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## Synthesis and characterization of new cathodic material for rechargeable Iron(VI) batteries

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**Abstract** 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. . Therefore, this study presents a procedure for the synthesis of cathode salts SrFeO<sub>4</sub> or strontium super-iron from K<sub>2</sub>FeO<sub>4</sub> 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 potassium ions of the ferrate VI obtained by strontium by mixing them with a saturated solution of strontium hydroxide Sr(OH)<sub>2</sub>, in order to study and optimize the essential parameters influencing the substitution yield as well. that the monitoring of its degradation over time, the reaction yield of which is of the order of 96.7% at a temperature of around [0°C - 60°C] and of pH = 12 for 25 minutes.

The phase obtained was characterized by XRD, Mössbauer spectroscopy as well as the UV spectrophotometer by measuring the optical density at the wavelength 507 nm to follow the degradation of the ferrate over time and determine its degree of purity by the titration method (volumetric).

**Keywords** Ferrate, oxidant, electrochemical, cathode, strontium ferrate (VI), Purity, Stability

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### Introduction

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 three-electron cathodic charge capacity Na<sub>2</sub>FeO<sub>4</sub>, K<sub>2</sub>FeO<sub>4</sub>, Rb<sub>2</sub>FeO<sub>4</sub>, Cs<sub>2</sub>FeO<sub>4</sub> (Fe(VI) alkali salts), alkaline earthy Fe (VI), salts BaFeO<sub>4</sub>, SrFeO<sub>4</sub>, as well as a transition salt Fe (VI) Ag<sub>2</sub>FeO<sub>4</sub> which exhibits a five-electron cathodic charge storage [1].

The development of iron (VI) synthesis processes is proving to be very delicate, this is due to the oxidizing power of iron (VI) and their value as a cathode for batteries. ferrates are very stressed because it has a standard potential of  $\text{FeO}_4^{2-} / \text{Fe}^{3+} = 2.2 \text{ V}$ .

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 and 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.

Licht and al [12] arrived at  $Ag_2FeO_4$ , with an unusual intrinsic capacity of 5 electrons was also presented, however, the impurity and instability detracts from it as a promising super-iron battery cathode. Attempts to search for alternative ferrate (VI) salts with high intrinsic storage capacity, such as  $CaFeO_4$  and  $MgFeO_4$ , etc. will be encouraging.

In 1954 J. R. Gump and al. [13] 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, however with  $Br_2$  preferred to  $Cl_2$  [14] as oxidant - of  $K_2FeO_4$  to which will be added a solution of  $CsOH$ ,  $Ba(OH)_2$ ,  $Ba(NO_3)_2$ ,  $BaCl_2$ ,  $2H_2O$  or  $Sr(OH)_2$  causing the precipitation of the alkaline or alkaline-earth ferrate corresponding to the cation of the salt used.

If Eidman and Moser [15], prepared it by the action of a solution of strontium bromide on potassium ferrate and Losana [16] by reaction of strontium nitrate on the same salt, Scholder [17] uses exactly the same same method as in the case of barium in order to obtain by this process a reddish powdery product which can be kept for a certain time in a sealed tube.

In recent years, a growing 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 literature [18, 19, 20, 21, 22, 23].

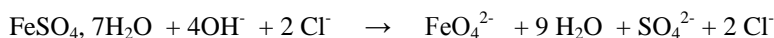
### Material and Method

The synthesis of  $SrFeO_4$  is done by treating the potassium ferrate salt prepared  $K_2FeO_4$  with an aqueous solution of strontium hydroxide  $Sr(OH)_2$  at pH around 12, temperature  $0^\circ C$  to  $60^\circ C$  for 25 minutes via a reaction of substitution of potassium ions of ferrate VI obtained by strontium in order to obtain a reddish powdery precipitate which deposits at the bottom of the tube spontaneously and immediately of strontium salt, according to the ion exchange reaction of the ferrate salt VI with strontium hydroxide:



The reddish powdery precipitate was filtered through filter paper, and washed three times with deionized water. The resulting product,  $SrFeO_4$ , was dried for 6 h under vacuum at room temperature to give the exact mass of  $SrFeO_4$ .

