

# Investigating Temperature-Dependent Synthesis of CuFeO<sub>4</sub> Cathode Salt

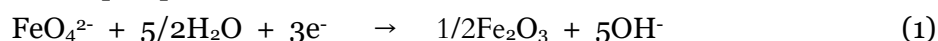
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**Abstract** Fe (VI) due to the high reduction potential, the large electrochemical capacity and the non-toxic discharge product, are useful for the formation of energetic super-iron batteries of compelling interest. As a result, the synthesis of high-quality cathodic salts proves to be very delicate according to the CuFeO<sub>4</sub> synthesis process which consists in substituting the Barium ions of the ferrate VI obtained by copper, by mixing the BaFeO<sub>4</sub> synthesized with a solution of copper nitrate Cu(NO<sub>3</sub>)<sub>2</sub>, in order to determine the optimum temperature of the good substitution purity as well as the monitoring of its degradation over time, of which the purity of the reaction is of the order of 99.7% at a temperature of around [20°C - 30°C] at pH = 11 for 40 minutes. The phase obtained was characterized by UV spectrophotometer by measuring the optical density at the wavelength 507 nm and analyzed by the volumetric titration method.

## Introduction

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



Efficient and economical energy storage is very important for the growing demand of society. Much 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 nontoxic character [7-12].

Currently, there is a need for research and innovation in order to improve the existing preparation methods and to develop new methods which would aim to increase the stability and the yield of the latter.

Scholder et al [13] recommended two methods of synthesizing M<sub>2</sub>FeO<sub>4</sub> if M is a divalent element (Ba<sup>2+</sup>, Sr<sup>2+</sup>) from Fe (III) or from the corresponding alkaline earth metaferrate.

Ferrates (VI) were also prepared from galvanized waste [14], the waste was mixed with ferric oxide in an oven at



800 ° C, the sample was cooled and mixed with sodium peroxide solid then gradually heated for a few minutes. Among the wet and electrochemical methods of synthesis, the dry method avoids the reaction of ferrates with water. This process for preparing ferrates is considered a green technology by recycling various waste iron compounds [15].

In recent years, an increasing number of investigations into the preparation, physico-chemical characterization and detailed performance of certain ferrates (VI). Such as SrFeO<sub>4</sub>, BaFeO<sub>4</sub>, Na<sub>2</sub>FeO<sub>4</sub>, Rb<sub>2</sub>FeO<sub>4</sub> and Cs<sub>2</sub>FeO<sub>4</sub>, have appeared in literatures [4, 6, 16, 17]. The solubility of BaFeO<sub>4</sub>, a salt more commonly studied in connection with super oxidant iron [18].

Recently, Ag<sub>2</sub>FeO<sub>4</sub>, with an unusual intrinsic capacity of 5 electrons has also been presented, however, the impurity and instability detract from it as a promising super-iron battery cathode [19]. Attempts to search for alternative ferrate (VI) salts with high intrinsic storage capacity, such as CaFeO<sub>4</sub> and MgFeO<sub>4</sub>, etc. will be encouraging. Calcium ferrate (VI) powders were synthesized from potassium ferrate (VI) and characterized by titration analysis, elemental analyzer, SEM, XRD, IR, TG and DSC. The results showed that the synthesized sample mainly consists of calcium ferrate (VI) and that calcium ferrate (VI) can exist as CaFeO<sub>4</sub> [20].

In 1925, Losana described the preparation of a variety of ferrate salts which included Ba<sup>2+</sup>, Ag<sup>+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Cu<sup>2+</sup> 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<sup>4+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> [21]. In a similar study, Gump described the preparation of metal salts (Li<sup>+</sup> -Cs<sup>+</sup>) and La<sup>3+</sup> ferrates [22].

## Material and Method

The synthesis of CuFeO<sub>4</sub> is done by dissolving the ferrate salt of BaFeO<sub>4</sub> prepared in an aqueous solution of copper nitrate Cu(NO<sub>3</sub>)<sub>2</sub> at a pH around 11 and temperature of [20°C- 30°C], for 40 minutes in order to obtain a heterogeneous black precipitate which deposits at the bottom of the tube spontaneously and immediately of copper salt, according to the ion exchange reaction (2) of the ferrate VI salt with copper nitrate:

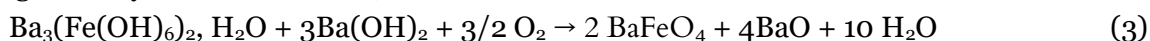


The heterogeneous black precipitate was filtered through filter paper, and washed three times with deionized water. The resulting product CuFeO<sub>4</sub> was dried for 6 h under vacuum at room temperature to give the exact mass of CuFeO<sub>4</sub>.

