



## $K_2FeO_4$ ELECTROCHEMICALLY STABLE SYNTHESIS PROCESS

Abdellatif EL MAGHRAOUI<sup>†</sup> --- Abdelaziz ZEROUALE<sup>2</sup> --- Mustapha IJJAALI<sup>3</sup>

<sup>1,2,3</sup>Laboratory of Chemistry of Condensed Matter (LCMC), Sciences and Technology Faculty, Sidi Mohammed Ben Abdellah University, Fez, Morocco

### ABSTRACT

*This work aims at preparing electrochemically the  $K_2FeO_4$  ambient stable phase and monitoring its degradation with time. The electrochemical method attracted more interest because of the high purity of the obtained product. Thus, we have identified, through the development of electrochemical method for the synthesis of the  $K_2FeO_4$  ambient stable phase, the optimizing parameters influencing the yield of the oxidation of Fe (II) to Fe (VI) in saturated alkaline (KOH) at a temperature of 60 ° C and at a current density of 1.3 A / dm<sup>2</sup> for a time electrolysis of an hour. This yield reached a value of 75%. It was characterized by UV spectrophotometer, measuring the optical density at a wavelength of 507 nm.*

**Keywords:** Ferrate, Bactericidal, Antioxidant, Flocculant, Coagulant, Water treatment, Electrochemical cathode.

### 1. INTRODUCTION

Ferrates (VI) are compounds containing iron in the oxidation state +6. Their growing importance appears in the treatment of sewage and industrial effluents from the multifunctional nature of Fe (VI) (oxidant, flocculant, disinfectant). [1]

The synthesis of ferrates (VI) is very delicate because of the instability that gives them their high oxidizing power although the existence of alkali ferrate is cited for a century [2-6]. Several efforts have been made to synthesize the ferrate (VI) solids [7-14]. However, it was all the time difficult to isolate the solid product from each of the resulting solutions and to stabilize it.

The  $K_2FeO_4$  phase was synthesized by electrochemical oxidizing power which allows it to be used as oxidant and disinfectant in water treatment [1].

The first electrochemical synthesis of ferrate (VI) was in Poggendorf [15]. This method is the most adequate to obtain the potassium ferrate in the form of a solution without impurities [16-19].

Denvir and Pletcher [20], Denvir and Pletcher [21] have shown that the synthesis of Fe (VI) needs highly concentrated alkali hydroxide solution (5M). Bouzek and Rousar [22], Bouzek

and Rousar [23], Bouzek, et al. [24] studied more precisely the influence of carbon speciation in the iron electrode

## 2. MATERIAL AND METHOD

The diagram below shows the experimental apparatus used for the electrochemical synthesis of  $K_2FeO_4$  with a current density of  $1.3A / dm^2$ , a temperature of  $60^\circ C$  and an electrolysis time of one hour.

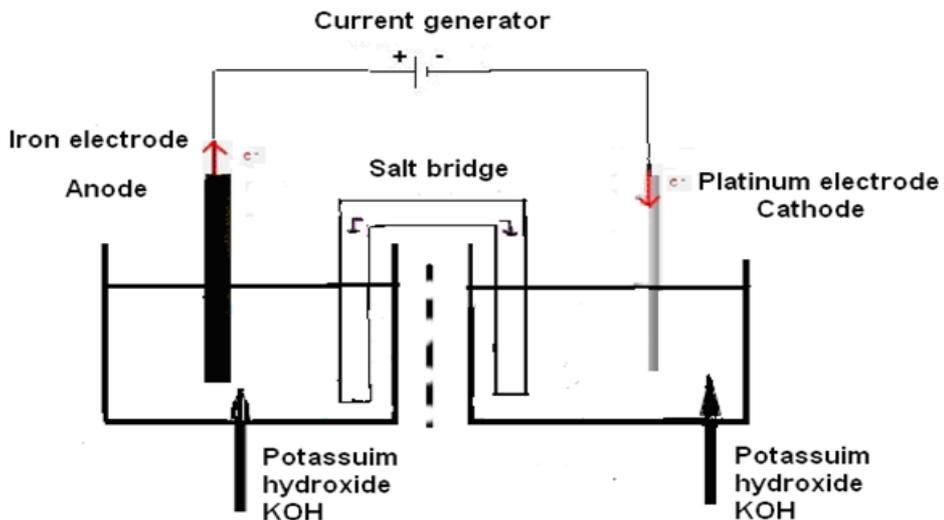


Figure-1. Schematic representation of the electrochemical cell for the synthesis of ferrate.