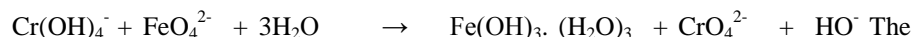
The preparation of  $K_2FeO_4$  is done by mixing hydrated iron sulfate  $FeSO_4 \cdot 7H_2O$  and concentrated  $ClO^-$  bleach at  $48^\circ F$  in the presence of  $KOH$ . The mixture is stirred for one hour at a temperature of around  $55^\circ C$  depending on the reaction:



$K_2FeO_4$  is recovered by vacuum filtration. This phase is dried at  $120^\circ C$  for 12 hours and then put in a desiccator for one hour at minimum before grinding [24], the dried  $K_2FeO_4$  product has been shown to be stable over time, and can be used for strontium ferrate syntheses directly or after storage.

The phase obtained was characterized by XRD, Mössbauer spectroscopy and by the volumetric chromite titration method, The latter method determines that the material obtained is 96.7% 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 excess iron exists as several amorphous ferric salts which can be generalized as a 3.3% ferric oxide impurity.

The volumetric titration method 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 [25].

The percentage of the original iron-containing material, which is converted to the solid Fe (VI) salt, was determined by the chromite method [26], to probe both the valence state of strontium and iron, measured by the reaction of salt to oxidize chromite. Then as title the chromate obtained by a solution of ferrous ammonium salt in the presence of sodium diphenylamine sulfonate as color indicator.



## Characterization

### Diffraction by RX:

The XRD spectrum obtained for the powdered  $\text{SrFeO}_4$  ferrate compound (Figure 1) makes it possible to verify the crystal structure of this phase and to demonstrate the existence of an isomorphism with  $\text{K}_2\text{FeO}_4$  and  $\text{BaFeO}_4$  found by Licht *et al* [3].

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

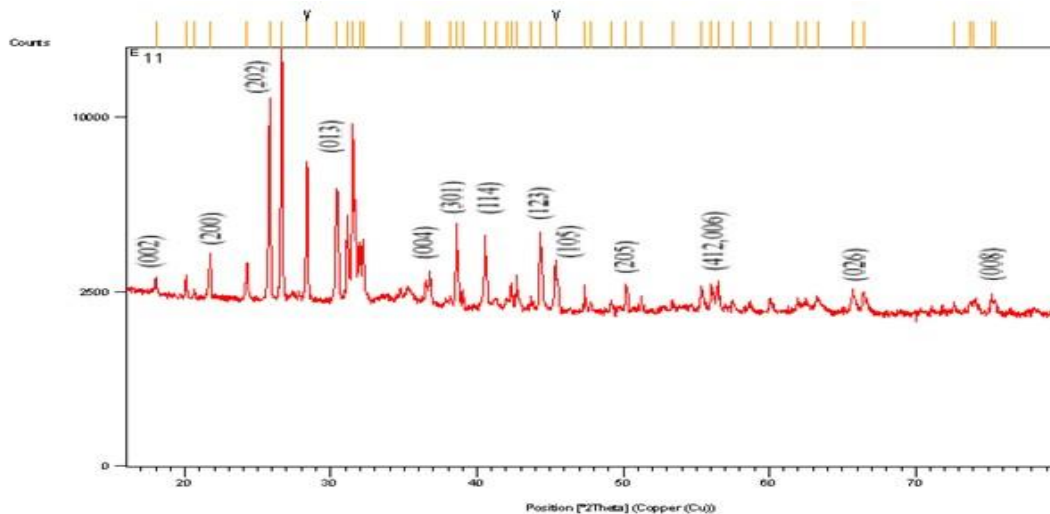


Figure 1: RX diffractogram of prepared  $\text{SrFeO}_4$

The spectrum of  $\text{SrFeO}_4$  obtained presents a similarity with that of isomorphous compounds, in particular  $\text{K}_2\text{FeO}_4$  (Figure 1) [27].

We note a doubling of the lines corresponding to the planes (102), (202), (013), (200), (002), (004), (105), (226), (114), (205), (412), (006), (026), (008), (301). [28], [29].

We note the existence of lines in the X-ray diffractogram of ferric impurities, which is difficult to distinguish, not observed in that of  $\text{K}_2\text{FeO}_4$ . These lines can be attributed to the excess iron that exists in the form of several amorphous ferric salts.

### Mössbauer Spectroscopy Analysis:

The Mossbauer spectrum obtained for the powdered  $\text{SrFeO}_4$  ferrate compound (Figure 2) allows the degree of oxidation of iron to ferrate VI to be observed.