The analysis of the purity of the CuFeO<sub>4</sub> product was determined by arsenite analysis and spectrophotometry. The material obtained contains less than 0.3% copper equivalent relative to barium as well as arsenite analysis determines that the material is 99.7% 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 as several amorphous ferric salts that can be generalized as a 0.3% ferric oxide impurity.

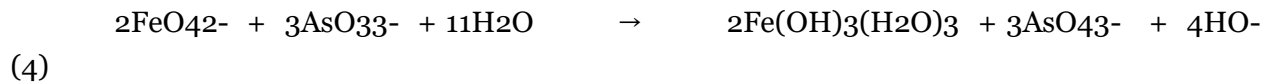
The preparation of BaFeO<sub>4</sub> is done by mixing Ba<sub>3</sub>(Fe(OH)<sub>6</sub>)<sub>2</sub>, H<sub>2</sub>O and Ba (OH)<sub>2</sub> pure in a platinum crucible in order to avoid side reactions. The mixture obtained is placed in an oven at a temperature of 850 ° C. under a stream of oxygen for a period of 12 hours with a Ba / Fe ratio = 3, and finally the molten mixture obtained is cooled in a ball dryer [ 23].

According to the synthesis reaction (3):

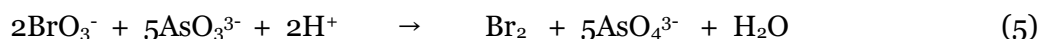


The phase found CuFeO<sub>4</sub> was analyzed and followed over time with UV spectrophotometry by measuring the optical density at 507 nm, which is used according to tsapin et al [24], to measure

the optical density of the ferrate solution (VI) at a wavelength of 507 nm and 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 reduction of ferrate in ion ferric in solution of excess alkaline arsenite according to reaction (4).



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



## Results

The yield of the reaction of the synthesis of the  $\text{CuFeO}_4$  phase as a function of the pH and the temperature of the reaction medium gives an idea of the progress of the synthesis reaction (Figure 1.2)

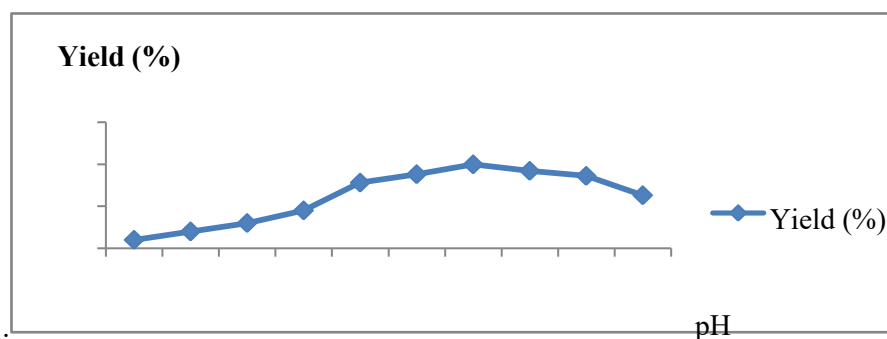


Figure 1: Reaction yield of the synthesis of ferrate (VI)  $\text{CuFeO}_4$  as a function of the pH of the reaction medium

From the curve (Fig. 1), it is observed that the yield of the ferrate (VI) obtained increases as a function of the pH of the reaction medium up to 99.71% at the value of pH = 11, which implies that the optimum pH of the synthesis reaction medium is around pH = 11. As a result the synthesized compound impurity is almost zero, which makes it more stable and promising for energy storage as cathode materials.

