



Development of a New Process for the Synthesis of Cathodic Salt Li_2FeO_4 based on Alkaline Iron VI by Ion Exchange

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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 cathodic salts Li_2FeO_4 or lithium super-iron, by substitution of barium ions of ferrate VI obtained by lithium, by mixing them with a saturated solution of lithium carbonate Li_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, of which the reaction yield is around 92.7% at a temperature around [20°C - 40°C] and pH = 11 for 50 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, oxidant, electrochemical, cathode, lithium ferrate (VI), Purity, Stability

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 a three-electron cathodic charge capacity.

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

Iron generally occurs as a metal or in the valence states of Fe (II) or Fe (III). Fe (VI) species have been known for over a century, although their chemistry remains relatively unexplored. Charging insertion or reduction of Fe (VI) represents an energetic and large capacity cathodic charge source, and Fe (VI) salts have been prepared as an environmentally safe cathode (due to the product of 'ferric oxide). Super iron batteries incorporating Fe (VI) cathode salts which have recently been shown, examples include alkali zinc, metal hydride batteries and non-aqueous lithium batteries, with several energy and environmental benefits [1-4].

Although the existence of alkaline ferrates has been cited for a century [5-13]. 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.



In 1925, Losana [14], described the preparation of a variety of ferrate salts which included Ba²⁺, Ag⁺, Sr²⁺, Ca²⁺, Pb²⁺, Ni⁺, 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⁺.

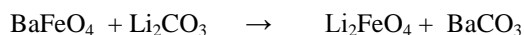
In 1954 J. R. Gump and al. [15] proposes the synthesis of other ferrate such as Cs₂FeO₄, BaFeO₄, SrFeO₄ by first formation - according to the method of J. M Shreyer, however with Br₂ preferred to Cl₂ [4] as oxidant - of K₂FeO₄ to which will be added a solution of CsOH, Ba(OH)₂, Ba(NO₃)₂, BaCl₂, 2H₂O 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 literature [16 - 19].

In a similar study, Gump [20], described the preparation of metal salts (Li⁺ - Cs⁺) and La³⁺ ferrates.

Material and Method

The synthesis of Li₂FeO₄ is done by dissolving the BaFeO₄ ferrate salt prepared in an aqueous solution of lithium carbonate Li₂CO₃ at a pH around 11 and temperature of [20°C- 40°C], for 50 minutes in order to obtain a heterogeneous red precipitate which deposits spontaneously and immediately at the bottom of the lithium salt tube, according to the ion exchange reaction of the ferrate VI salt with lithium carbonate:

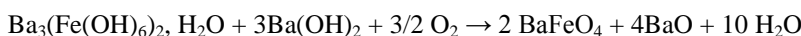


The heterogeneous red precipitate was filtered through filter paper, and washed three times with deionized water. The resulting product Li₂FeO₄ was dried for 6 h under vacuum at room temperature to give the exact mass of Li₂FeO₄.

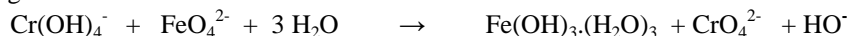
The analysis thus the purity of the product Li₂FeO₄ was determined by chromite analysis and spectrophotometry. Chromite analysis determines that the material is 92.7% pure based on the redox state and the remaining iron is in a lower valence state, although at these relatively low concentration levels, 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 7.3% ferric oxide impurity.

The preparation of BaFeO₄ is done by mixing Ba₃(Fe(OH)₆)₂, H₂O and Ba(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 Ba/Fe = 3, and finally the molten mixture obtained is cooled in a ball dryer [21].

The synthesis reaction is as follows:



The phase Li₂FeO₄ found 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 [22], 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 [23].

Results

The reaction yield of the synthesis of the Li₂FeO₄ 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).



