Scope
Volume 16 Number 01 March 2026

Quantitative and Qualitative Evaluation of Iron VI in the Compound ($CuFeO_4$) Synthesized by Wet Method

Abdellatif El Maghraoui[1], Mustapha Ijjaali[1], Rachida Bouagaga[2]

1. Laboratory: Processes, Materials and Environment (LPME), Sciences and Technology Faculty, Sidi Mohammed Ben Abdellah University. P. O. Box 2202 Fez (Morocco).
2. Laboratory of Human Pathology, Biomedicine and Environment, Faculty of Medicine, Pharmacy and Dentistry of Fez, Sidi Mohammed Ben Abdellah University. P. O. Box 2202 Fez (Morocco).

Correspondance Author : **Abdellatif El Maghraoui**

Abstract: Due to its high reduction potential, large electrochemical capacity, and non-toxic discharge product, Fe(VI) is of compelling interest for the formation of high-energy super-iron batteries. Therefore, the synthesis of high-quality cathodic salts is very challenging. The CuFeO4 synthesis process involves substituting the barium ions of the ferrate(VI) obtained with copper. This is achieved by mixing the synthesized BaFeO4 with a copper nitrate (Cu(NO3)2) solution to determine the optimal temperature for achieving good substitution purity and to monitor its degradation over time. The reaction purity is approximately 99.7% at a temperature of around 20°C–30°C and pH 11 for 40 minutes. The resulting phase was characterized by UV spectrophotometry by measuring the optical density at a wavelength of 507 nm and analyzed by volumetric titration.
Keywords: Ferrate, oxidant, electrochemical, cathode, copper ferrate(VI), Purity, Stability.

I. Introduction

Ferrate(VI) is the high-oxidation iron compound that possesses strong oxidizing power, a relatively high redox potential, and an environmentally friendly reduction product. Due to these advantages, ferrate(VI) has been used as an alternative to common oxidants, such as toxic chlorine and chromate, in organic synthesis and wastewater treatment. Recently, "super-iron" batteries have been shown to have higher capacity and energy efficiency than conventional alkaline batteries. As summarized in equation (1), ferrate(VI) salts undergo three-electron reduction at relatively higher potentials [1–6].

$$FeO_4^{2-} + 5/2H_2O + 3e^- \rightarrow 1/2Fe_2O_3 + 5OH^- \quad (1)$$

Efficient and economical energy storage is very important for the growing demand of society. Just like fuel cells and lithium-ion batteries, ferrate (VI) materials have also received a lot of attention for their potential used as cathode materials in the development of "super-iron" batteries since the late 1990s due to their energetic, but non-toxic nature [7-12].

Currently, there is a need for research and innovation to improve existing preparation methods and develop new ones aimed at increasing their stability and yield.

Scholder et al., 1956-b [13] proposed two methods for synthesizing M_2FeO_4 if M is a divalent element (Ba^{2+}, Sr^{2+}): either from Fe(III) or from the corresponding alkaline earth metaferrates.

Ferrates(VI) have also been prepared from galvanized waste [14]. The waste was mixed with ferric oxide in a furnace at 800°C, the sample was cooled and mixed with solid sodium peroxide, then gradually heated for a few minutes. Among the wet and electrochemical synthesis methods, the dry method avoids the reaction of the ferrates with water. This ferrate preparation process is considered a green technology because it recycles various residual iron compounds [15].

In recent years, a growing number of investigations into the preparation, physicochemical 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 literature [4, 6, 16, 17]. The solubility of $BaFeO_4$, a salt more commonly studied in the context of super-oxidizing iron [18], has also been investigated.

Recently, Ag_2FeO_4, with an unusual intrinsic capacity of 5 electrons, has also been presented; however, its impurity and instability hinder its potential as a cathode for a promising super-iron battery [19]. Attempts to search for alternative ferrate (VI) salts with high intrinsic storage capacity, such as $CaFeO_4$ and $MgFeO_4$, etc., will be encouraging.

