



Method of Synthesis and Characterization of a New Material based on Iron VI by Solid Way

Abdellatif EL MAGHRAOUI, Abdelaziz ZEROUALE, Mustapha IJJAALI, Ahmed HARRACH

Laboratory: Processes, Materials and Environment (LPME), Sciences and Technology Faculty, Sidi Mohammed Ben Abdellah University. P. O. Box 2202 Fez, Morocco
Correspondence: E-mail: elmaghraabdellatif@yahoo.fr

Abstract The development of iron (VI) synthesis processes is very delicate, this is due to the oxidizing power of iron (VI) and their interest as battery cathode. As a result, this work consists in developing a new material based on iron VI, in particular $ZnFeO_4$, 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 their degradation over time.

The synthesis of this phase was carried out by a solid process using the reaction of ZnO with Fe_2O_3 under a stream of oxygen at a temperature of $800^\circ C$ for a period of 2 hours and with a ratio of $Zn/Fe = 3$, 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

Introduction

The importance of the study of ferrates (VI) lies in their considerable increasingly diversified and innovative applications such as water treatment and the storage of loads considerably higher than conventional cathode materials.

Constituents based on iron and iron oxide have shown enormous practical uses in different fields, the best known and best studied are ferrates VI ($Fe^{VI}O_4^{2-}$) which have attracted particular interest from researchers due to their very high oxidative power for the degradation of recalcitrant and non-biodegradable compounds, such as pharmaceuticals, personal care products and heavy metals, as well as charge insertion or reduction of Fe(VI) represents an energetic and high-capacity cathodic charge source, and Fe(VI) salts were prepared as an environmentally safe cathode (due to the ferric oxide product). 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 Ba²⁺, Ag⁺, Sr²⁺, Ca²⁺, Pb²⁺, Ni²⁺, Co²⁺ and Cu²⁺ by direct precipitation from an aqueous solution of sodium ferrate. / potassium with salts of the desired counterion, as well as the preparation of impure salts of Th⁴⁺, Fe²⁺, Fe³⁺ and Al³⁺.

In 1954 J.R. Gump et al. [12] proposes the synthesis of other ferrate such as Cs₂FeO₄, BaFeO₄, SrFeO₄ by first formation – according to the method of J. M Shreyer, with however Br₂ preferred to Cl₂ [4] as oxidant – from K₂FeO₄ to which a solution of CsOH, Ba (OH)₂, Ba(NO₃)₂, BaCl₂, 2H₂O or Sr(OH)₂ causing 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 SrFeO₄, BaFeO₄, Na₂FeO₄, Rb₂FeO₄ and Cs₂FeO₄, have appeared in the literatures [13 , 14, 15, 16].

In a similar study, Gump [17], described the preparation of metal salts (Li⁺- Cs⁺) and La³⁺ ferrates.

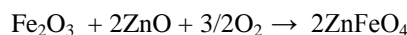
According to jiang and lloyd [18], dry synthesis at a temperature greater than or equal to 500°C seems unconvincing because of the explosiveness of the reaction medium and makes the high temperature synthesis process very dangerous.

Material and Method

ZnFeO₄ lead ferrate was prepared by heating a mixture of Fe₂O₃ and pure ZnO under a stream of oxygen in a platinum crucible at a temperature of 800°C and a Pb/Fe ratio = 3 for a treatment period of 2 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 800°C.

The synthesis reaction is the following:

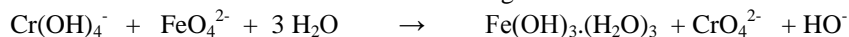


Analysis of the purity of the ZnFeO₄ product was determined by chromite analysis and spectrophotometry.

Chromite analysis determines that the material is 80% 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 20% ferric oxide impurity.

The ZnFeO₄ 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].

Characterization

X-ray diffraction

The XRD spectrum obtained for the ferrate compound ZnFeO₄ powder (Figure 1) makes it possible to verify the crystal structure of this phase and to demonstrate the existence of an isomorphism with K₂FeO₄ and BaFeO₄ found by Licht et al [21].

