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ELECTROCHEMICAL SYNTHESIS OF FERRATE (VI) FOR THE WASTEWATER TREATMENT**

Abstract

Ferrate ion, FeO_4^{2-} or Fe(VI) , has long been known as a very powerful and environmentally benign oxidizing agent suitable for a wide range of applications: organic synthesis, water and wastewater treatment, corrosion protection, and as a cathode material in the new super iron batteries. Several techniques have been developed for the synthesis of ferrates including the thermal, wet chemical and electrochemical. The electrochemical approach has received the most attention of the three synthesis methods because it is easier to perform, does not require harmful and costly chemicals and provides the possibility for continuous production. The electrochemical synthesis of ferrate (VI) is reviewed in this work. Particular attention is paid to the influence of factors such as the anode material, electrolyte composition, temperature and current density. Mechanism of ferrate synthesis and recent advances in this field are discussed as well.

Keywords: ferrate(VI), electrochemical synthesis, wastewater treatment

1 INTRODUCTION

Iron usually exists in the 0, +2 and +3 oxidation state, however, it is possible to obtain the higher oxidation states of iron, theoretically up to +8. These high oxidation states of iron are in the form of oxyanions, called ferrates, and the most stable is +6 or FeO_4^{2-} . Ferrate (VI) has a dark purple color similar to permanganate, MnO_4^{2-} .

Ferrate (VI) has been considered for years as a possible alternative to the most commonly used oxidants in the water treatment plants (chlorine, hydrogen peroxide and ozone). The unique characteristics of this compound are: high redox potential ($E = +2,2 \text{ V}$, under acidic conditions), as well as the non-toxic by-product - Fe (III) hydroxide which has the properties of an effective coagulation agent. Therefore, in literature, ferrate (VI) is often called a

“green” oxidant. In most cases, ferrate (VI) provide a complete degradation of the pollutants without harmless by-products.

The superior performance of ferrate (VI) as an oxidant/disinfectant and coagulant in water and wastewater treatment has been extensively studied. Separate laboratory studies have confirmed the ferrate (VI) efficiency in removal the various pathogenic microorganisms, bacteria [1], and viruses [2], among which are those resistant to chlorine. By comparing the disinfection ability of ferrates and other oxidants, it can be concluded that ferrate (VI) exhibits the same or better effect even in smaller doses and shorter operating times.

Ferrate has also been proven to be a good pre-oxidant in the removal of algae and for a biofilm growth control. It has

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** The authors are grateful to the Ministry of Education and Science of the Republic of Serbia for the financial support of the Project TR34004

been demonstrated that many organic compounds can be easily oxidized by potassium ferrate. Alcohols, phenols [3-5], carboxyl compounds, amines, thiourea [6], thioacetamide, hydrazine and monomethyl hydrazine [7] are just some of them. Ferrate (VI) decomposes rapidly many recalcitrant pollutant such as antibiotics and endocrine disruptors.

Potassium ferrate, thanks to its dual role, as an oxidizing agent and coagulant, can break down and remove a range of inorganic impurities in the treatment of wastewater. Some of these pollutants are: cyanides, ammonia, hydrogen sulphide [8], heavy metals (Mn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Cr^{2+} , and Hg^{2+}) [9,10]. Removal of radioactive elements from wastewater with potassium ferrate was also studied. In addition, potassium ferrate is effective in oxidation of As (III) to As (V), and its subsequent removal by adsorption onto $\text{Fe}(\text{OH})_3$.

In the field of the corrosion protection, ferrate(VI) can be utilized for passivation of aluminum, zinc and iron products, or to dissolve the resistant deposits from the different metal surfaces [11].

In the organic synthesis, ferrate (VI) can be a substitute and safer alternative to the other highly toxic oxidizing compounds, e.g. CrO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 .

Ferrate has also been used in a new class of environment-friendly high capacity batteries, referred to as the super-iron batteries, as cathode material instead of hazardous MnO_2 [12].

Generally, three kinds of technique are used to synthesize ferrate (VI): (i) wet chemical synthesis, implies oxidation of ferric compounds by hypochlorite in highly alkaline environment (ii) thermal chemical synthesis, implies oxidation of ferric compounds at high temperature in molten state with alkaline peroxide and (iii) electrochemical synthesis, implies anodic dissolution of iron or its alloys in strongly alkaline solution in the low trans-passive region of potential. Chemical synthesis of ferrate (VI) must be

conducted under the strictly controlled conditions in consideration a danger of poisoning and explosion. The additional problem is a separation and purification of the obtained ferrate (VI), because the toxic oxy-chlorine compounds are always present [13].

The electrochemical technique is the most promising because it uses electrons as the "clean" reactants and produces a pure dissolved Fe (VI) product with better yields [14]. However, the obtained maximal concentration of Fe(VI) is limited by the low stability of Fe(VI) species and deactivation of the anode surface.