The reactions involved are the following:

### Anode

Simultaneous oxidation of the iron and of the solvent according to the reaction:



### Cathode

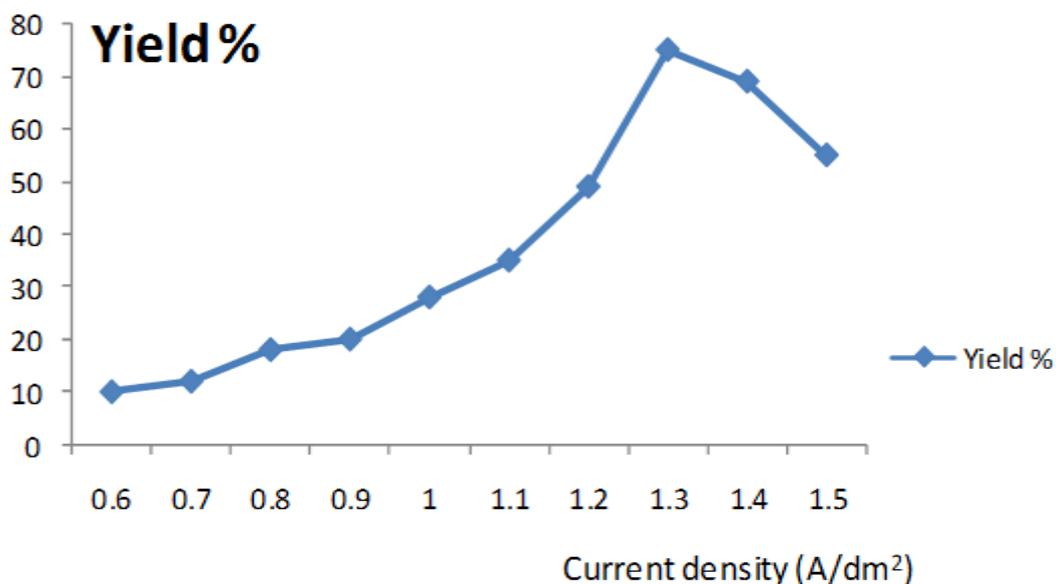
Only the reduction of hydrogen solvent occurs:



This synthesis has attracted numerous studies to optimize all the parameters that influence the performance. Retrieving synthesized ferrate is by vacuum filtration followed by a drying phase at  $120^\circ C$  FOR 12 HOURS.

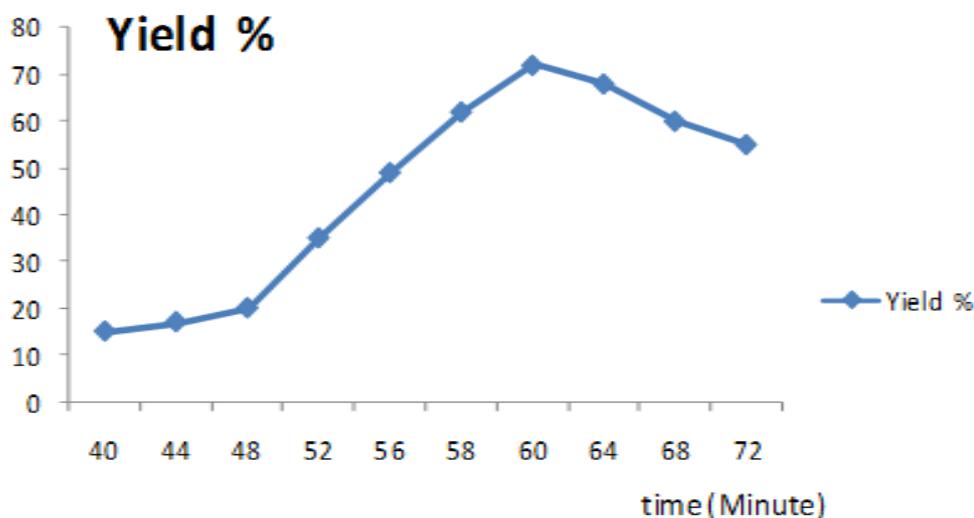
## 3. RESULTS

According to the  $K_2FeO_4$  ambient stable phase electrochemical synthesis with the previous arrangement (Figure 1), we found that the yield of the oxidation of iron (II) to iron (VI) varies depending on the current density, the temperature and the time of the electrolysis (Figure 2, 3 and 4).



