

Electrochemical study of the stability of ferrates(VI) in low temperature molten hydroxide

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Abstract: During last decades interest in ferrates(VI) has increased significantly. On one hand they serve as strong, non-toxic oxidants without harmful by-products and, on the other hand, as an efficient coagulant in both drinking and waste water treatment technology. In this work we focused on the electrochemical preparation of ferrate (VI) salts in eutectic low temperature molten sodium hydroxide – water mixture using pure iron anodes. Some information on the stability and kinetics of decomposition of sodium ferrate(VI) prepared by molten-system electrolysis is discussed. An assumption that electrochemically prepared ferrate(VI) in molten hydroxide media are stable enough to be used especially in the field of waste water treatment was confirmed by our observation.

Keywords: electrolysis, ferrates, melts, stability

Introduction

The most common oxidation states in which iron is usually found are Fe(II) and Fe(III). Other, rare oxidation states, e.g. ferrate(VI) $[\text{Fe}^{\text{VI}}\text{O}_4]^{2-}$, have been also detected (Macova et al. 2009). One of the most potentially important application of ferrates(VI) is closely connected with both drinking water and wastewater treatment. The main advantage of ferrates(VI) is their high oxidation potential that allows the decomposition of even very stable inorganic, organic and microbiological contaminants. In most cases, ferrates(VI) provides a complete degradation of the pollutant without harmless by-products (Licht et al. 2005). A key factor for ferrate(VI) utilization for water treatment is a product of the ferrate (VI) reduction – ferric hydroxide. $\text{Fe}(\text{OH})_3$ does not burden the environment, it is non-toxic and it is also an excellent coagulant and flocculent (Jiang and Lloyd 2002, Jiang and Wang 2003, Lee et al. 2003, Sharma et al. 2005).

According to the literature data, the oldest information about ferrates(VI) is dated back to 1702 (Macova et al. 2009). Electrochemical dissolution of Fe in various alkaline media has been investigated by several research groups for decades. It can be summarized that in alkaline solutions iron can be electrochemically dissolved as ferrous(II), ferric(III) and finally ferrate(VI) species depending on the electrode potential, both solution and anode composition as well as the temperature (Armstrong and Baurhoo 1972, MacDonald and Roberts 1978, Serebrennikova et al. 2009, Zhang and Park 1994, Denvir and Pletcher 1996, Macova and Bouzek

2011, Macova and Bouzek 2012, Macova et al. 2010, Bouzek et al. 1999, Hives et al. 2008, Pick 1901, Lapique and Valentin 2002, He et al. 2005). It was also found that the current yield increased with an electrolyte concentration and composition, temperature, as well as with iron electrode composition (Serebrennikova et al. 2009). Grube et al. utilized direct current (DC) with a superimposed alternating current (AC) in order to increase a reaction yield (Grube and Gmelin 1920).

Several attempts to describe the reaction mechanism of ferrate(VI) formation during electrochemical treatment were made (Beck et al. 1985, Bouzek et al. 1999, Bouzek et al. 1998, Bouzek and Roušar 1993, Bouzek et al. 1997, De Koninck and Bélanger 2003, De Koninck et al. 2003, Hives et al. 2006, Hives et al. 2008, Hives et al. 2008, Macova et al. 2010, Toušek 1962, Venkatadri et al. 1974).

Three basic methods of ferrates(VI) preparation are reported in the literature (Macova et al. 2009). The first one is called dry oxidation or thermal method, the second one is so-called wet oxidation and the last one is an electrochemical anodic dissolution (oxidation) of iron or cast iron in the concentrated hydroxide solutions. Using electrochemical methods the high purity ferrates(VI) are prepared (Macova et al. 2009, Sharma 2002). However, even a small amount of water presented in the highly alkaline paste decomposes ferrate(VI) within hours.

To minimize disadvantages of previous aqueous approach an electrochemical treatment of iron in low-temperature melts binary hydroxide systems has been proposed (Hives et al. 2006). The major advantage of this treatment is, usually, the negli-

gible presence of water. Another advantage of this technology is the fact that the reaction rate can be easily and continuously controlled by adjusting temperature and potential in order to achieve the optimum anodic dissolution conditions. Ferrates(VI) are easily detected by observing the colour change of the electrolyte during electrolysis. Titration, chemical precipitation and UV-Vis spectroscopy methods are used for the quantitative determination of ferrates(VI) concentration (Delaude and Laszlo 1996, Licht et al. 2001, Licht et al. 2001).

The main goal of this work was to study the stability of electrochemically prepared ferrates(VI) by transpassive oxidation in molten sodium hydroxide at relatively low temperatures in order to optimize preparation process for further utilization of ferrates(VI) in waste water treatment.

