Synthesis and Characterization of Ferrate(VI) Alkali Metal by Electrochemical Method

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ABSTRACT
This works aims at preparing at room stable Na2FeO4 and tracking its degradation over time. The synthetic, during this step, was carried out by electrochemical method. The latter was given maximum focus because of its simplicity and the high degree of purity of the resulting product with respect to wet and dry method. This paper reviews the development of the electrochemical method applied to the synthesis of stable at room Na2FeO4, optimizing the parameters impacting the performance of the oxidation of iron(II) in to iron(VI) in alkaline NaOH, saturated at a temperature of 61˚C and a current density of 1.4 A/dm2, in order to simplify the synthesis process, to minimize the cost and to improve the production of iron(VI) to meet the growing demand of ferrate(VI) useful for water treatment. The supervision of the degradation of synthesized Na2FeO4 shows its stability over a period of 10 months, which makes storage and transport easier. The phases obtained were characterized by IR spectrometry, X-ray, Mössbauer, spectroscopy and thermogravimetric analysis.

Keywords: Ferrate; Bactericidal; Oxidant; Flocculants; Coagulant; Conductivity; Cathode

1. Introduction
Iron compounds in the oxidation state (VI) have the advantage of being powerful antioxidants and bactericides, which explains their particular interest in water treatment. Moreover, their results in reduction of ferric hydroxide, their flocculating power contributes to the elimination of organic pollutants, minerals (hydrocarbons, heavy metals, radioactive isotopes...) and industrial effluents.

The synthesis of ferrate(VI) appears to be very delicate, because of the instability that gives them their high oxidizing power. Although the existence of alkaline ferrate has been testified for a century [1,2]. Several efforts have been made to synthesize the solid sodium ferrate [3-7]. Difficulties were encountered in isolating the solid product from each of the resulting solutions and stabilizing it.

The Na2FeO4 phase was synthesized by electrochemical way. Its oxidizing power makes it possible to use it as an oxidizing agent and a disinfectant in water treatment. It first reacts as iron(VI) causing an oxidation process during which the iron(VI) is reduced to Fe(III) that is itself used in the treatment of waste water to precipitate phosphate. The induced oxidation is not accompanied by unwanted byproducts. The aim of our work is to synthesize compounds based on iron(VI) Fe6+O42− stable at room temperature and replace potassium hydroxide by sodium hydroxide to obtain a significant reduction in the cost of synthesis of these ferrates. The electrochemical method used can provide a useful way for the industrial mass production of iron(VI).

2. Experimental
2.1. Synthesis
The first electrochemical synthesis of ferrate(VI) is due to Poggendorff (Poggendorff, 1841) [8]. This method is the easiest way to obtain the sodium ferrate in solution without impurities. The principle of the synthesis involves the oxidation of pig iron or iron salts in alkaline solutions using concentrated NaCl as a stabilizer. Figure 1 shows the experimental synthesis.

Next the various tests made by G. Grube [9,10], in concentrated NaOH environment by varying the Current density and temperature and the electrolysis time. During these tests, we found out that the performance of the iron oxidation varies depending on the current density, the temperature and the electrolysis time, according to Figure 2.
Figure 1. Schematic representation of the electrochemical cell for the synthesis of ferrate.

Figure 2. Performance of the oxidation of iron as a function of the current density $I$ at $T = 61^\circ C$ in concentrated NaOH for $I = 1.4 \text{ A/dm}^2$. Performance reaches a maximum value of 60%.

The increase in temperature leads to higher yields but with a maximum at $T = 61^\circ C$ Figure 3. Indeed, it catalyzes the oxidation of iron. Regarding the electrolysis time, it is obvious, from a first abort, that the number of moles of ferrates produced will increase if the reaction time is longer. But, alongside with this, we must not forget that we operate in aqueous media and that in contact with water, ferrate is reduced to form a precipitate of ferric hydroxyl according to the reaction:

$$2\text{Na}_2\text{FeO}_4 + 5\text{H}_2\text{O} \leftrightarrow 4\text{NaOH} + 2\text{Fe(OH)}_3 + 3/2\text{O}_2$$

In fact, from Figure 4, we can notice that beyond about an hour, the rate of decomposition $\text{FeO}_4^{2-}$ exceeds that of synthesis, since the over all performance drops.

The reactions involved are:

Anode
- Simultaneous oxidation of iron and solvent according to the reaction:
  $$\text{Fe} + 8\text{OH}^- \rightarrow \text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 6\text{e}^-$$
  $$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 6\text{e}^-$$

To obtain sufficiently high concentration ferrate, we use another source of Fe(III), that is the ferric salt FeCl$_3$, 6H$_2$O according to the following reaction:

$$\text{FeCl}_3 + 8\text{OH}^- \rightarrow \text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^-$$

FeO$_4^{2-}$ Formation process
- Trivalent iron reacts with the OH$^-$ to form an oxohydroxyl complex of FeO$_4$-nH$_2$O type which will then be oxidized electrochemically in the presence of ferrate halide (NaCl).