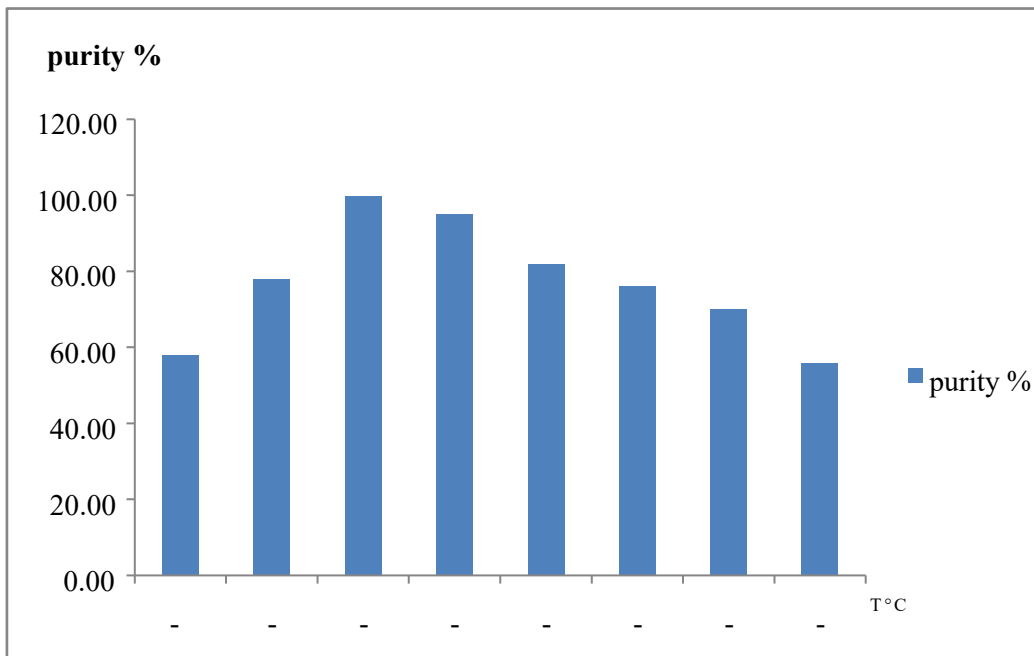


Figure 2: Purity of the ferrate (VI)  $\text{CuFeO}_4$  synthesized as a function of the temperature of the reaction medium According to the curve (Fig. 2), it can be seen that the purity of the ferrate (VI) synthesized decreases with the increase in temperature from [30°C- 40°C], which implies that the optimum temperature of the medium of the synthesis reaction is around [20°C - 30°C], because in this temperature range the purity reaches its maximum.

### Evaluation of the stability of synthesized cathodic salt as a function of time

The results of the evaluation of the stability of  $\text{CuFeO}_4$  show that the shelf life can reach 12 months with a degradation rate in the first six months is limited to 0.8%.

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

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

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

**D.O<sub>i</sub>**: Optical densities of iron (VI) respectively in the initial state

**D.O<sub>f</sub>**: Optical densities of iron (VI) in the final state

**Table 1:** Optical density of the  $\text{CuFeO}_4$  solution synthesized according to the rate of degradation between the initial state of production and different months of storage of ferrate VI (%) as well as according to the rate of degradation between the months of storage of ferrate VI (%).

t (Months)	The rate of deterioration from baseline in the production and storage of ferrate VI different month ferrate VI (%)	The monthly rate of degradation of ferrate VI (%)
0.04		0.04
0.05		0.01
0.06		0.01

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0.07	0.01
0.1	0.03
0.8	0.7
1.3	0.5
1.8	0.5
2.3	0.5
3.4	1.1
3.6	0.2
3.9	0.3

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

### Discussion

The pH required for the synthesis of iron (VI) stable at room temperature for a yield of 99.7% is of the order of 11 (Figure 1), this is compatible with the results of various preliminary studies [20-21], which show that the adjustment of the pH, the modification of the concentrations of the reagents and the improvement of the procedures of synthesis of ferrate salts like  $\text{CuFeO}_4$  by wet way is required.

According to previous studies on the effect of temperature on the purity of the cathodic salt synthesized, it is deduced that the optimum temperature for having pure  $\text{CuFeO}_4$  of the order of 99.7% is around [20°C- 30°C], (Fig. 2). Therefore this work is an encouraging progress for the development of industrial processes for the production of ferrates (VI). As this result confirms the studies made by Zhihua Xu and col., 2007 [20], and meant that the decrease in impurities leads to better stability and increases the discharge performance of the copper ferrate sample with a higher intrinsic capacity. Climate change also influences the rate of degradation and the storage time of ferrate (VI) in the room.

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### Conclusion

This article reviews the effect of temperature on the reaction of synthesis of ferrate (VI)  $\text{CuFeO}_4$  pure and stable at room temperature from the reaction of copper nitrate  $\text{Cu}(\text{NO}_3)_2$  and  $\text{BaFeO}_4$  whose pH is around of 11, at a temperature of around [20°C - 30°C] for a reaction time of the order of 40 minutes.

The process for the wet synthesis of ferrate (VI) of  $\text{CuFeO}_4$  from  $\text{BaFeO}_4$  is a very easy and very promising method, although there is still a need for further technical, economical improvement regarding industrial application.

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