Experimental

Sodium hydroxide (p.a., Mikrochem Ltd. Pezinok, Slovakia) was used for electrolyte preparation. An oil thermostat JULABO (Germany) with calibrated sensor, stainless steel box and PTFE crucible with the sample was utilized for our experiments. Reference connection of thermocouple was immersed in a Dewar flask filled with ice-water and measuring connection was immersed into the melt at the same level as electrodes (Hrnčiariková et al. 2010).

Electrochemical measurements were performed using AUTOLAB instrument PGSTAT 20 (ECO Chemie, The Netherlands). Five working electrodes (WE) were made from pure iron (Fe) (99.95 %

(w/w) Fe, 0.005 % (w/w) C, 0.0048 % (w/w) Ni and 0.0003 % (w/w) Mn) with total geometric area of 60 cm². Quasi-reference electrode (RE) was made from the same material as WE. Counter electrode (CE) was made from mild steel (steel class 11). Cathodic and anodic compartments were divided by polypropylene textile-like diaphragm. Electrolysis were carried out in a PTFE crucible containing 200 g of melt (100 g of anolyte) (NaOH:NaOH. H₂O) at 80 °C, 3.5 V and 25 mA cm⁻².

The amount of ferrates(VI) in the sample were determined by UV-Vis spectrometry at $\lambda = 505$ nm. Each solidified sample was prior to analysis dissolved in NaOH solution in ultrasonic bath. Calibration curve were constructed by measuring an absorbance of various concentrations of commercial K₂FeO₄ (98 %, Sigma-Aldrich) in 13 M NaOH. Samples were stable for at least one hour. Each measurement was repeated three times.

Results and discussion

The aim of this contribution was to study the stability of ferrates(VI) in molten NaOH:NaOH. H₂O mixture during and after the galvanostatic electrolysis at 80 °C.

Current efficiency, η , of the overall electrolysis time, τ_{el} is illustrated in the next Fig. 1.

One can see that the current efficiency slightly decreases during electrolysis. It may be connected with the formation of protective passive layer at the electrode surface during electrochemical treatment as it was observed previously (Hrnčiariková et al.

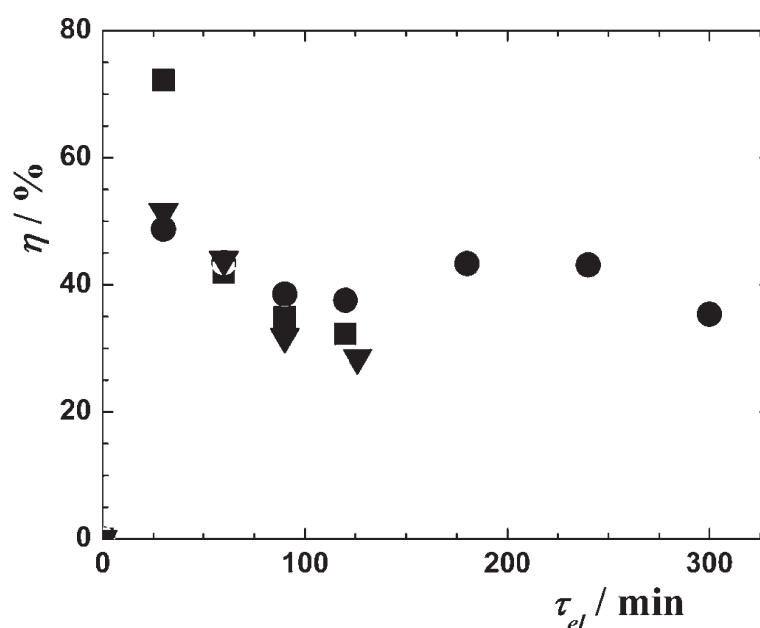


Fig. 1. Dependence of the current efficiency (%) on the time of the electrolysis. Electrolysis duration, τ_{el} : ■ 120 min; ▼ 126 min; ● 300 min.

2013, Hrnčiariková et al. 2010, Hrnčiarikova et al. 2013). After certain electrolysis time the formation and subsequent disintegration of passive layer due to the oxygen evolution and/or high potential is balanced. Therefore the plateau on the curve describing the dependence the electrolysis current efficiency against electrolysis time is reached.

In Fig. 2 the dependence of the mass fraction, w of ferrates(VI) on the measuring time, τ is plotted. Measuring time means that the amount of ferrates in the system was measured not only during the electrolysis time, τ_{el} but also a certain time after the current was switched off. From Fig. 2 it is clearly

visible that during the electrolysis the amount of ferrates(VI) increased with time. When the current was switched off the amount of ferrates(VI) remains almost constant or slightly decreases for further tens or hundreds of minutes. The amount of ferrates(VI) in anodic compartment was not above 3 % (w/w). This is because our aim was not to prepare as much ferrates(VI) as possible but to study their stability and kinetics of their decomposition in molten hydroxide in order understand their behaviour at elevated temperatures.

