^{2+} led to the consumption of hydroxyl radicals generated alongside the BDD electrode. High concentrations of Fe^{3+} in solution inhibited the formation of FeO_4^{2-} [48]. Additionally, the reactions of synthesizing ferrates and hydroxyl radicals to produce oxygen on the BDD electrode surface exhibited a competitive relationship [60].

Different additives in electrolytes have varying mechanisms of influence, closely related to the electronegativity of additives. One type of electrolyte ion (F^-, I^-, MoO_4^{2-}, WO_4^{2-}, SiO_3^{2-}, PO_4^{3-}, IO_4^-, ClO_3^-, BrO_3^-) adsorbs around Fe^{3+}, reducing the catalytic decomposition of FeO_4^{2-} by Fe^{3+}. Another type of electrolyte ion (Cl^-, Br^-) can trigger the generation of OH radicals, promoting higher ferrate production. SO_4^{2-} can also facilitate the production of hydroxyl radicals in alkaline conditions. However, under acidic conditions, it reacts rapidly with electron-donating groups. There is yet another type of electrolyte ion (NO_3^-) that does not react with OH radicals and remains inert during the electrooxidation process.

2.4 Reaction Temperature

The influence of reaction temperature on the electrochemical synthesis of FeO_4^{2-} can be summarized in two main aspects. Firstly, raising the temperature can enhance reaction activity, alleviate electrode surface passivation, and consequently improve reaction rate. Secondly, elevated temperatures can lead to side reactions involving oxygen, accelerating the decomposition of FeO_4^{2-}.

In the first aspect, Lijuan Xi [90] proposed that increasing temperature can enhance the activity of hydroxide ions and the rate of conversion of intermediate products into ferrate ions, thus favouring FeO_4^{2-} synthesis. Sibel Barışçı [91] investigated the effect of temperature (20°C-65°C) and found that the highest ferrate yield was obtained at 65°C with an electrolysis time of 75 minutes, while the lowest yield was observed at 20°C. However, both the 65°C and 50°C experimental groups exhibited a decrease in ferrate concentration after 75 minutes. This phenomenon was attributed to the formation of a passivating oxide-hydroxide layer on the anode surface during electrolysis, which dissolves more rapidly at higher temperatures, mitigating anode passivation. Additionally, the decomposition of FeO_4^{2-} also accelerated with rising temperature. Thus, the impact of temperature on FeO_4^{2-} synthesis is the combined result of these two competing factors. Similar findings have been reported by other researchers [52,92].

In the second aspect, Xuhui Sun [47] studied the effect of temperature on the electrochemical synthesis of ferrates. It was found that at temperatures exceeding 65°C, more iron oxide accumulated on the electrode surface, leading to increased current consumption, the occurrence of side reactions involving oxygen evolution, and accelerated ferrate decomposition. Other researchers have also obtained similar results [36,75,93-96]. Although some variations exist in the research outcomes, they mainly stem from differences in experimental conditions. If effective measures to overcome passivation issues are implemented, higher temperatures may primarily impact the thermal decomposition of ferrates. Experimental results indicate that raising the reaction temperature without limitations does not necessarily have a promoting effect on the experimental outcomes.

2.5 Current Density

The current density has an impact on the yield and rate of electrochemical synthesis of FeO_4^{2-}. On the surface, higher current density seems to lead to higher FeO_4^{2-} yield, but the actual situation is more intricate. Diaz [86] suggested that the reactions for synthesizing ferrates using different electrolytes are reversible. Furthermore, it was found that the current only affects the efficiency of ferrate production within a specific range of current density (less than 7 mA/cm^2), which is related to the saturation of lower oxidation states of iron in the electrolyte [96]. Increasing current density facilitates iron dissolution and hydroxyl radical generation [97], which are closely connected to the formation of FeO_4^{2-} and can promote its generation [23,67]. Nevertheless, continuously increasing current density can also lead to slight decreases in certain performance metrics, including yield and purity. This is because higher current density leads to increased oxygen evolution at the electrode and elevated electrode surface temperatures due to Joule heating, accelerating the decomposition of Fe(IV).

Current density not only influences FeO_4^{2-} synthesis but also affects the appearance of other byproducts. In this context, the oxygen evolution reaction and ferrate generation seem to be in competition [98]. Traditional electrochemical methods appear to be constrained in this aspect. However, K. Bouzek [55] altered the way the current was applied by superimposing sinusoidal alternating current onto the direct current. The maximum current yield after 180 minutes of electrolysis was 33%. Ruobing Pi *et al.,* [99] overcame anode passivation issues through periodic

reverse current. Similar research outcomes were reported by K.M. Wang [100]. Samimi-Sedeh [101] utilized the solution plasma process (SPP) to produce Na_2FeO_4. The same synthesis has been studied by others [107]. SPP did not follow Faraday's law, resulting in higher current efficiency compared to regular electrochemical processes. Under the conditions of an initial electrolyte solution temperature of 30°C and voltage of 35 V, the optimal conditions for generating Na_2FeO_4 in a 16 M NaOH solution were achieved. Due to the formation of OH- ions and H_2O_2, the current efficiency increased by up to 512%, presenting a novel method for large-scale production of Na_2FeO_4. The efficiency of the current action is also affected by the electrode surface structure resistance and isolation membrane.

