



Synthesis Process for New Cathode Materials based on Alkaline Iron VI: Cs_2FeO_4

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Abstract Recent advances in super-iron batteries, based on unusual Fe (VI) cathodic charge storage, are presented. Fe (VI) cathodes that have been demonstrated in super-iron batteries include the Fe (VI) compound synthesized with a three-electron cathodic charge capacity. Therefore, this study presents a procedure for the synthesis of cathode salts Cs_2FeO_4 or cesium super-iron from BaFeO_4 chemically synthesized from ferric salts, in an alkali hydroxide medium and hypochlorite which is a particularly oxidizing agent. efficient in the synthesis, respecting the filtration, purification and drying processes required for the synthesis, because each change can lead to decomposition and decrease in purity. This method consists of substituting the barium ions of the ferrate VI obtained by cesium by mixing them with a saturated solution of cesium carbonate Cs_2CO_3 , in order to study and optimize the essential parameters influencing the substitution yield as well as the monitoring of its degradation. Over time, the reaction yield of which is of the order of 95.7% at a temperature of around $[30^\circ\text{C}-45^\circ\text{C}]$ and of $\text{pH} = 11$ for 45 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.

Keywords Ferrate, Oxidizer, Electrochemical, Cathode, Cesium Ferrate (VI), Purity, Stability

Introduction

Batteries are based on unusual Fe (VI) redox couple and multi-electron cathode charge storage, such Fe (VI) cathodes can be "green", cost effective and store considerably higher charge than conventional cathode materials. . The development of iron (VI) synthesis processes is proving to be very delicate, due to the oxidizing power of iron (VI). Among all the oxidants / disinfectants, practically used for the treatment of water and pollutants in water [1]. Ferrates are in high demand because it has a standard potential of $\text{FeO}_4^{2-}/\text{Fe}^{3+} = 2.2\text{V}$. The evolution of water pollution presents very dangerous statistics thanks to the appearance of new pollutants. Although the existence of alkali ferrates has been cited for a century [2-10]. 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, 1956-b [11] recommended two methods of synthesizing M_2FeO_4 if M is a divalent element (Ba^{2+} , Sr^{2+}) from Fe (III) or from the corresponding alkaline earth metaferrate.

Kopelev et al [12] prepared sodium ferrate Na_4FeO_5 and Na_2FeO_3 according to the procedure of Kisselev et al [13]. 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 synthesis methods, 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_4 , BaFeO_4 , Na_2FeO_4 , Rb_2FeO_4 and Cs_2FeO_4 , have appeared in the literature [16, 17, 18, 19]. The solubility of BaFeO_4 , a salt more commonly studied in connection with super oxidant iron [20].

In 1925, Losana [21], 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 ferrate. / potassium 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 a similar study, Gump [22], described the preparation of metal salts (Li^+ - Cs^+) and La^{3+} ferrates.

L. Moser and al. [23, 24] has spoken well about the manner and mixing of the reaction of obtaining rubidium cesium ferrate in solution and the double decomposition between barium ferrate and cesium carbonate.

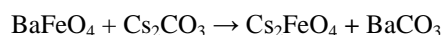
In 1954 J. R. Gump and al. [25] proposes the synthesis of other ferrate such as Cs_2FeO_4 , BaFeO_4 , SrFeO_4 by first formation - according to the method of JM Shreyer, however with Br_2 preferred to Cl_2 [4] as oxidant - of K_2FeO_4 to which will be added a solution of CsOH , $\text{Ba}(\text{OH})_2$, $\text{Ba}(\text{NO}_3)_2$, BaCl_2 , $2\text{H}_2\text{O}$ or $\text{Sr}(\text{OH})_2$ causing the precipitation of the alkaline or alkaline-earth ferrate corresponding to the cation of the salt used.

Scholder and al. [26] seems to achieve a purer salt in the case of cesium by performing a reaction similar to that which they describe for potassium; that is to say, oxidation of ferric hydroxide by potassium hypobromite, but in a mixed solution of potash - cesium hydroxide (in order to limit the quantities of cesium used). We tried this reaction, but failed to separate the ferrate formed with the excess hydroxide.