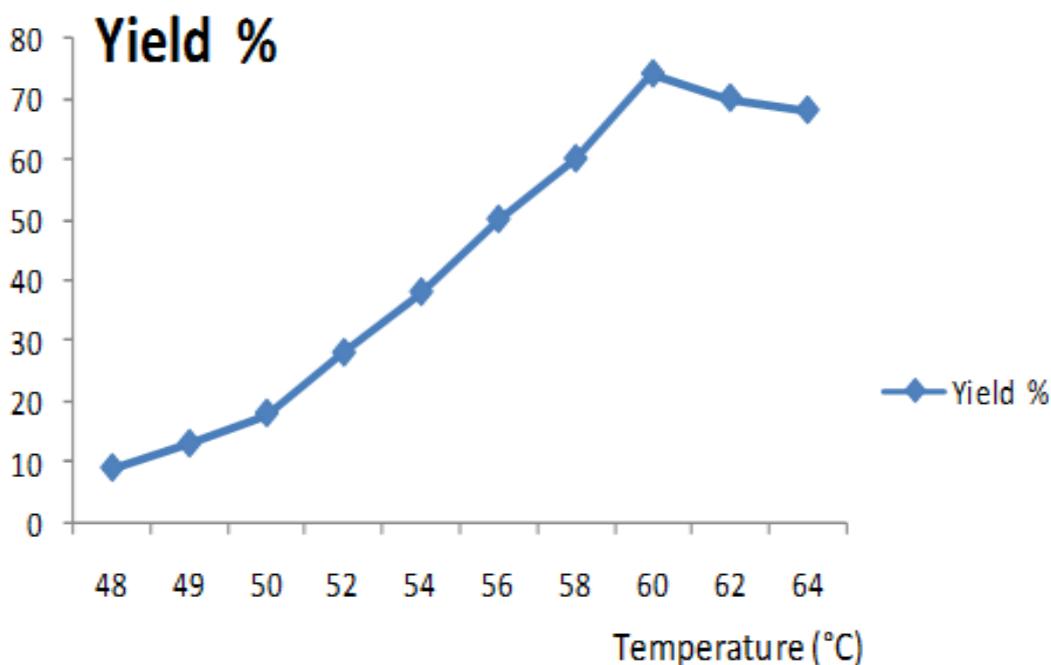
**Figure-2.** Performance of the oxidation of iron depending on the current density  $I$  ( $T = 60^\circ\text{C}$ , the electrolysis time of 60 minutes, and concentrated solution of KOH).

According to Figure 2, the yield of the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe(VI)}$  increases with the current density until it reaches the value of  $1.3\text{A}/\text{dm}^2$  and then begins decreasing. The best yield is 75% at a current density of  $1.3\text{A}/\text{dm}^2$  with a temperature of  $60^\circ\text{C}$  for an electrolysis time period of 60 minutes.



**Figure-3.** Influence of the electrolysis time the performance of the anodic oxidation of the iron ( $T = 60^\circ\text{C}$ ,  $I = 1.3\text{A}/\text{dm}^2$ , concentrated solution of KOH).

From Figure 3, the anodic oxidation of the  $\text{Fe}^{2+}$  into  $\text{Fe(VI)}$  increases over time up to 60 minutes. Beyond this value, the oxidation decreases. The maximum efficiency is obtained at a time period of 60 minutes with a temperature of  $60^\circ\text{C}$  and a current density of  $1.3\text{A}/\text{dm}^2$ .



**Figure-4.** The oxidation of the iron yield according to Temperature T (time of electrolysis 60 minutes,  $I = 1.3 \text{ A / dm}^2$ , concentrated solution of KOH).

The oxidation of Fe (II) into Fe (VI) is achieved at 75 % with a temperature of 60°C for an electrolysis time of 60 minutes and a current density of  $1.3 \text{ A / dm}^2$  (Fig. 4).

The previous results show the importance of the parameters influencing the optimization of electrochemical synthesis of ambient stable  $\text{K}_2\text{FeO}_4$ .