Calcium (VI) ferrate powders were synthesized from potassium (VI) ferrate and characterized by titration analysis, elemental analyzer, SEM, XRD, IR, TG and DSC. The results showed that the synthesized sample consists mainly of calcium (VI) ferrate and that calcium (VI) ferrate can exist in the form of $CaFeO_4$ [20].

In 1925, Losana described the preparation of a variety of ferrate salts, including 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+} [21].

In a similar study, Gump described the preparation of the metallic salts (Li^{+}- Cs^{+}) and La^{3+} ferrates [22].

II. Materials and Methods

The synthesis of $CuFeO_4$ is carried out by dissolving the prepared $BaFeO_4$ ferrate salt in an aqueous solution of copper nitrate $Cu(NO_3)_2$ at a pH around 11 and a temperature of [20°C-30°C], for 40 minutes in order to obtain a heterogeneous black precipitate which settles spontaneously and immediately at the bottom of the tube of copper salt, according to reaction (2) of ion exchange of the ferrate salt VI with copper nitrate:

$$BaFeO_4 + Cu(NO_3)_2 \rightarrow CuFeO_4 + Ba(NO_3)_2 \quad (2)$$

The heterogeneous black precipitate was filtered through filter paper and washed three times with deionized water. The resulting $CuFeO_4$ product was dried for 6 h under vacuum at room temperature to determine the exact mass of $CuFeO_4$.

The purity of the $CuFeO_4$ product was determined by arsenite analysis and spectrophotometry.

The material obtained contains less than 0.3% copper equivalent relative to barium. Arsenite analysis determined the material to be 99.7% pure based on its redox state, and the remaining iron is in a lower valence state. However, 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 to a 0.3% ferric oxide impurity.

The preparation of $BaFeO_4$ is carried out by mixing pure $Ba_3(Fe(OH)_6)_2$, H_2O, and $Ba(OH)_2$ in a platinum crucible to avoid side reactions. The resulting mixture is placed in a furnace at a temperature of 850°C under a stream of oxygen for 12 hours with a Ba/Fe ratio of 3, and finally the molten mixture is cooled in a ball dryer [23]. According to synthesis reaction (3):

$$Ba_3(Fe(OH)_6)_2, H_2O + 3Ba(OH)_2 + 3/2\ O_2 \rightarrow 2\ BaFeO_4 + 4BaO + 10\ H_2O \quad (3)$$

The $CuFeO_4$ phase was analyzed and monitored over time using UV spectrophotometry by measuring the optical density at 507 nm, which, according to Tsapin et al. [24], is used to measure the optical density of the ferrate(VI) solution at a wavelength of 507 nm and a pH greater than 10. The characteristic peak of iron(VI) appears at this wavelength, as does the volumetric titration method, which is based on the reduction of ferrate to ferric ions in an excess of alkali arsenite solution according to reaction (4).

$$2FeO_4^{2-} + 3AsO_3^{3-} + 11H_2O \rightarrow 2Fe(OH)_3(H_2O)_3 + 3AsO_4^{3-} + 4HO^- \quad (4)$$

The excess arsenite is then back-titrated with bromate according to reaction (5), and the equivalent of the ferrate is thus deduced.

$$2BrO_3^- + 5AsO_3^{3-} + 2H^+ \rightarrow Br_2 + 5AsO_4^{3-} + H_2O \quad (5)$$

III. Results

The yield of the $CuFeO_4$ phase synthesis reaction as a function of pH and temperature of the reaction medium gives an idea of the evolution of the synthesis reaction (figure 1,2).