Cathode
- Only the reduction in hydrogen of the solvent was held.
  $$\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$
2.2. Characterizations

2.2.1. X-Ray Diffraction
Measures by a radiation ray diffractometer CuK of a compound of ferrate powder Na₂FeO₄ Figure 5 proves the crystal structure of ferrate [11,12] and demonstrates the existence of an isomorphism with K₂FeO₄ and BaFeO₄ as found by Stuart Licht, Vera. Naschitz and collaborators [13]. From the analytical point of view, the X-ray diffraction is one of the means used to verify the presence of ferrate.

The spectrum obtained on Na₂FeO₄ bears a strong similarity with that of isomorphous compounds. There is a splitting of the lines corresponding to planes (102), (202), (013), (200), (002), (004) [14-16].

2.2.2. Infrared Spectrum
The appearance of an infrared spectrum is related to the symmetry of the molecule or study group. We expected for FeO₄⁻, with tetrahedral structure, to find: first, the fundamental bands characteristic of a symmetry 2d: either bands \( \sqrt{3} \) and \( \sqrt{4} \) from the two degenerate modes of vibration: the symmetric stretching and angular deformation within the tetrahedron resulting in inactive modes in infrared absorption, bands \( \sqrt{1} \) and \( \sqrt{2} \) must be absent from the spectra [17]. On the other hand, a similarity is among infrared spectra of isomorphism series [18]. The presence of a band \( \sqrt{1} \) and a triplet for \( \sqrt{3} \) (elongation of the tetrahedron) have led W. Griffith [19] to consider a lower symmetry in 2d, very close to 2s the FeO₄⁻ anion.

IR spectroscopy is a quantitative method for the determination of iron(VI) compounds in the ferrate. The shape of the spectra is related to the symmetry of the molecule or FeO₄⁻ groups (tetrahedral structure) the IR spectrum of Na₂FeO₄. Figure 6 showed a similar pace in the field of high frequency to similar that obtained (mode 825 cm⁻¹ and 780 cm⁻¹) by P. Tarte and G. Nizete [20].

The IR results support those obtained by XRD.

2.2.3. ATG Spectrum
In general, two stages of decomposition were obtained in the TGA curve up to 500°C Figure 7. A first one above 100°C corresponding to the evolution of water weakly adsorbed by the sample and a second step between 210°C and 310°C corresponding to the release of O₂ Scholder et al. [21] and [22].

The two stages of decomposition were accompanied by endothermic heat effects as measured by TGA.

3. Tracking the Degradation of Ferrates as Function of Time
Analysis by Mössbauer Spectroscopy
The Mössbauer effect highlights the absorption of apha-
Figure 8. Mössbauer Na$_2$FeO$_4$ spectrometer after ten months of storage.

Figure 7. TGA spectrum of Na$_2$FeO$_4$.

Table 1. Hyperfine parameters deduced from the calculation of the spectrum after ten months of storage.

<table>
<thead>
<tr>
<th>Broadened component</th>
<th>Paramagnetic component</th>
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<tbody>
<tr>
<td>Sextuplet 1</td>
<td>Sextuplet 2</td>
</tr>
<tr>
<td>H$_{hyp}$ (kOe)</td>
<td>ISO (mm/s)</td>
</tr>
<tr>
<td>E4</td>
<td>490</td>
</tr>
</tbody>
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ton Y by a nucleus of $^{57}$Fe (present at a rate of about 2.6 percent in the natural iron): we varied gradually the energy of the photon emitted by variation of the speed of the source ($^{57}$Co. When it reaches a value equal to the difference between the energy level of the core in its ground state ($l = 1/2$) and its level in the excited state ($l = 3/2$) the photon is absorbed. This phenomenon results in a peak on the spectrum.

Mössbauer spectroscopy also helped to highlight the existence of a magnetic order at low temperature [23-27]. Na$_2$FeO$_4$ characterization by Mössbauer spectroscopy, after ten months of storage at room temperature, reveals a degradation of iron(VI) over time according to the Mössbauer spectrum Figure 8. We have a broad magnetic component calculated by the superposition of two sextuplets and a paramagnetic component adjusted by a paramagnetic doublet. The hyperfine parameters deduced from the calculation of the spectrum are given in Table 1.

This isomer shift is due to degradation of Fe(VI) to iron(III) because of moisture.

4. Conclusions

From the results, it’s possible to synthesize at room stable sodium ferrate Na$_2$FeO$_4$ electrochemically at a temperature of 61°C and a current density of $I = 1.4$ A/dm$^2$ in an alkaline medium saturated NaOH.

Infrared spectroscopy shows that we are dealing with a compound containing the FeO$_2^−$ group.

Mössbauer spectroscopy of iron allowed us to visualize the oxidation of iron and therefore to control the rate of iron(VI), and track its degradation in iron(III) over time.

The XR spectrum of Na$_2$FeO$_4$ is isomorphic to that given by K$_2$FeO$_4$ literature.

The spectrum shows a peak ATG at 100°C corresponding to the release of water and a peak at 295°C corresponding to the decomposition of Na$_2$FeO$_4$.

REFERENCES


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