The impact of current is not only related to the magnitude of current density but also to the way the current is applied. Increasing current density promotes the generation of FeO_4^{2-}, but at high current densities, more oxygen is produced at the electrode. Meanwhile, the increase in temperature due to current-induced heating of the electrode accelerates the decomposition of Fe(IV). Changing the method of current application can reduce the likelihood of electrode passivation and improve current efficiency.

2.6 Membrane (Ion Exchange Membrane)

In the electrochemical synthesis process, to prevent the diffusion of FeO_4^{2-} generated at the anode to the cathode for reduction, a membrane is introduced between the anode and cathode of the reaction. This membrane not only needs to hinder the diffusion of ferrate but also must permit the flow of electric current and the exchange of necessary ions. A. Sánchez-Carretero [69] employed the STEREOM L-105 ion exchange membrane for the reaction. M. A. Cataldo-Hernández [61] used a proton exchange membrane (PEM) to isolate the anode and cathode compartments. The PEM selectively allows protons (H+) formed at the anode to pass through, leading to the generation of hydrogen gas at the cathodeas shown in Figure 2 and Figure 3.
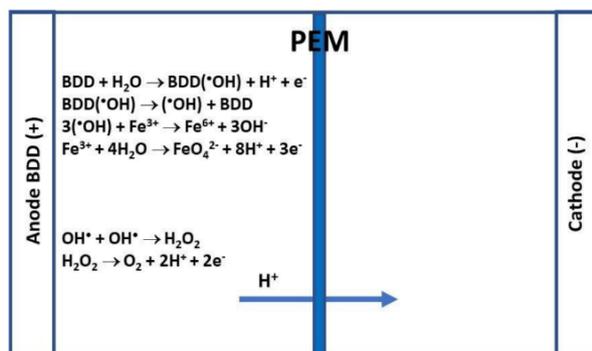
Fig. 2. Membrane isolation in the electrolysis process
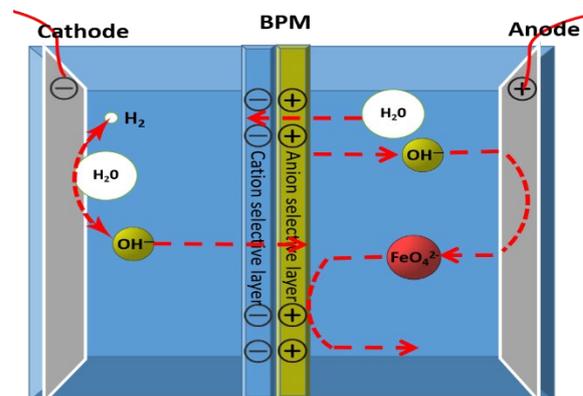
Fig. 3. Principle of the bipolar membrane's function

Zeng [66] utilized a cation exchange membrane, Nafion 117, in a dual cathode chamber setup to synthesize FeO_4^{2-}. This membrane is composed of polytetrafluoroethylene grafted with sulfonic acid groups, allowing for the exchange of Na^+ ions. Nafion membranes have also been used by other researchers [37,102]. Lin Zhihong [103] studied solid polymer electrolyte (SPE) anion exchange membranes as separators between the anode and cathode chambers. These membranes effectively impede the diffusion of FeO_4^{2-} into the cathode chamber. Simultaneously, they allow the timely replenishment of OH- ions from the cathode chamber to counteract the consumption of OH- during the generation of FeO42- in the anode chamber.

Y. Ren [104] employed a self-assembled monolayer on support of carboxymethyl cellulose-chitosan (SAMS-CMC-CS) bipolar membrane as a separator for electrochemical FeO_4^{2-} synthesis. This bipolar membrane not only effectively obstructs the diffusion of FeO_4^{2-} into the cathode chamber but also promptly replenishes the consumed OH- ions during the ferrate synthesis process. Xu [105] synthesized a sodium alginate-polyvinyl alcohol-chitosan (SA–PVA–CS) bipolar membrane using a two-step method. Combining the findings of Ren's research, the principle of the bipolar membrane's role is illustrated in Figure 3.