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



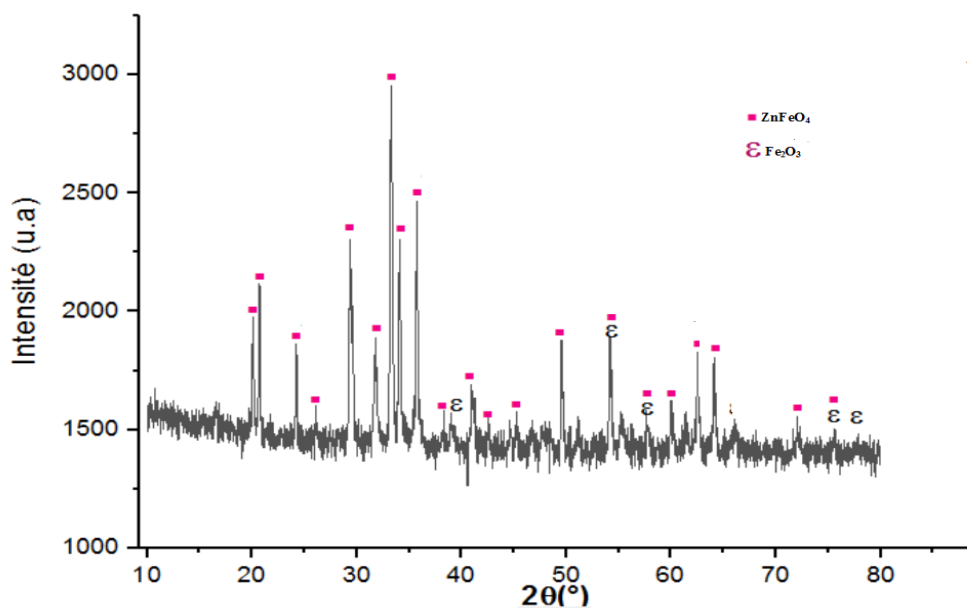


Figure 1: X-ray diffractogram of prepared $ZnFeO_4$

The spectrum of $ZnFeO_4$ obtained presents 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

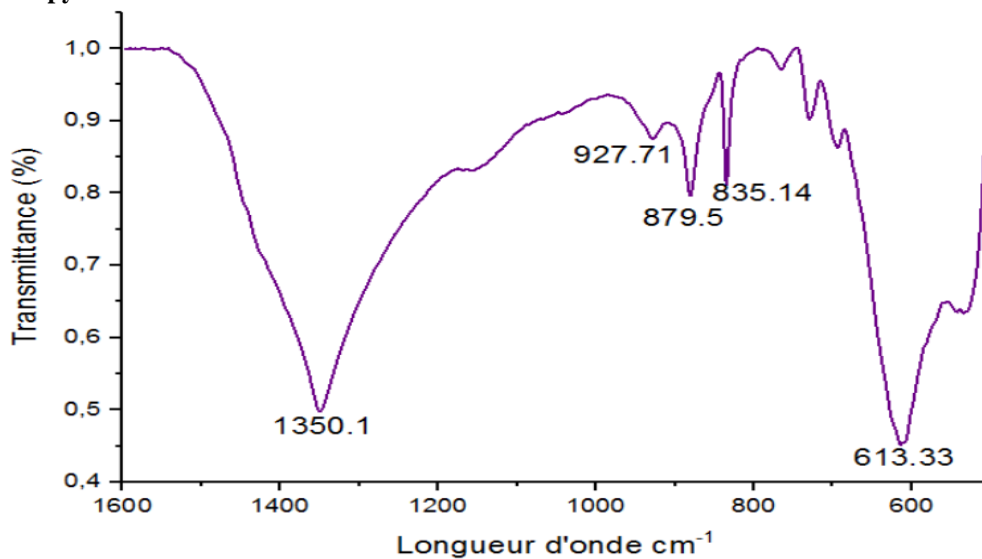


Figure 2: $ZnFeO_4$ infra-red spectrometer

IR spectroscopy is a quantitative method for the determination of iron (VI) in ferrate compounds. The appearance of the spectra is linked to the symmetry of the molecule or of the FeO_4^{2-} groups (tetrahedral structure) the IR spectrum of $ZnFeO_4$ (figure. 2) revealed an identical appearance in the high frequency range to that obtained (mode 1350.1, 881 and 616 cm^{-1}) by P. Tarte and G. Nizete [23]. The results obtained by IR support those obtained by XRD.



Monitoring ferrate degradation over time

The ZnFeO₄ 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 6.3%.

The results of calculation 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:

$$\% \text{ iron (VI) degradation} = (D.O_i - D.O_f) / D.O_i$$

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

Table 1: Optical density of the ferrate (VI) solution of the synthesized ZnFeO₄ phase as a function of the degradation rate between the initial state of production and different months of ferrate VI storage (%) as well as a function of 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	0.5	0.5
2	1	0.5
3	1.6	0.6
4	2	0.4
5	5	3
6	6.3	1.3
7	6.6	0.3
8	8	1.4
9	9	1
10	10.2	1.2
11	10.6	0.4
12	11	0.4

According to these results (tab.1), we note 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).

Discussion

According to our results, the Zn/Fe ratio necessary for the synthesis of iron (VI) stable at room temperature for a high yield is of the order of 3, this is compatible with the results of the various preliminary studies [11], [24], [25], which show that the optimal Zn/Fe ratio for the synthesis of iron (VI) by the solid route is greater than 2.

The optimum temperature (T = 800°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 et al [24].

The synthesis reaction time (t = 2 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.

Conclusion

This manuscript reviews the most suitable method for the synthesis of ferrate (VI) (ZnFeO₄) stable at ambient temperature from the reaction of Fe₂O₃ with ZnO under a current of oxygen whose Zn/Fe ratio = 3, a temperature of 800° C. and a reaction time of the order of 2 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.