2 ELECTROCHEMICAL SYNTHESIS

The process of electrochemical generation of ferrate (VI) usually consists of a sacrificial iron anode in strongly alkaline solution with electric current serving to oxidize iron to Fe (VI), Eq. (1), while the hydrogen gas is generated on a cathode, Eq. (2) [15,16]:

Anode reaction:

Cathode reaction:

Overall reaction:

The electrochemical generation of ferrate is significantly affected by many factors, mainly, the anode composition, type and concentration of electrolyte, temperature and current density. Thus, many researchers have focused their attention on optimization of these parameters. These parameters influence the structure of passive layer and possibility of its dissolution during the electrochemical synthesis of ferrate. Parameters should be selected in such way to avoid blocking the anode surface with poorly soluble species.

1.1 Anode Material Composition

Carbon content in the anode material has a crucial impact on the anode dissolution process. There is a general agreement that only carbon in the form of iron carbide (Fe_3C) positively influences the anode material dissolution. White cast iron (WCI), containing 3.17 wt.% of carbon in the form of Fe_3C is a typical representative. For a grey cast iron (GCI), where carbon is present in a form of graphite, the efficiency of ferrate (VI) synthesis is even lower than for a pure iron anode. Graphite on the surface of the GCI anode lowers the over potential to the competing oxygen evolution reaction and reduces the current efficiency of the electrochemical process. On the contrary, the Fe_3C readily dissolves in the concentrated NaOH exposing a fresh anode surface to the anolite. It was reported that the silicon content has the similar influence on the protective layer as iron carbide [17].

1.2 Temperature

The influence of temperature on the efficiency of electrochemical synthesis of ferrate (VI) has been studied from the earliest stage of research. There are two basic impacts of temperature on ferrate (VI) production. The first, rise in temperature increases the activity of OH^- ions and their interaction with the oxo-hydroxide layer, thus accelerates de-passivation of anode. This is especially important for materials that tend to build a compact protective layer, such as pure iron. In contrast, using an anode material with a high iron carbide content such as white cast iron (WCI), the high yields can be achieved at 20 °C. The second, increase in temperature causes an enhancement in the rate of ferrate (VI) decomposition [17].

Conclusion is that by the appropriate selection of anode material and electrolyte composition, the effect of temperature on the efficiency of electrochemical synthesis of ferrate can be minimized.

1.3 Electrolyte Composition

The electrolyte composition and its concentration is one of the most important factors that affect the synthesis of ferrate (VI). It was found that using more concentrated OH^- solution, both surface layer disintegration and ferrate (VI) stability are increased [17].

Stability of ferrate (VI) in a highly concentrated NaOH solution was investigated by L. Ding et al. Under these conditions, a ferrate ion undergo the spontaneous decomposition described by the following reaction, Eq. (5):

A set of experiments was carried out with initial ferrate (VI) concentration of 0.145mM in aqueous NaOH solution with concentration in a range of 1.5 – 14M. It was assumed that the reaction of ferrate (VI) decomposition follows the first order kinetics. A decomposition rate constant k_d and half-life of ferrate (VI) in different NaOH solutions were calculated. These results demonstrated a great effect of NaOH concentration on the aqueous decomposition of ferrate (VI). Free water activity in NaOH solution from 1.5 M to 14 M decreases and inhibits the redox reaction Eq. (6). For example, a half-life of ferrate (VI) in 1.5 M NaOH was found to be 0.48 h, in 8 M NaOH ten times longer 4.8 h, but in 14M NaOH was greatly extended to even 43h [18,19].

Numerous researches reported a maximum current efficiency of ferrate (VI) generation in 14M NaOH solution. Further increase in NaOH concentration causes a decrease in current efficiency and ferrate (VI) yield. When the concentration of sodium hydroxide approaches to its saturated value of around 20M, the electrolyte solution will become very viscous and solution conductivity will decline significantly resulting in a lower rate of electron transfer on the anode surface and ferrate (VI) generation [20].

Although NaOH is the leading electrolyte for electrochemical preparation of ferrate, the electrolyte solution may include a hydroxide selected from potassium hydroxide, lithium hydroxide, cesium hydroxide, barium hydroxide and combinations between them [15]. It was reported that when comparing LiOH, NaOH and KOH solutions, the NaOH solution provides the highest ferrate and current yields [21]. On the contrary, He et al. [8] reported that KOH is far better electrolyte for electro-synthesizing ferrate (VI) than NaOH. The results showed that under the similar conditions, the obtained current efficiency in the concentrated NaOH solution was 55%, while it could reach 73.2% in a solution of KOH for temperature higher than 50°C. Ferrate produced in KOH was more stable and with purity.

1.4 Other Important Synthesis Parameters

Anode activation before or during the electrolysis significantly improve ferrate (VI) synthesis efficiency. The following methods have been proposed for this purpose: mechanical polishing, chemical etching, ultrasound and cathodic pre-polarization.

Anode geometry is another important factor in the electrochemical synthesis of ferrate. Generally, increasing the specific surface area of the anode yields a significant enhancement of production rates. Several authors reported the utilization of three-dimensional iron anodes in a form of iron wire gauze [22,23], porous magnetite electrode [24], pressed iron powder [12,24], iron chunks [25], and sponge iron [20].

The efficiency of ferrate (VI) formation is also affected by the electrolysis time. Increasing the electrolysis time will decrease the amount of ferrate (VI) due to a decomposition, and anode deactivation. This represents a serious hurdle for the industrial continuous production [17].

