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Voltammetric and impedance study of the influence of the anode composition on the electrochemical ferrate(VI) production in molten NaOH

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ABSTRACT

Three typical anode materials: pure iron (Fe), silicon-rich steel (FeSi) and white cast iron (FeC) electrodes were used in the process of electrochemical ferrate(VI) synthesis in the molten sodium hydroxide. The voltammetric peak current densities corresponding to the first and second step of the anode dissolution in the case of FeC as well as FeSi electrode are higher compared to the pure iron electrode. After passivity region subsequently the transpassive iron dissolution, including ferrate(VI) formation together with an oxygen evolution occurs and the current shoulder is visible for all electrodes used. Measured electrochemical impedance spectra confirm the physical model of the polarized surface based on the concept of two macrohomogeneous surface layers. In all cases the resistance of both inner and outer layer decrease with increasing applied potential. With increasing temperature the resistance of inner and outer layer decreases. The capacity of inner and outer layer increases with increasing potential. This is in agreement with decrease of the resistances of both layers: layers are getting thinner or more disintegrated by oxygen evolution or strong anodic dissolution. The number of exchanged electrons calculated from a static polarization curve at the potentials in ferrate(VI) formation region is $z = 3$ for all electrode materials used.

1. Introduction

Generally, Fe(II)/Fe(III) are the typical oxidation states in which iron can be usually found. However, other not very stable states have been also observed, e.g. ferrate(VI) $[Fe^{VI}O_4]^{2-}$ [1]. The very first information about ferrates(VI) is dated back to 1702 [1]. In 1715 Stahl prepared K_2FeO_4 by oxidation of iron filings in molten KNO_3 [1]. After the dissolution of residues in alkaline solution and during the smelting of iron ore with potassium carbonate the violet coloration was observed. Fremy assumed that the violet color of this product was caused by the presence of $Fe^{VI}O_4^{II}$ [1]. Electrochemically ferrates(VI) were prepared for the first time by using anodic oxidation of iron in alkaline electrolyte by Poggendorf in 1841 [1,2]. At the beginning of the 20th century huge development of Ni–Fe alkaline batteries increased the interest in ferrates(VI). Haber and Pick [3,4] focused on the production of ferrates(VI) for electrochemical synthesis [2]. In the early fifties, Touška [5,6] and Helferich [7] began intensive research in the preparation of ferrates(VI) by chemical synthesis (wet process) due to their excellent oxidation capability.

One of the most promising application of ferrates(VI) is, nowadays, connected with, both drinking water and wastewater treatment. The main advantage of ferrates(VI) is the high oxidation potential that allows the decomposition of stable inorganic, organic and microbiological contaminants. Another reason for ferrates(VI) utilization for water treatment is a product of the ferrates(VI) reduction – ferric hydroxide [8]. $Fe(OH)_3$ does not burden the environment, is non-toxic and is excellent coagulant and flocculant. In most cases, ferrates(VI) provide a complete degradation of the pollutant without harmless by-products [9]. Therefore, it can be nominated as a “green” environmental friendly oxidant [10]. In organic synthesis, ferrates(VI) are used for the selective oxidation of primary and secondary alcohols to aldehydes and ketones [11]. In the field of the corrosion protection, ferrates(VI) can be utilized for passivation of aluminium, zinc and iron products, or to dissolve resistant layer of deposits [12].

Three basic methods of ferrates(VI) preparation are reported in the literature [1]. The first one is called dry oxidation: iron or iron oxide is heated to a high temperature in the melt of alkali metal compounds (e.g. oxides, peroxides). The resulting product is corresponding ferrate of the alkali metal. The second one is wet

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oxidation: its principle is in the absorption of chlorine in solution of concentrated sodium hydroxide and subsequent reaction of the resulting hypochlorite with ferric ion to form ferrates(VI). The last one is the electrochemical anodic dissolution (oxidation) of iron or cast iron in the concentrated hydroxide solutions or melts until ferrates(VI) are prepared. There has been a gradual increase in attention to this method because it can provide solution for a majority of the problems associated with the previous ones [10]. In the case of the melt suitable temperature for ferrates(VI) synthesis is up to 200 °C. In water solutions the typical temperature range is from 20 to 70 °C [1]. Utilizing electrochemical method the high purity ferrates(VI) are prepared. However, the stability of the product in the presence of water remains the weak point of this approach. Even a small amount of water presented in the highly alkaline paste decomposes ferrate(VI) within hours. Sharma [10] suggested the utilization of organic solvents instead of usual ones. However, the lower electrical conductivity on the one side and higher toxicity on the other side disadvantage this method.

An electrochemical treatment of iron in low-temperature melt binary hydroxide systems, e.g. KOH–LiOH, NaOH–KOH, CsOH–LiOH, KOH–RbOH has been proposed for ferrates(VI) preparation to minimize disadvantages of previous approaches [13]. The major advantage is usually the negligible presence of water: ferrates(VI) are prepared in dry form and therefore are stable. Another advantage of this technology is the fact that the reaction rate can be easily and continuously controlled by adjusting temperature in order to achieve the optimum anodic dissolution conditions. Híveš et al. [13] also reported the minimal thermal decomposition of ferrates(VI) during their electrochemical preparation. The most suitable eutectic mixture of NaOH and KOH (51.5% (n/n) of NaOH) was found in our previous studies [13–15]. This mixture is characterized by a relatively low eutectic melting point and high electrical conductivity [15]. In addition, the iron anode passivation is significantly reduced [1,14]. Ferrates(VI) formation can be detected easily by observing color change of the electrolyte. Titration, chemical precipitation, spectral and electrochemical methods can be used for the quantitative determination of ferrates(VI) concentration [11,16].