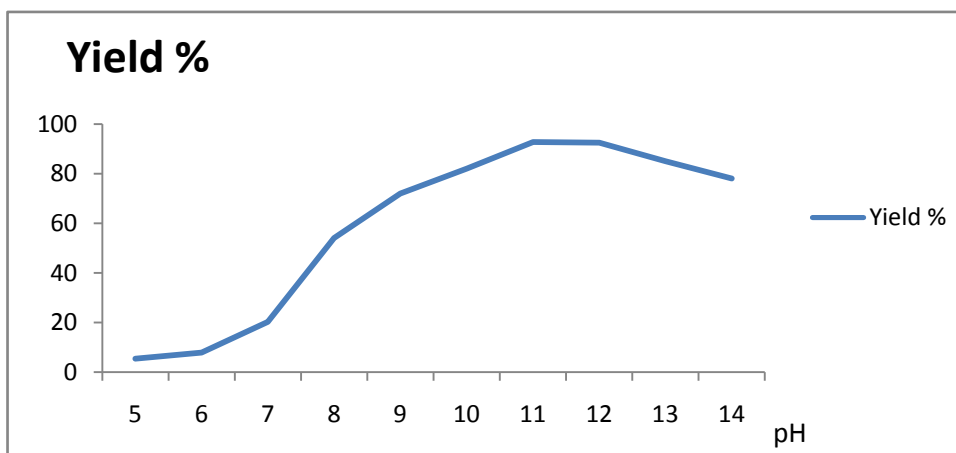


Figure 1: Reaction yield of the synthesis of ferrate (VI) Li_2FeO_4 as a function of the pH of the reaction medium. According to the curve (Fig. 1), it can be seen that the yield of the ferrate (VI) obtained increases as a function of the pH of the reaction medium up to 92.71% at the value of pH = 11, which implies that the optimum pH of the synthesis reaction medium is around pH = 11.

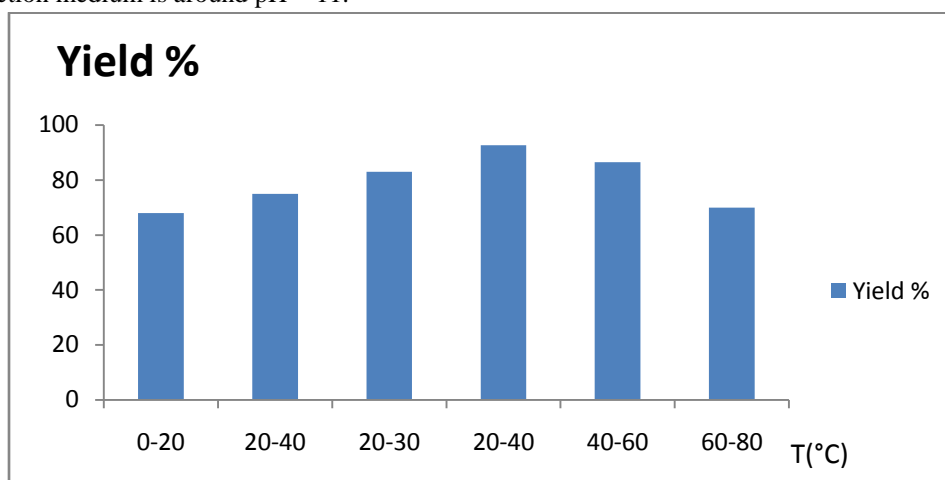


Figure 2: Reaction yield of the synthesis of ferrate (VI) Li_2FeO_4 as a function of the temperature of the reaction medium.

From the curve (Fig. 2), it can be seen that the yield of ferrate (VI) decreases with increasing temperature from [20°C- 40°C], which implies that the optimum temperature of the medium of the synthesis reaction is around [20°C - 40°C], because in this temperature range the yield reaches its maximum.

Monitoring of the degradation of ferrate as a function of time

The Li_2FeO_4 degradation monitoring results show that the storage period can reach 12 months with a degradation rate in the first six months is limited to 3.1%.

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_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 Li_2FeO_4 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	0.6	0.6
2	1.1	0.5
3	1.6	0.5
4	2	0.4
5	2.5	0.5
6	3.1	0.6
7	3.7	0.6
8	4.3	0.4
9	4.5	0.2
10	4.8	0.3
11	6	1.2
12	7	1

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 required for the synthesis of cathodic salt Li_2FeO_4 for a yield of 92.7% is of the order of 11 (Figure 1), this is compatible with the results of the various preliminary studies [15,17, 18, 19, 20], 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 such as Li_2FeO_4 by the wet route is required.

The optimum temperature, which is around [30°C- 40°C], for the synthesis of Li_2FeO_4 (Fig. 2) is an encouraging progress for the development of industrial processes for the production of ferrates (VI). This result confirms the studies made by J. R Gump and al [15, 20], as the decrease in impurities leads to better stability and increases the discharge performance of the calcium ferrate (VI) sample with a 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 suitable method for the synthesis of ferrate (VI) Li_2FeO_4 from the reaction of cesium carbonate Li_2CO_3 and BaFeO_4 whose pH is around 11, at a temperature around [20°C- 40°C] and a reaction time of the order of 50 minutes.

The process for the wet synthesis of Li_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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