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Material and Method

The synthesis of Cs_2FeO_4 is carried out by dissolving the ferrate salt of BaFeO_4 prepared in an aqueous solution of cesium carbonate Cs_2CO_3 at a pH of around 11 and temperature of [30°C - 45°C], for 45 minutes in order to obtain a heterogeneous red precipitate which deposits spontaneously and immediately at the bottom of the tube of the cesium salt, according to the ion exchange reaction of the ferrate VI salt with the cesium carbonate:



The heterogeneous red precipitate was filtered through filter paper, and washed three times with deionized water. The resulting product Cs_2FeO_4 was dried for 6 h under vacuum at room temperature to give the exact mass of Cs_2FeO_4 .

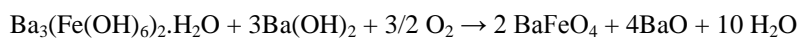
The analysis thus the purity of the product Cs_2FeO_4 was determined by chromite analysis and spectrophotometry.

Chromite analysis determines that the material is 95.7% pure based on the redox state and the remaining iron is in a lower valence state, although at these relatively low concentration levels, nature specific to this ferric impurity is difficult to distinguish. It can be assumed that excess iron exists as several amorphous ferric salts which can be generalized as a 4.3% ferric oxide impurity.

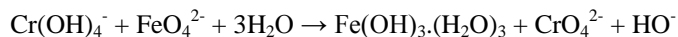
The preparation of BaFeO_4 is done by mixing $\text{Ba}_3(\text{Fe}(\text{OH})_6)_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{OH})_2$ pure in a platinum crucible in order to avoid side reactions. The mixture obtained is placed in an oven at a temperature of 850°C . under a stream of oxygen for a period of 12 hours with a ratio of $\text{Ba} / \text{Fe} = 3$, and finally the molten mixture obtained is cooled in a ball dryer [31].

The synthesis reaction is as follows:





The phase found CuFeO_4 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* [32], 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 does 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 solution of ferrous salt with sodium diphenylamine sulfonate as an indicator [33].

Results

The yield of the reaction of the synthesis of the Cs_2FeO_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 (Figures 1 and 2).

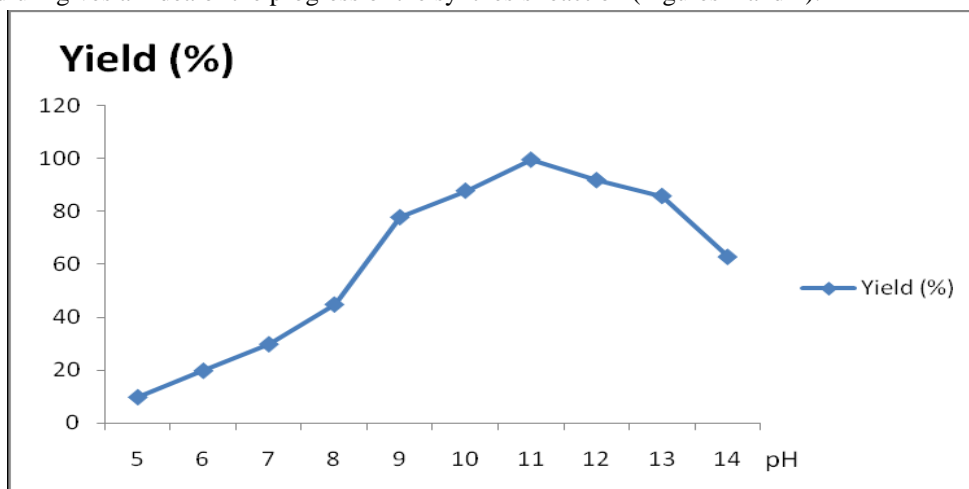


Figure 1: Reaction yield of the synthesis of ferrate (VI) Cs_2FeO_4 as a function of the pH of the reaction medium.

According to the curve (Fig. 1), it can be seen that the yield of the ferrate (VI) obtained increases as a function of the pH of the reaction medium up to 95.71% at the value of pH = 11, which implies that the optimum pH of the synthesis reaction medium is around pH = 11.

