



Synthesis and Characterization of Ambient Stable PbFeO_4 by Solid Way

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Abstract Iron compounds in the oxidation state (VI) have the advantage of being powerful oxidants and coagulants as well as "Super Iron" battery cathode; which explains in particular their interest in the treatment of water and the storage of loads considerably higher than conventional cathode materials.

The aim of this work is to prepare a new compound based on iron VI, in particular PbFeO_4 which is stable at ambient temperature by a solid process in order to optimize the essential parameters of the oxidation of iron (III) to iron (VI), as well as monitoring its degradation over time.

The synthesis of this phase was carried out by a solid method using the reaction of PbO with Fe_2O_3 under a stream of oxygen at a temperature of 750°C for a period of 3 hours and with a ratio of

$\text{Pb/Fe} = 2.5$, in order to simplify the synthesis process, minimize the cost and strengthen the production of iron (VI) to meet the growing demand for ferrate (VI) for their interest in water treatment and in cell cathodes.

The phase obtained was characterized by IR and DRX spectrometry as well as the UV spectrophotometer by measuring the optical density at the wavelength of 507 nm to follow the degradation of the ferrate over time as well as determine the degree of purity by the method of volumetric titration.

Keywords Ferrate, oxidant, cathode, Purity, Stability, physicochemical characterization.

1. Introduction

Ferrate (VI) is a supercharged iron compound in which iron is in the +6 oxidation state, it is known as iron (VI) is extremely potent as it can provide multiple treatments from single application, creates no disinfection by-products and is environmentally friendly and solves difficult treatment challenges that other oxidants cannot address, as well as recent advances in super-iron batteries, based on an unusual Fe(VI) cathodic charge storage, are presented. The Fe(VI) cathodes that have been demonstrated in super-iron batteries include the synthesized Fe(VI) compound with a three-electron cathodic charge capability.

Charge insertion or reduction of Fe(VI) represents an energetic and high capacity cathode charge source, and Fe(VI) salts have been prepared as an environmentally safe cathode (due to the product of ferric oxide). Super-iron batteries incorporating Fe(VI) cathode salts which have been recently introduced, examples include alkaline zinc, metal hydride batteries and non-aqueous lithium batteries, with several energy and environmental benefits [1].

Although the existence of alkaline ferrates has been cited for a century [2-10]. Currently, there is a need for research and innovation to improve existing methods of preparation and to develop new methods that would aim to increase the stability and yield of the latter.

In 1925, Losana [11] described the preparation of a variety of ferrate salts which included Ba^{2+} , Ag^+ , Sr^{2+} , Ca^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} and Cu^{2+} by direct precipitation from an aqueous solution of sodium/ potassium ferrate with salts of the desired counterion, as well as the preparation of impure salts of Th^{4+} , Fe^{2+} , Fe^{3+} and Al^{3+} .

In 1954 J.R. Gump and al. [12] proposes the synthesis of other ferrate such as Cs_2FeO_4 , BaFeO_4 , SrFeO_4 by first formation – according to the method of J. M Shreyer, with however Br_2 preferred to Cl_2 [4] as oxidant – from K_2FeO_4 to which a solution of CsOH , $\text{Ba}(\text{OH})_2$, $\text{Ba}(\text{NO}_3)_2$, BaCl_2 , $2\text{H}_2\text{O}$ or $\text{Sr}(\text{OH})_2$ leading to the precipitation of the alkaline or alkaline-earth ferrate corresponding to the cation of the salt used.

In recent years, an increasing number of investigations into the preparation, physico-chemical characterization and detailed performance of certain ferrates (VI), such as SrFeO_4 , BaFeO_4 , Na_2FeO_4 , Rb_2FeO_4 and Cs_2FeO_4 , have appeared in the literatures [13, 14, 15, 16].

In a similar study, Gump [17], described the preparation of metal salts (Li^+ , Cs^+) and La^{3+} ferrates.

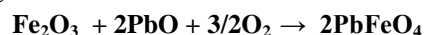
According to jiang and lloyd [18], dry synthesis at a temperature greater than or equal to 500°C seems unconvincing because of the explosiveness of the reaction medium and makes the high temperature synthesis process very dangerous.

2. Material and Method

Lead ferrate PbFeO_4 was prepared by heating a mixture of Fe_2O_3 and pure PbO under a stream of oxygen in a platinum crucible at a temperature of 750°C and a Pb/Fe ratio = 2.5 for a treatment period of 3 hours temperature of the reaction mixture.

The molten mixture obtained is cooled in a ball desiccator to avoid moisture absorption and above all we worked at a temperature of 750°C .

The synthesis reaction is the following:



The image below illustrates the color of the ferrates obtained by the solid process. In fact, FeO_4^{2-} ferrate ions are easily recognized by their purple color.

