THE FERRATES(VI) – THE NEW MATERIAL FOR HIGH CAPACITY BATTERY

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Introduction

Ferrates (ferrate means ferrate (VI) throughout the text) are compounds distinguishing by unique oxidizing properties. It is due to their unusual oxidation state of +VI. The first description of ferrate is dated to year 1702 [1] and as early as in 1715 [2] K_2FeO_4 was firstly prepared by Stahl through an oxidation of iron in molten nitrate salt. The first wave of attention to this compound could be noticed at the beginning of the 20th century in connection with a development of an alkaline battery, when Haber and Pick [3, 4] focused on the electrochemical way of its synthesis. They studied the influence of the process parameters on the reaction efficiency widely. Another time of interest in ferrates came in fifties and sixties due to their application as a powerful oxidizing agent. In those days Schreyer [5] investigated the chemical ferrate production and Toušek [6] was solving the problems of the electrochemical synthesis. A new interest steeply increasing in the last decade is caused by possibility of ferrate use as a strong oxidizing agent for environmental uses [7-10] and as a high capacity source of cathodic charge [11-13].

Due to its aforementioned strong oxidizing properties, ferrate is very unstable, especially in acidic and neutral media [14]. Thus the synthesis has to be carried out in high concentrated alkali environment. There are three basic methods of the ferrate synthesis developed:

1. The wet way of chemical oxidation consists of absorption of chlorine in concentrated NaOH solution and consequent reaction of forming hypochlorite with ferric ions to form ferrate.
2. Within the thermal way is the oxidation of Fe conducted at high temperatures in molten nitrate salts, oxides, peroxides or hydroxides of alkali metals.
3. Electrochemical oxidation of an iron anode to ferrate is conducted in concentrated solution of hydroxide of alkali metals. Despite its higher cost the electrochemical way doesn’t handle with toxic chloro-compounds and provides very pure final product.

The present work is focused on the process parameters of the electrolysis especially the role of a cation of the hydroxide solution used.

The problematic of the solution composition was studied already by Pick [4], who realized that the process efficiency is higher in NaOH solutions than in KOH. Hills [15] showed that addition of LiOH to KOH improves the efficiency of ferrate production by affecting the oxy-hydroxide layer forming on the anode surface. Beck *et. al.* [16] focused on the mechanism of ferrate production and compared KOH and NaOH solutions. As well as Pick [4] he observed lower current densities and lower current efficiency for ferrate synthesis in 50 %

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KOH solution. Lapicque [17] synthesized ferrate from mixed solution of KOH and NaOH. The current efficiency of ferrate production in solution of 7.1-8.6 M KOH with 10.1-8.1 M NaOH respectively was well comparable with that in 15.2 M NaOH. KOH does not affect the efficiency of the process but the low solubility of generated K_2FeO_4 provides a continual process of ferrate synthesis. However, further increase of KOH concentration lowered the ferrate yield. Similar suggestion about solubility in mixed KOH-NaOH solutions was made previously by Bailie in [18]. According to Licht [11], the ferrate with highest stability and very high charge capacity (313 mA h/g) is the ferrate of barium. In [19] Licht studied the direct electrochemical synthesis of solid $BaFeO_4$ from $NaOH/Ba(OH)_2$ electrolyte at 45 °C and current density of 1.6 $mA.cm^{-2}$. When pure $Ba(OH)_2$ solution was used only poor $BaFeO_4$ yield was observed. In solution of 14 M NaOH with 45 mM $Ba(OH)_2$ a product of high purity (95.0 %) and through easy procedure was obtained. The process efficiency exceeded a value of 60 %.

The aim of presented work was to identify the role of the solution cation in the whole process of ferrate production in highly concentrated solutions of alkali metal hydroxide solutions.

Experimental

Analytical grade purity NaOH, KOH and LiOH were used for solution preparation. The pure iron anode contained 99.95 wt. % Fe and less than 0.005 wt. % C, the white cast iron contained 3.16 wt. % C in the form of iron carbide (Fe_3C).

Solutions of 14 M KOH, 14 M NaOH, 5 M NaOH, 5 M LiOH and mixed LiOH-NaOH solutions (total hydroxide concentration of 5 M) were studied at various temperatures (20-40°C) and current densities (2-43 $mA.cm^{-2}$).

A conventional three-electrode configuration of a cell with compartments divided by PVC diaphragm (1mm thick of 43.4 % porosity and medium pore size 28 μm) was used for the experiments. The anolyte volume was 92 ml. The anodes were in the form of plates of active electrode surface area of 55.4 cm^2. An EG&G Potentiostat/Galvanostat Model 283 was used to obtain the polarisation data. The electrode potential values reffer to a HgO/Hg reference electrode.

The chromite method was used for the ferrate analysis. The Reihard-Zimmermann method was used to estimate the total iron concentration.

Results and Discussion

When results in KOH and NaOH solutions of same alkalinity were compared, strong differences came out. Using the KOH solution both ferrate concentration and from that arose ferrate current yield were much lower on both anode materials investigated. Moreover the maximum yield was obtained at lower current density than it was in the case of NaOH. The concentration of iron in oxidation states lower than Fe^{6+} is also significantly lower except for the experiment with pure iron at 30°C (what is still under discussion).

The low solubility of LiOH in water (5.3 M at 20°C) does not favor a direct comparison with previous experiment with KOH and NaOH. Despite low stability of ferrate at low solution alkalinity a comparable study of 5 M NaOH, LiOH and different mixtures of NaOH-LiOH was done. Decreasing current yield with increasing Li^+ content in the anolyte was observed. The only exception was noted within the experiment with white cast iron at 40°C. Also lower concentration of iron in oxidation states lower than Fe^{6+} in comparison with experiments in pure 5 M NaOH solution were observed for solutions with Li^+ concentration lower than 0.5 M. These both phenomena could be explained by different solubility of coming up iron species in different hydroxide solutions as it was done in [18] in case of KOH-NaOH mixtures. Two effects could be caused by lower solubility of ferrate or other iron species in the studied solution. It could results in higher anode passivation by coming up oxidation products and in lower concentration of ferrate intermediates in the near anode electrolyte layer.

Conclusions

Experiments in NaOH, KOH and LiOH solutions in temperature range of 20 to 40 °C led to conclusion that at these conditions the NaOH solution provides the highest ferrate current yields. No positive effect of Li^+ addition was observed.

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