The primary function of the membrane is to facilitate the migration and inhibition of specific ions. For example, an anion exchange membrane allows the free migration of OH- ions, while a cation exchange membrane can impede the migration of FeO_4^{2-}. Dual ion-exchange membranes possess both of these abilities concurrently, indicating higher potential. Furthermore, ensuring the flow of current is also a crucial factor to consider.

2.7 Reactor Types

Batch electrolytic cells are commonly used for the electrochemical synthesis of FeO_4^{2-} and are relatively simple, as shown in Figure 4. The reaction Eq. (18)-(20) [74] was applicable to batch electrolytic cells. This type of cell has been widely applied and various designs have been developed to optimize the synthesis process and enhance the yield [108]. Examples included membrane-separated electrolytic cells [61] and dual cathode chamber cells [66].
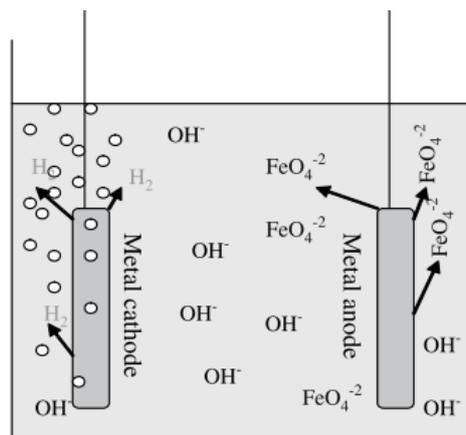
Fig. 4. Batch electrolytic cell

Anodic reaction:

$$3H_2O \rightarrow 3H_2 + 6OH^- - 6e \tag{18}$$

Overall reaction:

$$Fe + 2OH^- \rightarrow FeO_4^{2-} + 3H_2 + H_2O \tag{19}$$

$$FeO_4^{2-} + 2K^+ \rightarrow K_2FeO_4 \tag{20}$$

Some researchers [22] employed a membrane-separated electrolytic cell with a mixed alkaline solution of 400g/L KOH and NaOH as the electrolyte and gray cast iron with a silicon content of 2.8%

as the anode. This setup resulted in a solid K_2FeO_4 with a purity of 54%. Liu [43] employed a titanium-ruthenium alloy as the cathode and gray iron as the anode in a dual cathode/one anode electrolytic cell for FeO_4^{2-} synthesis. This configuration was about four times more effective in producing iron (VI) than a single cathode/single anode setup, a similar approach as in [66], as shown in Figure 5.H. Wang [106] compared the results of electrochemical Fe(IV) generation using different types of intermittent electrolytic reactors by periodically changing the anode. This practice significantly improved the efficiency of hexavalent chromium iron generation. Additionally, some researchers have proposed that using porous electrodes and electrolytic reactors with two cathode chambers could further enhance the concentration of hexavalent chromium iron.
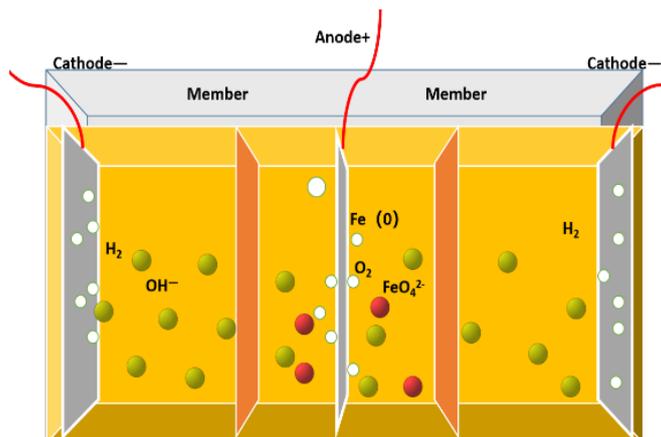
Fig. 5. Dual cathode chamber electrolytic cell

Ren [104] utilized a cylindrical electrolytic cell for their experiments, achieving a FeO_4^{2-} salt concentration of 48.0 mmol/L after a reaction time of 6 hours. The setup of the electrolytic cell was depicted in Figure 6. The choice of reactor can be selected and designed based on actual needs.