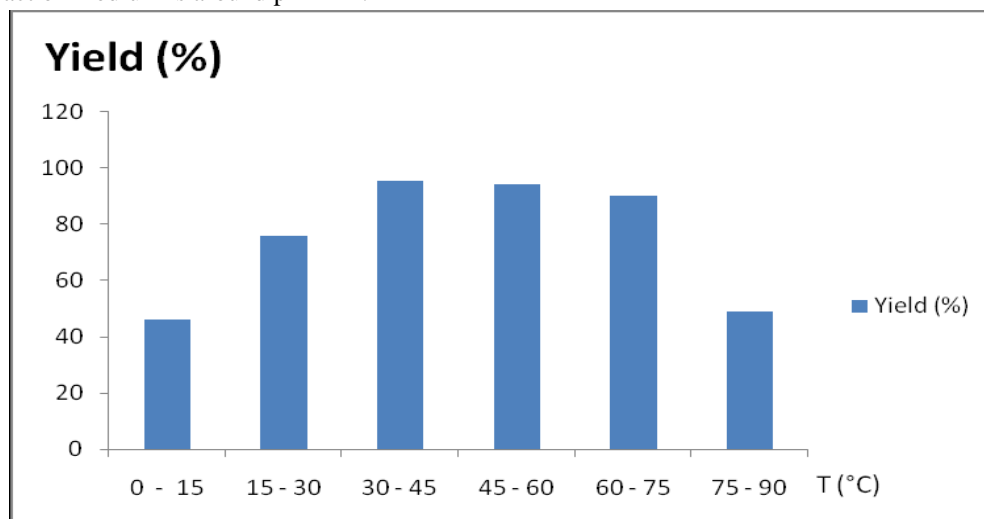


Figure 2: Reaction yield of the synthesis of ferrate (VI) Cs_2FeO_4 as a function of the temperature of the reaction medium

According to the curve (Fig. 2), we see that the yield of ferrate (VI) decreases with the increase in temperature from [30°C- 45°C], which implies that the optimum temperature of the medium of the synthesis reaction is around [30°C - 45°C], because in this temperature range the yield reaches its maximum.

Monitoring of the degradation of ferrate as a function of time

The results of Cs₂FeO₄ degradation monitoring show that the storage period can reach 12 months with a degradation rate in the first six months is limited to 2.3%.

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:

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

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

Tables 1: Optical density of the solution of ferrates (VI) of the synthesized phase Cs₂FeO₄ according to the rate of degradation between the initial state of production and various months of storage of ferrate VI (%) as well as according to the rate degradation between 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	0.8	0.8
2	1	0.2
3	1.6	0.6
4	1.8	0.2
5	2	0.2
6	2.1	0.1
7	2.7	0.6
8	3	0.3
9	3.5	0.5
10	4.5	1
11	6	1.5
12	8	2

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

Discussion

The pH necessary for the synthesis of iron (VI) stable at room temperature for a yield of 95.7% is of the order of 11 (Figure 1), this is compatible with the results of the various preliminary studies [25, 26, 27, 28, 29, 30], which show that the adjustment of the pH, the modification of the concentrations of the reagents and the improvement of the procedures for the synthesis of ferrate salts like Cs₂FeO₄ by the wet route is required.

The optimum temperature, which is around [30°C- 45°C], for the synthesis of Cs₂FeO₄ (Figure 2) is an encouraging progress for the development of industrial processes for the production of ferrates (VI). This result confirms the studies made by JR Gump and al [25], Scholder and al [26], as well as the reduction of impurities leads to better stability and increases the discharge performance of the calcium ferrate (VI) sample with greater intrinsic capacity



and better throughput capacity. Climate change also influences the rate of degradation and the storage time of ferrate (VI) in the room.

Conclusion

This manuscript reviews the most adequate method for the synthesis of ambient stable ferrate (VI) Cs_2FeO_4 from the reaction of cesium carbonate Cs_2CO_3 and BaFeO_4 whose pH is around 11, at a temperature around $[30^\circ\text{C}-45^\circ\text{C}]$ and a reaction time of the order of 40 minutes. The process for the wet synthesis of Cs_2FeO_4 ferrate (VI) from BaFeO_4 is a very easy and very promising method, although there is still a need for further technical, economical improvement in industrial application.

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