References

- [1]. S. Licht, V. Naschitz, S. Ghosh, 2002, Silver mediation of Fe(VI) charge transfer: Activation of the K_2FeO_4 super-iron cathode, *J. Phys. Chem., B*, 106, p. 5947, 2002.
- [2]. H. J. Hrostowski, A.B. Scott, 1950, The magnetic susceptibility of potassium ferrate, *J. Chem. Phys.*, 18, pp. 105-107, 1950.
- [3]. L. Ockerman, J. M. Schreyer, G. W. Thompson, 1951, Preparation and purification of potassium ferrate VI, *J. Am. Chem. Soc.*, 73, pp.1379-1381,1951.
- [4]. J. M. Schreyer, G. W. Thompson, L.T. Ockerman, 1953, Potassium ferrate (VI), *Inorg. Synthesis*, 4, pp. 164-169, 1953.
- [5]. A. Hooker, 1920, *Chem. and Met. eng.*, 23, p. 961, 1920.
- [6]. G. W.Thompson, L.T. Ockerman, J. M. Schreyer, 1951, Preparation and purification of potassium ferrate VI, *J. Am. Chem. Soc.*, 73, pp. 1379-1381, 1951.
- [7]. R. Scholder, H. Bunsen, F. Kin, W. Zeiss and Z. Anorg, 1955, "Zur Kenntnis der Ferrate(VI)," *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 282, No. 1-6, 1955, pp. 268-279, 1955. doi:10.1002/zaac.19552820129.
- [8]. R. Scholder, 1965, Über alkali-oxo-metallate (V) der elemente chrom, mangan, eisen und kobalt, *Bull. Soc. Chem. Fr.*, 7, pp. 1112-1114, 1965.
- [9]. W. F. Wagner, J. R. Gump and E. N. Hurt, 1952 "Factors Affecting Stability of Aqueous Potassium Ferrate(VI) Solutions," *Analytical Chemistry* Vol. 24, No. 9, pp. 1497-1498, 1952. doi: 10.1021/ac60069a037.
- [10]. R. J. Audette, J.W. Quail, 1972, Potassium, Rubidium, Cesium, and barium ferrates VI: préparations, infrared spectra, and magnetic susceptibilities, *Inorg. Chem.*, 11, pp. 1904 -1908, 1972.
- [11]. L. Losana, 1925, *Gazz. Chim. Ital*, vol. 55, pages 468-97, 1925.
- [12]. J. R. Gump, W. Wagner, J. M. Schreyer, *Anal. Chem.*, 26, p. 1957, 1954.
- [13]. S. Licht, S. Ghosh, *Journal of power sources* 109, 465, 2002.
- [14]. K. E. Ayers, N. C. White, 2005, *Journal of the Electrochemical Society* 152A467, 2005.
- [15]. S. Licht, V. Naschitz, S. Ghosh, L. Lin, 2001, *Electrochemical communication*. 3, 340, 2001.
- [16]. S. Licht, R. Tel-redded, 2004, *Chemical communications*, 628, 2004.
- [17]. J. Gump., E. Hart, W. Wagner. 1952, *Analyt. Chem.* Vol. 24, pages 1497-1498, 1952.
- [18]. J. Q. Jiang, B. Lloyd, 2002, « Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and waste water treatment» *Water Research*, 36, pp 1397-1408, 2002.
- [19]. A. I. Tsapin, M. G. Goldfeld, G. D. McDonald, K. H. Nealson, B. Moskovitz, p. Solheid, W. Klemner, S. D. Kelly, K. A. Orlandini, 2000, iron (VI): Hypothetical candidate for The Martian Oxidant *Icarus* 147, pp. 68-78, 2000.
- [20]. J. Q. Jiang, B. Lloyd, 2002 « Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and waste water treatment» *Water Research*, 36, pp 1397-1408, 2002.
- [21]. S. Licht, V. Naschitz, L. Halperin, N. Halperin, L. Lin, J. Chen, S. Ghosh and B. Liu, 2001, Analysis of ferrate (VI) compounds and super-iron Fe (VI) battery cathodes: FTIR, ICP, titrimetric, XRD, UV/VIS, and electrochemical characterization, *J. Power Sources*, 101, pp. 167–176, 2001.
- [22]. Y.L. Wang, S.H. Ye, Y.Y. Wang, J.S Cao and F. Wu, 2009, Structural and Electrochemical Properties of a K_2FeO_4 Cathode for Rechargeable Li Ion Batteries, *Electrochimica Acta*, 54, 16, P. 4131-4135, 2009, doi:10.1016/j.electacta.2009.02.053.
- [23]. P. Tarte, G. Nizet, 1964, *spectrochimica acta*, 20, p. 503, 1964.



- [24]. E. Martinez-Tamayo, A. Beltran-porter, D. Beltran-porter, 1986, Iron compounds in high oxidation states: II. Reaction between Na_2O_2 and FeSO_4 , *Therm. Acta*, 97, pp. 243-255, 1986.
- [25]. Y. M. Kisselev, N. S. Kopelev, N. A. Zavyalova, perfiliev , Y. D. Kazin P. E., 1989, The preparation of alkali métal ferrates VI, *Russ. J. Inorg. Chem.*, 34, pp. 1250 -1253, 1989.