three-dimensional picture

planform   *cross-section view*
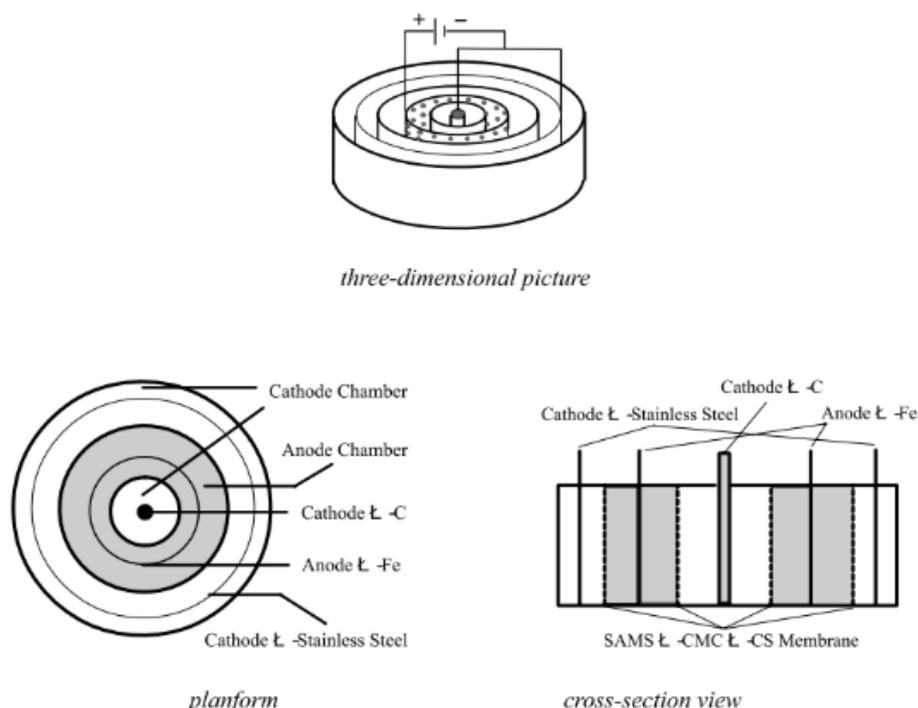
Fig. 6. Circular electrolytic cell used in Ren

3. Conclusion

This paper critically analyzes the various factors affecting the synthesis of ferrate(VI) by the electrochemical method. Regarding the choice of electrode, using high-surface-area alloy materials or porous carrier electrodes as anode materials exhibits superior electrochemical performance. The composition of the electrolyte significantly affects the pH environment of the electrochemical reaction; achieving efficient reaction rates requires optimizing the diffusion of reactants within an appropriate pH range. The choice of electrolyte can have varying impacts on the reaction outcome, and the underlying mechanisms can differ depending on the electrolyte used.

Maintaining an appropriate temperature is beneficial for the electrochemical reaction, as it enhances reactivity, but excessively high temperatures can lead to the decomposition of synthesized FeO_4^{2-}. The impact of current density is notable mainly at lower values, while high current densities can lead to electrode passivation. Techniques such as alternating current or plasma-based methods can increase FeO_4^{2-} yield under certain conditions.

Various types of ion exchange membranes, including anion, cation, and bipolar membranes, can serve as separators in the electrochemical synthesis of FeO_4^{2-}. The focus is on achieving high ion flux and current efficiency. Different types of electrolytic cells, including conventional, double cathode/single anode, and cylindrical cells, can be used as reaction devices based on specific needs.

The paper also introduces the direct synthesis of Ferrate (VI) using inert electrodes (e.g., BDD). Its merit lies in the direct utilization of iron ions in the solution to synthesize Ferrate (VI) and apply it for pollutant degradation. Furthermore, the paper mentions plasma technology (SPP), which offers an efficient synthesis approach for electrochemical Ferrate (VI) production.

4. Future Perspectives:

As research continues, addressing these areas could advance the efficiency, effectiveness, and applicability of electrochemical synthesis of Ferrate (VI), contributing to the broader understanding of this promising technology for sustainable applications in water treatment and beyond.

i. Anode Material Exploration: Research on anode materials can be expanded in two directions: exploring various alloy materials beyond FeC and FeSi systems, and developing porous electrode carriers. Investigating conductive and cost-effective inert electrodes like carbon electrodes can be particularly beneficial.

ii. Enhancing Diffusion Rates: Overcoming the limitation of reactant diffusion rates in the electrolyte can be addressed through methods such as agitation, ultrasonication, or improved convection to accelerate the diffusion of species and enhance reaction rates.

iii. Synergistic Effects with Different Electrolytes: Investigate the synergistic effects between generated FeO_4^{2-} and various electrolyte compositions in electrochemical systems.

iv. Explore the electrochemical synthesis in NaOH and KOH molten systems under low-temperature conditions.

v. Alternate Current Processes: Employ techniques like alternating current or plasma processes to modify current application methods and mitigate electrode passivation.

vi. Novel High-Performance Membranes: Develop new membranes with high ion flux and current efficiency for improved electrochemical synthesis.

vii. Optimized Reaction Equipment: Design reaction devices that optimize membrane functionality, facilitate continuous production, and integrate synthesis and degradation for wastewater treatment.

viii. Product Separation and Purification: Focus on research into the separation and purification of electrochemically synthesized Ferrate (VI) products.

Acknowledgements

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