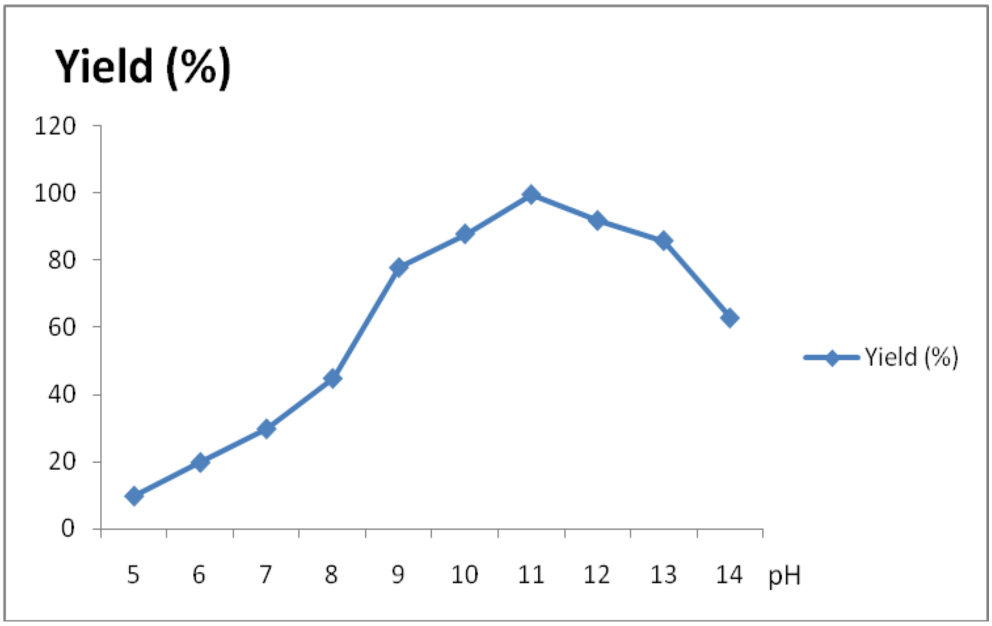

Figure 1: Yield of the $CuFeO_4$ ferrate(VI) synthesis reaction as a function of the reaction medium's pH.

According to the curve (Fig. 1), the yield of the ferrate(VI) obtained increases with the reaction medium's pH, reaching 99.71% at pH 11. This implies that the optimum pH of the synthesis medium is around pH 11. Consequently, the impurity of the synthesized compound is almost zero, making it more stable and promising for energy storage as a cathode material.