1.5 Mechanism

The anodic behavior of an iron electrode in alkaline solutions has been studied in detail by numerous authors. The reason of an intensive research of this system were mainly the investigation of corrosion protection and improvement the construction of alkaline Ni-Fe cells. More recently, a trend in ferrate (VI) research has turned from optimization of electrochemical production toward a deeper understanding of the electrode reaction mechanism [26,17].

Anodic dissolution of iron takes place in several successive processes. Various ferrous and ferric oxides, hydroxides and oxihydroxides are formed on the anode surface, among which the ferric compounds are particularly poorly soluble and lead to the anode passivation. With an increase in anodic potential the conditions for formation of soluble compounds of iron in higher valence state are obtained, i.e. trans passive dissolution [17,27].

Voltametric studies of iron behavior in the alkaline media exhibit several peaks and shoulders within the potential range of water stability, corresponding to the active dissolution of anode material and surface layer restructuring. The anodic current peak a_1 at a potential of about -0.1V (depends on the electrolysis conditions and electrode composition) corresponds to the active iron dissolution to Fe^{2+} according to Eq. (6). Oxidation reactions, Eqs. (7,8), may occur simultaneously [17,13,26]:

Current peak a_2 corresponds to a continuous oxidation of $Fe(OH)_2$ to Fe_3O_4 , according to Eq.(9). Parallel oxidation of Fe_3O_4 is possible, according to Eq.(10) [13,26]:

It is assumed that the reactions of passive layer with OH⁻ ions, Eqs. (11-13), causes the iron surface to break down and enables continuous dissolution of the anode, corresponds to the current peak a₃ [1,14].

After the active dissolution region, a broad passivity plateau follows. At the potential of about 0.6V, the oxygen evolution commence, Eq. (16). At the same time, the oxidation reaction, Eq.(14), takes place, followed by the subsequent disproportionation reaction, Eq. (15). Peak a₄ the corresponds to the reactions (14-16) cannot always be observed because an intensive oxygen evolution overlaps the trans-passive iron dissolution, including ferrate (VI) formation [17,13].

During the negative scan of the potential, the three cathodic current peaks are often observed and attributed to the reduction of Fe(VI) to Fe(III), Fe(III) to Fe(II), and Fe(II) to Fe(0) [13].

3 THE NEW APPROACHES IN THE ELECTROCHEMICAL SYNTHESIS OF Fe(VI)

Ferrate can be synthesized by the oxidation of ferric ion with an inert electrode (Pt, BDD, SnO₂-Sb₂O₃/Ti) as well as in hydroxide melts by the oxidation of an iron anode.

In recent years, the electrochemical oxidation with conductive diamond anodes converted into very promising technology for electro synthesis of powerful oxidants such as peroxodisulfates, peroxodifosfates and percarbonates. Electrochemical generation of ferrate (VI) using BDD (boron-

doped diamond electrode) was successfully performed by Canizares et al. [28,29]. Within this research research, it was demonstrated that the application of ultrasound and iron powder as the raw material during the electrochemical synthesis of ferrate using conductive diamond electrode, enhances the efficiency of process. While high current density and hydroxide concentration increase the yield and stability of the generated ferrate product [29].

The formation of ferrate (VI) in molten NaOH – KOH system was studied by Hiveš et al. [30,11]. The most important advantages of these method are: (1) there is no decomposition of the resulting ferrate due to the absence of water in electrolyte, (2) after cooling down of the reaction mixture, ferrate (VI) is in a solid dry form and thus stable, (3) lack of passive layer formation on the iron electrode, (4) chemical step in the ferrate (VI) formation mechanism is accelerated by raise the operational temperature of electrolysis.

The main issue in this synthetic approach that requires attention is the stability of ferrate (VI) product at the temperature of a suitable molten hydroxide mixture (170 - 200°C). Therefore, this group of authors chose the eutectic mixture of the NaOH – KOH (51,5 mol% NaOH), characterized by a relatively low eutectic melting point of 170°C and high electrical conductivity of 0.588 Ω⁻¹cm⁻¹.

CONCLUSION

It has been demonstrated by numerous studies that ferrate (VI) is one of the most powerful oxidants for water and wastewater treatment. However, the challenges have still existed to the implantation of ferrate (VI) technology in practice due to poor stability of Fe (VI) solutions and high cost of the solid ferrate salts as they require costly chemicals and multiple purification steps.

Of the three synthesis methods – electrochemical, chemical and thermal, the electrochemical method is the most promising due to its simple performance, high

purity of product and absence of hazardous chemicals. Many factors affect the electrochemical ferrate (VI) production, such as anode composition, type and concentration of electrolyte, temperature, cell design, etc. Further work on optimization of these parameters is necessary. Although the electrochemical generation of ferrate (VI) has been known for almost two centuries and many advances have been made over this period, there are still many unresolved questions that should be overcome, such as: passivation of the anode surface during the electrolysis, self-decomposition and low yields of ferrate product. It can be concluded that ferrate (VI) represents vital and continuing field of research.

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