This work is focused on the preparation of ferrates(VI) by anodic oxidation of pure iron (Fe), silicon-rich steel (FeSi) and white cast iron (FeC) electrodes in the molten sodium hydroxide. All three electrodes were chosen in order to compare our results in molten hydroxide with previous reports by Mácová et al. [18–20] in strong alkaline aqueous solutions. The advantage of molten hydroxide to Mácová's approach is almost water-free environment, higher temperature and, therefore, higher reaction kinetics and efficiency of the ferrate(VI) production.

2. Experimental

2.1. Chemicals

Sodium hydroxides (Mikrochem Ltd., Pezinok, Slovakia) in p.a. grade with distilled water were used to prepare electrolytes. The purity of NaOH ranged from 72 to 82% (w/w), carbonate content of up to 0.6% (w/w) and water. Determination of NaOH purity was performed by acidimetric titration with HCl (Mikrochem Ltd., Pezinok, Slovakia, p.a.), using Methyl red indicator (Lachema Neratovice, Czech Republic, p.a.). Carbonates were determined gravimetrically, by precipitation with barium chloride (p.a., Lachema Neratovice, Czech Republic).

2.2. Apparatus and procedures

An oil thermostat with calibrated sensor, stainless steel box and PTFE crucible with the sample was used for our experiments. Reference connection of thermocouple was immersed in a Dewar flask with ice-water. Measuring connection of thermocouple was immersed into the melt at the same level as electrodes [17].

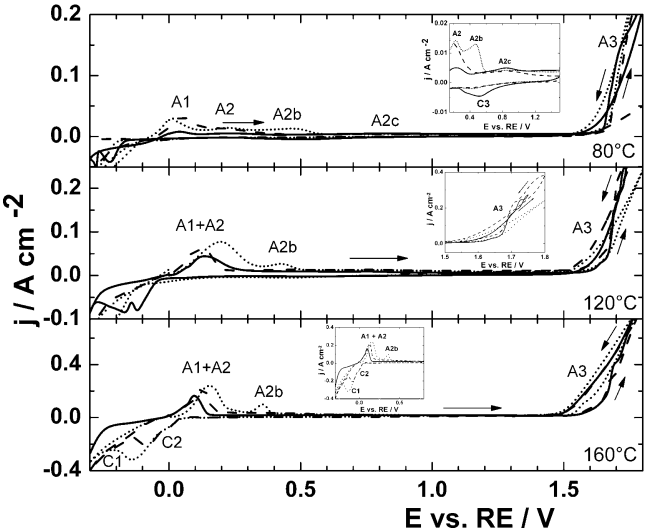

Fig. 1. Cyclic voltammograms of working electrodes, i.e. pure iron (solid line), FeSi (dashed line), and FeC (dotted line) at different temperatures in molten NaOH at scan rate of 400 mV s^{-1}; temperatures are indicated on the graph; arrows indicate the potential sweep direction; insets represent zoomed part of CVs in order to make peaks better visible.

Electrochemical measurements were performed using AUTOLAB instrument PGSTAT 20 equipped with FRA2 module (ECO Chemie, The Netherlands). A three electrode electrochemical cell was used for all experiments. Working electrodes (WE) were made from: (A) pure iron (Fe) (99.95% (w/w) Fe, 0.005% (w/w) C, 0.0048% (w/w) Ni and 0.0003% (w/w) Mn), (B) silicon steel (FeSi) (96.1% (w/w) Fe, 3.17% (w/w) Si, 0.47% (w/w) Cu, 0, 23% (w/w) Mn, 0.03% (w/w) Ni), and (C) white cast iron (FeC) (96.354% (w/w) Fe, 3.17% (w/w) C in the form of Fe_3C, 0.44% (w/w) Mn and 0.036% (w/w) Ni). The geometric area of the working electrodes varied from 0.2 to 0.7 cm^2. The same material (Fe) served as the reference electrode (RE) in all cases. Counter electrode (CE) was made from mild steel (steel class 11). Measurements were carried out in a PTFE crucible containing the melt of 50 g (NaOH–NaOH·H_2O). The temperature was varied in the range 70–160 °C. The lower limit is given by the temperature and composition of eutectic mixture NaOH–NaOH·H_2O which is 62.5 °C and 74% (w/w) of NaOH in mixture. Cyclic voltammograms were recorded in the potential range from −0.3 to 1.8 V vs. RE.

Impedance measurements were carried out in the same systems immediately after the measurement of polarization curves. The potential of the working electrode was gradually increased by 25 mV from 1.35 up to 1.75 V vs. RE. In this area, the formation of ferrates(VI) was expected. Frequency range used for the impedance measurements was from 10 Hz to 100 kHz. Perturbation signal had a sinusoidal shape with amplitude of 5 mV.

3. Results and discussion

3.1. Voltammetric analysis

In Fig. 1 cyclic voltammograms of Fe, FeSi and FeC electrodes in the molten NaOH at various temperatures are shown. The anodic part of the potential window is limited by the decomposition of the melt and subsequent oxygen evolution while the hydrogen evolution limits cathodic one.