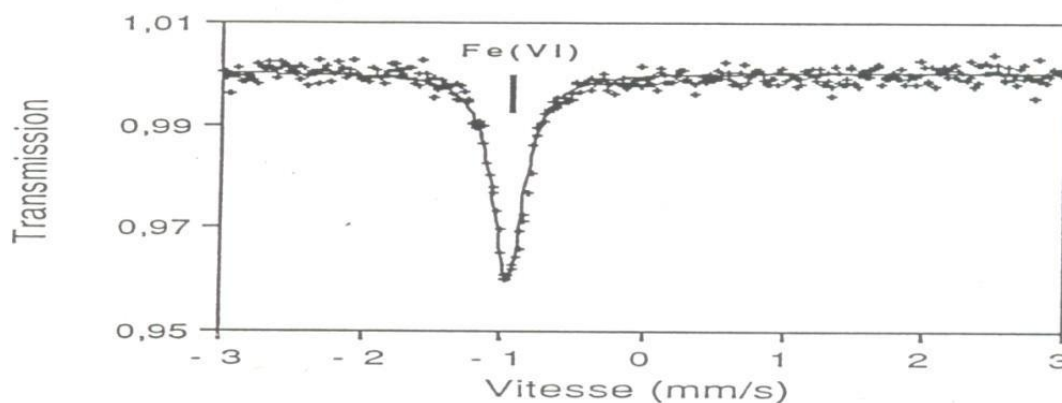


Figure 2: Mössbauer spectrum of  $\text{SrFeO}_4$



According to Figure. 2 below, it can be seen that the compound obtained is almost pure, which confirms the results found previously concerning the level of iron VI (96.7%) of the compound obtained from SrFeO<sub>4</sub>, because the Mossbauer spectrum remains the best for controlling the rate of iron oxidation.

### Periodic monitoring of iron VI degradation

According to tsapin et al [30], the phase found was analyzed and followed over time with UV spectrophotometry by measuring the optical density at 507 nm at pH greater than 10, because the characteristic peak of iron (VI) comes out at this wave length.

The results of monitoring degradation of SrFeO<sub>4</sub> shows that the storage period can reach 12 months with a degradation rate in the first six months is limited to 2%.

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<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

**Tables 1:** Optical density of the solution of ferrates (VI) of the synthesized phase SrFeO<sub>4</sub> 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 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	0.3	0.3
2	0.6	0.3
3	1	0.4
4	1.2	0.2
5	1.4	0.2
6	2.2	0.8
7	2.3	0.1
8	2.9	0.6
9	3.1	0.2
10	3.4	0.3
11	3.7	0.3
12	3.9	0.4

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) due to changes in humidity as well as crystalloid and / or absorbent water, and the stronger polarization effect of the Sr<sup>2+</sup> ion on FeO<sub>4</sub><sup>2-</sup>.

### Discussion

According to the results obtained, it is possible to synthesize strontium ferrate SrFeO<sub>4</sub> stable at room temperature by wet process at a temperature of around 0°C to 60°C at a pH of around 12, this is compatible with the results of different preliminary studies [13], [14]. [16]. [17]. [18]. [19].

The characterization of compounds synthesized by XRD and Mössbauer spectroscopy confirms the purification rate of 96.7% found by the volumetric titration method and present diffractograms resembling those given in the literature [27], [28].

The monitoring of the degradation of SrFeO<sub>4</sub> over time varies in a different way from one month to another during storage as a consequence of climate change which influences the rate of degradation and the duration of storage of



ferrate (VI) at the time of storage ambient. this is compatible with crystalloid and / or absorbent water, and the strongest polarization effect of the  $\text{Sr}^{2+}$  ion on  $\text{FeO}_4^{2-}$  [30].

### Conclusion

According to the experiments and the characterizations made to have the ferrate (VI)  $\text{SrFeO}_4$  compound stable at room temperature, it results that the most adequate method for the synthesis, requires the reaction of strontium hydroxide  $\text{Sr}(\text{OH})_2$  and  $\text{K}_2\text{FeO}_4$  whose pH is around 12, at a temperature varying from  $[0^\circ\text{C} - 60^\circ\text{C}]$ , and a reaction time of the order of 25 minutes.

The choice of the wet method, for the synthesis of ferrate (VI)  $\text{SrFeO}_4$  from  $\text{K}_2\text{FeO}_4$  returns to profitability, ease, very promising and less expensive compared to other synthesis methods, although there is still need more technical, economic improvement concerning industrial application.

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