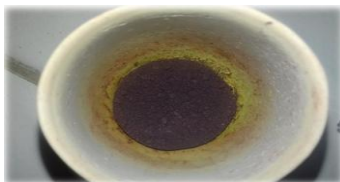


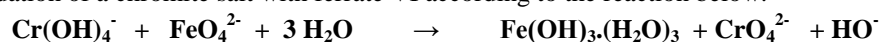
Image representing the color of synthesized lead ferrate

Analysis of the purity of the PbFeO_4 product was determined by chromite analysis and spectrophotometry.

Chromite analysis determines that the material is 69.7% pure based on the redox state and the remaining iron is in a lower valence state, although at these relatively low concentration levels the specific nature of this ferric impurity is difficult to distinguish. It can be assumed that the excess iron exists in the form of several amorphous ferric salts which can be generalized as a 30.3% ferric oxide impurity.

The PbFeO_4 phase found was analyzed and monitored over time with UV spectrophotometry by measuring the optical density at 507 nm, which is used according to tsapin et al [19], to measure the optical density of the solution of ferrate (VI) at a wavelength of 507 nm and a pH greater than 10.

The characteristic peak of iron (VI) comes out at this wavelength, as well as the volumetric titration method which is based on the oxidation of a chromite salt with ferrate VI according to the reaction below.



The resulting chromate is titrated with a ferrous salt solution with sodium diphenylamine sulfonate as an indicator [20].



3. Characterization

Diffraction by RX:

The XRD spectrum obtained for the ferrate compound PbFeO_4 powder (Figure 1) makes it possible to verify the crystal structure of this phase and to demonstrate the existence of an isomorphism with K_2FeO_4 and BaFeO_4 found by Licht *et al* [21].

X-ray diffraction is one of the means used to verify the presence of ferrates (VI).

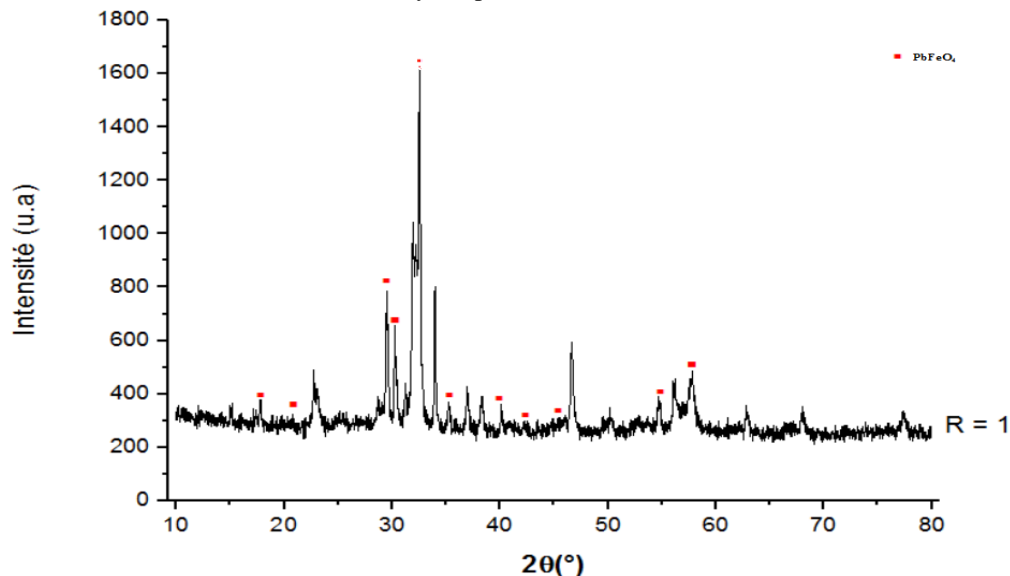


Figure 1: X-ray diffractogram of prepared PbFeO_4

The spectrum of PbFeO_4 obtained shows a similarity with that of isomorphous compounds, in particular K_2FeO_4 (Figure. 1) [21].

We note a splitting of the lines corresponding to the planes (102), (202), (013), (200), (002), (004), (105), (226), (114), (205), (412), (006), (026), (008), (301). [19], [22].

Note the existence of lines in the X-ray diffractogram of ferric impurities is difficult to distinguish, not observed in that of K_2FeO_4 . These lines can be attributed to excess iron existing in the form of several amorphous ferric salts.