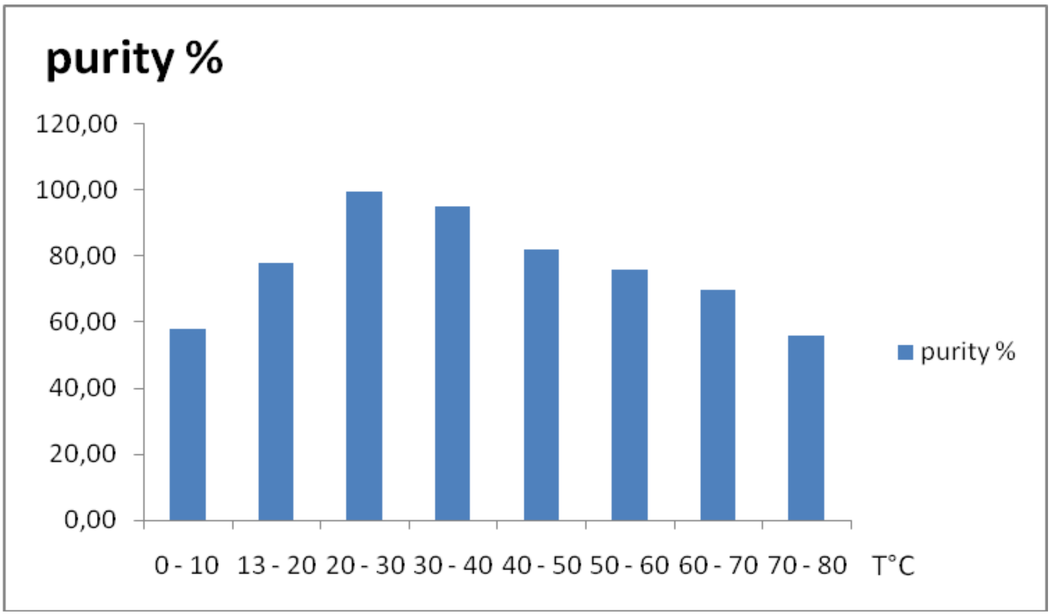

Figure 2: Purity of the synthesized $CuFeO_4$ ferrate(VI) as a function of reaction medium temperature.

According to the curve (Fig. 2), the purity of the synthesized ferrate(VI) decreases with increasing temperature from [30°C– 40°C], implying that the optimum temperature of the synthesis medium is around [20°C–30°C], as purity reaches its maximum within this temperature range.

IV. Evaluation of the stability of synthesized cathodic salt as a function of time

The stability evaluation results for $CuFeO_4$ show that storage can last up to 12 months, with a degradation rate limited to 0.8% during the first six months.

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

The formula used to calculate the percentage of iron(VI) degradation is as follows:

% degradation of iron (VI) = $(D.O_i - D.O_f)/D.O_i$

$D.O_i$: 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 synthesized $CuFeO_4$ solution as a function of the degradation rate between the initial state of production and different months of storage of ferrate VI (%) as well as as a function of the degradation rate between the months of storage of ferrate VI (%).

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	**0.04**	**0.04**

2	**0.05**	**0.01**
3	**0.06**	**0.01**
4	**0.07**	**0.01**
5	**0.1**	**0.03**
6	**0.8**	**0.7**
7	**1.3**	**0.5**
8	**1.8**	**0.5**
9	**2.3**	**0.5**
10	**3.4**	**1.1**
11	**3.6**	**0.2**
12	**3.9**	**0.3**

According to these results (table 1), we note that the rate of degradation of iron (VI) remains almost invariable over time, registering a small degradation in a different way from one month to another during storage, which shows the stability of this compound over time.

V. Discussion

The pH required for the synthesis of room-stable iron(VI) with a yield of 99.7% is approximately 11 (Figure 1). This is consistent with the results of several previous studies [20], [21], which show that pH adjustment, modification of reagent concentrations, and improvement of the wet synthesis procedures for ferrate salts such as $CuFeO_4$ are necessary.
Based on previous studies on the effect of temperature on the purity of synthesized cathodic salt, the optimal temperature for obtaining pure $CuFeO_4$ of approximately 99.7% is around 20°C–30°C (Fig. 2). Therefore, this work represents encouraging progress for the development of industrial processes for the production of ferrates (VI). This result confirms the studies conducted by Zhihua Xu et al., 2007 [20], and indicates that reducing impurities leads to improved stability and increases the discharge performance of the copper ferrate sample, resulting in a greater intrinsic capacity and improved flow rate.
Climate change also influences the degradation rate and storage duration of ferrate (VI) at ambient temperature.

VI. Conclusion

This article reviews the effect of temperature on the synthesis reaction of pure and room-stable $CuFeO_4$ ferrate(VI) from the reaction of copper nitrate $Cu(NO_3)_2$ and $BaFeO_4$, with a pH of approximately 11, at a temperature of approximately 20 –30°C and a reaction time of about 40 minutes.
The wet process for synthesizing $CuFeO_4$ ferrate(VI) from $BaFeO_4$ is a very easy and promising method, although further technical and economic improvements are still needed for industrial application.