Kinetics of ferrates(VI) decomposition prepared in sodium hydroxide melt and the decomposition of

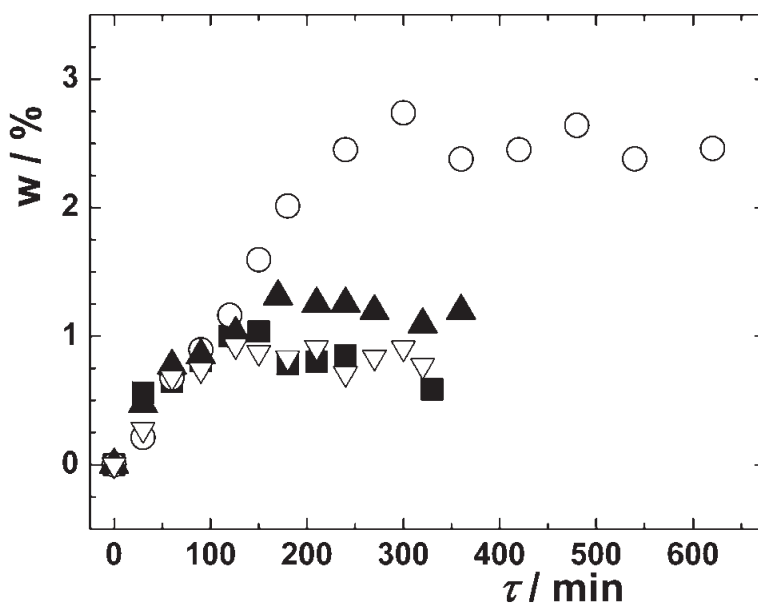


Fig. 2. Dependence of the mass fraction of ferrates(VI) on the measuring time, τ . Electrolysis time, τ_{el} : ■ 120 min; ▽ 126 min; ▲ 170 min; ○ 300 min.

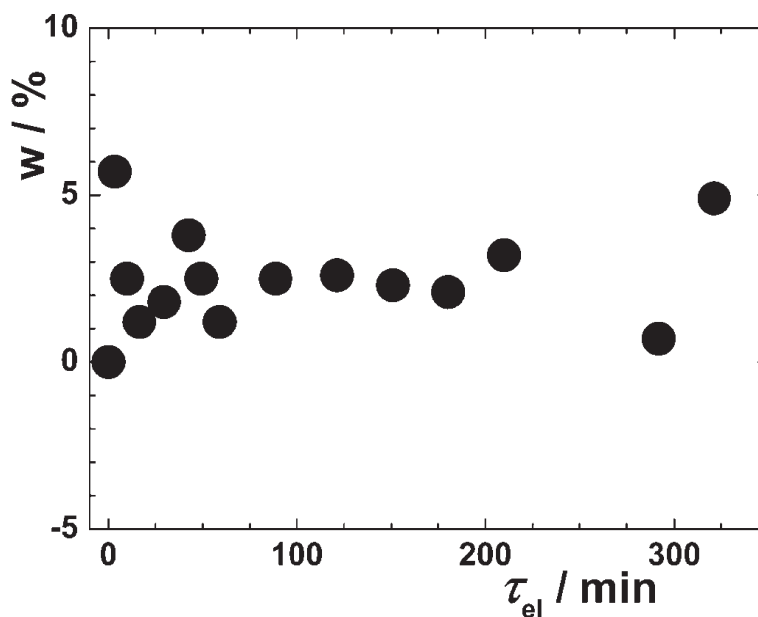


Fig. 3. Kinetics of ferrates(VI) decomposition.

K₂FeO₄ standard in alkaline aqueous solution were compared. In this reference solution ferrates(VI) were not detectable after ca. 30 minutes. However, ferrates(VI) prepared electrochemically in molten NaOH environment remained stable for several hours in molten form as shown in Fig. 3.

The stability of ferrates(VI) in dried, solidified form was also checked. It was found that ferrates(VI) after solidification and cooling were stable for several months in an air-moisture free environment. These observations confirm our assumption that electrochemically prepared ferrates(VI) in molten sodium hydroxide are very stable not only in molten form (during electrolysis and/or after electrolysis) but also in dried, solidified form. It can be summarized that ferrates(VI) prepared in this way are undoubtedly suitable for utilization at waste water treatment.

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