IR spectroscopy:

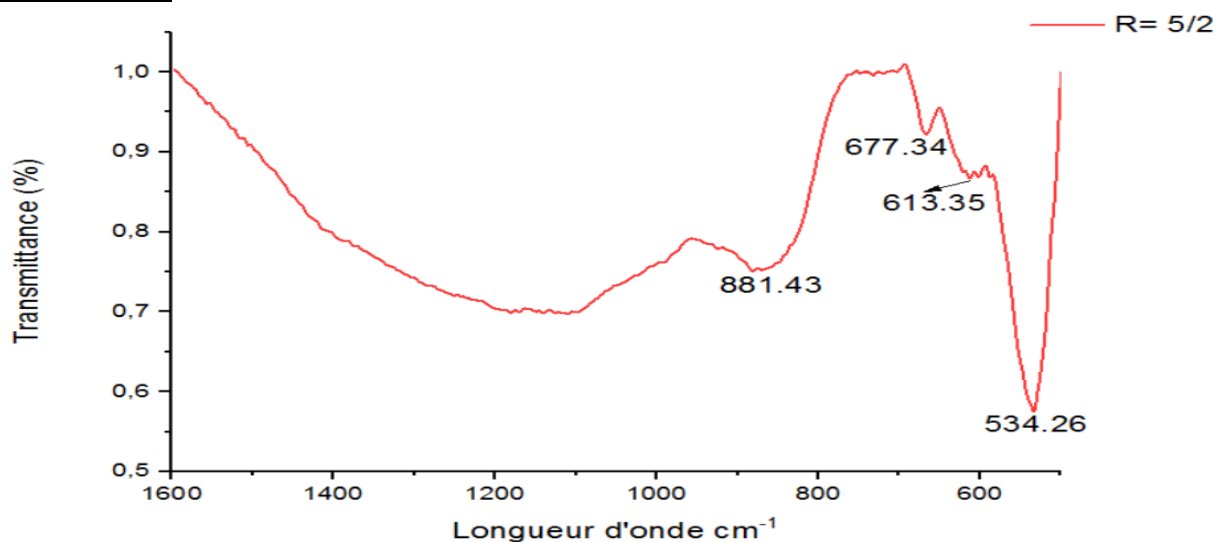


Figure 2: PbFeO_4 infra-red spectra



IR spectroscopy is a quantitative method for the determination of iron (VI) in ferrate compounds. The shape of the spectra is linked to the symmetry of the molecule or of the FeO_4^{2-} groups (tetrahedral structure) the IR spectrum of PbFeO_4 (figure. 2) revealed an identical shape in the high frequency range to that obtained (mode 881, 613 and 534 cm^{-1}) by P. Tarte and G. Nizete [23]. The results obtained by IR support those obtained by XRD.

4. Monitoring ferrate degradation over time

The PbFeO_4 degradation monitoring results show that the storage period can reach more than 10 months with a degradation rate in the first six months is limited to 3.3%.

The calculation results of the degradation rate between the months as well as between the state of production and ferrate (VI) and the different months of storage are given in Table 1.

The relation which allows to calculate the percentage of degradation of Iron (VI) is given by the following formula:

$$\% \text{ degradation of iron (VI)} = (\text{D.O}_i - \text{D.O}_f) / \text{D.O}_i$$

D.O_i: Optical densities of iron (VI) respectively in the initial state

D.O_f: Optical densities of iron (VI) in the final state

Tables 1: Optical density of the solution of ferrates (VI) of the synthesized phase PbFeO_4 according to the degradation rate between the initial state of production and different months of storage of ferrate VI (%) as well as according to the rate degradation between months of ferrate VI storage (%)

t (Months)	The rate of deterioration from baseline in the production and storage of different month ferrate VI (%)	The monthly rate of degradation ferrate VI (%)
1	0.6	0.6
2	1	0.4
3	1.6	0.6
4	2	0.4
5	2.9	0.9
6	3.1	0.2
7	3.7	0.6
8	4.7	1
9	4.9	0.2
10	5	0.1
11	6.2	1.2
12	7	0.8

According to these results (Table 1), we notice that the degradation rate of iron (VI) remains variable slightly as a function of time and varies in a different way from one month to another during storage, which means that the climate change influences the rate of degradation of ferrate (VI).

5. Discussion

According to our results, the Pb/Fe ratio necessary for the synthesis of iron (VI) stable at room temperature for a high yield is of the order of 2.5, this is compatible with the results of the various preliminary studies [11], [24], [25], which show that the optimal Pb/Fe ratio for the synthesis of iron (VI) per solid route is greater than 2.

The optimum temperature ($T = 750^\circ\text{C}$) for the synthesis of ferrates (VI) is encouraging progress for the development of industrial processes for the production of ferrates (VI). This result confirms the studies done by Martinez-Tamayo and al [24].



The synthesis reaction time ($t = 3$ h) is an important parameter for producing ambient stable ferrates (VI) by the solid-state route [11], [25]. As well as climate change influence on the degradation rate and the duration of storage of ferrate (VI) at ambient.

6. Conclusion

This manuscript reviews the most suitable method for the synthesis of ambient stable ferrate (VI) (PbFeO_4) from the reaction of Fe_2O_3 with PbO under oxygen flow whose Pb/Fe ratio = 2.5, a temperature of 750°C and a reaction time of the order of 3 hours.

The method of synthesizing ferrate (VI) by solid route is a very easy and very promising method, although there is still need for more technical, economic improvement concerning the application of industrial policy.

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