VII. References :

1. Sharma V. K., Advances in Environment Research 6, 143, 2002.
2. Delaude L., Laszlo P., Journal of Organic Chemistry 61, 6360, 1996.
3. Licht S., Wang B., Ghosh, S., Science 285, 1039, 1999.
4. Licht S., Ghosh S., Journal of Power Sources 109, 465, 2002.
5. Walz K.A., Suyam a A.N., Suyama W.E., Sene J.J., Zeltner W.A., Armacanqui E.M., Roszkowski A.J., Anderson M.A., Journal of Power Sources 134, 318, 2004.
6. Ayers K.E., White N.C., Journal of the Electrochemical Society 152 ,A467, 2005.
7. Wang Z.B., Yin G.P., Shi P.F., "Microwave heated polyol synthesis of carbon-supported PtSn nanoparticles for methanol electrooxidation ", Electrochem. Commun., 8(1), 83-90, 2006.
8. Sari A, Kaygusu K., "First and second laws analyses of a closed latciir heat thermal energy storage system", Chin. J. Chenz. En., 12(2), 290-293, 2004.
9. Zhong L., Zhang T.Y., Chen, J.J., Wei G.L., Luo J.L., Chung K., "Effect of H_2S flow rate and concentration on performance of H_2S/air solid oxide fuel cell", Chin. J. Chem. Eng., 12(2), 306-309,2004.
10. Yu L.J., Yuan J.Q., Cao G.Y., Jiang X.M., "Numerical simulation of dynamic performance of the molten car- bonate fuel cell", Chin. J. Chem. Eng., 12(2), 272- 276, 2004.
11. Kim J.W., Ryu J.H., Lee K. T., Oh S. M., "Improve- ment of silicon powder negative electrodes by copper electroless deposition for lithium secondary batteries", J. Power Sources, 147(1/2), 227-233, 2005.
12. Tang Z.Y., Feng J.J., Peng Y.N., "Studies on spinel LiMnO, cathode material synthesized from different Mn sources", Chin. J. Chem. Eng., 12(2), 124-127, 2004.
13. Scholder R., Kindervater F., Zeiss W., 1956-b, Uber orthoferrate IV, Z. Anorg. Allg. Chem., 283, pp. 330-337, 1956.
14. Cici M., Cuci Y., 1997, production of some coagulant materials from galvanizing workshop waste, Waste manage., 17,7, pp. 407 – 410, 1997.
15. Lee Y.H., M. Cho., Kim J.Y., Yoon J., 2004, Chemistry of ferrate Fe (VI) in aqueous solution and its application as a green chemical, J. Ind. Eng. Chem., 10, pp. 161-171, 2004.
16. Licht S., Naschitz, Ghosh V., Lin, S., L., Electrochemical communication. 3, 340, 2001.
17. Licht S., Tel-reded R., Chemical communications 628, 2004.
18. Licht S., Naschitz V., Wang B., J. Power sources 109, 1(67), 2002.
19. Licht S. , Yang L. , Wang, B. , Electrochemistry Communications, 7 , p. 931, 2005.
20. Zhihua Xu a,b, Jianming Wang , Haibo Shao , Zheng Tang , Jianqing Zhang, Preliminary investigation on the physicochemical properties of calcium ferrate(VI), Electrochemistry Communications,9,pp. 371–377,2007.
21. Losana L., Gazz. Chim. Ital, vol. 55, pages 468-97, 1925.
22. Gump, J.., Hart, E., Wagner, W.. Analyt. Chem. Vol. 24, pages 1497-1498, 1952.
23. El maghraoui A, Zerouale A, Ijjaali M, SYNTHESIS PROCESS OF STABLE $BaFeO_4$ BY DRY METHOD, International Journal of Chemistry and Materials Research, 3(4): 100-106, 2015. ISSN(e): 2311-763X/ISSN(p): 2312-0991.
24. Tsapin A. I., Goldfeld M. G., Mcdonald G.D., Nealson K.H., Moskovitz B., Solheid p., Klemner W., Kelly S.D., Orlandini K.A., iron (VI): Hypothetical candidate fort he Martian Oxidant Icarus 147, pp. 68-78, 2000.