#### 4. DEGRADATION AND MONITORING FERRATE OVER TIME

According to Tsapin, et al. [25], measuring the optical density of the solution of ferrate (VI) is done at a wavelength of 507 nm with a pH greater than 10. The characteristic peak of iron (IV) appears at this wavelength.

Table 1 shows the rate of degradation of ferrate (VI) over the months and also between the state of the production of ferrate (VI) and the different months of storage from the optical density measured. The relation used to calculate the percentage of degradation of Iron (VI) is given by the following formula:

$$\% \text{ Degradation of the iron (VI)} = (D.O_i - D.O_f) / D.O_i$$

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

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

**Table-1.** Optical density of the solution of ferrate (VI) ( $K_2FeO_4$ ) depending on the degradation rate between the initial state of the production and storage of ferrate VI (%) during different months and 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 months of ferrate VI (%)	The monthly rate of degradation ferrate VI (%)
1	1.75	1.75
2	7.01	5.35
3	8.77	1.88
4	10.52	1.92
5	12.63	2.35
6	15.08	2.81
7	22.45	8.67
8	30.52	10.40
9	44.91	20.70
10	64.56	35.66
11	69.19	12.87
12	72.63	11.36

According to these results, we find that the rate of degradation of iron (VI) remains variable over time and varies differently from one month to the other during storage, which means that climate change influences the degradation rate of ferrate (VI) due to changes in humidity.

## 5. DISCUSSIONS

According to our results, the optimal current density to reach a 75% yield of the oxidation of iron (II) to iron (VI) is of the order of 1.3 A / dm<sup>2</sup>. The temperature and the required electrolysis time are 60 ° C and 60 minutes, which is comparable with the results of various preliminary studies [26, 27]. The degradation of the synthesized phase  $K_2FeO_4$  rate does not exceed 15.08% in the first 6 months of which the storage time reaches 12 months for easy transport.

## 6. CONCLUSION

This work examines the electrolysis time, the synthesis temperature and the current density required for electrochemically ambient stable  $K_2FeO_4$ . Values are respectively T = 60 minutes, T = 60 ° C and current density of 1.3A / dm<sup>2</sup>. The stocking rate exceeds 12 months, which encourages bulk synthesis of ferrate (VI). During the first 6 months, the rate of degradation does not exceed 15.08 %.

## REFERENCES

- [1] E. M. Abdellatif, Z. Abdelaziz, I. Mustapha, and F. B. Kawtar, "The role of ferrates (VI) as a disinfectant: Quantitative and qualitative evaluation for the inactivation of pathogenic bacteria," *African Journal of Microbiology Research*, vol. 7, pp. 3690-3697, 2013.
- [2] R. J. Audette and J. W. Quail, "Potassium, rubidium, cesium, and barium ferrates VI: Preparations, infrared spectra, and magnetic susceptibilities," *Inorg. Chem.*, vol. 11, pp. 1904-1908, 1972.

- [3] R. Scholder, F. Kindervater, and W. Zeiss, "Uber orthoferrate IV," *Z. Anorg. Allg. Chem.*, vol. 283, pp. 330-337, 1956-b.
- [4] R. Scholder, "Uber alkali-oxo-metallate (V) der elemente chrom, mangan, eisen und kobalt," *Bull. Soc. Chem. Fr.*, vol. 7, pp. 1112-1114, 1965.
- [5] R. Scholder, H. V. Bunsen, F. Kindervater, and W. Zeiss, "Zur kenntnis der ferrate (VI)," *Z. Anorg. Allg. Chem.*, vol. 282, pp. 268-279, 1955.
- [6] J. A. Thompson, "Process for producing alkali metal ferrates utilising hematite and magnetite, patent Américan, No.4545974, No. Application: 590567, filing date: March 16, 1984, date of publication: October 8, 1985," 1985-a.
- [7] J. A. Thompson, "Process for preparing alkali métal ferrates, patent Américan, No.4551326, No. Application: 468487, filing date: February 22, 1983, date of publication, November 5, 1985," 1985-b.
- [8] J. M. Schreyer, G. W. Thompson, and I. T. Ocherman, "Potassuim ferrate VI, inorg," *Synthesis*, vol. 4, pp. 164-169, 1953.
- [9] B. Helfrich and K. Lang, "Uber salze der eisensaure," *Z. Anorg. Allg. Chem.*, vol. 263, pp. 169-174, 1950.
- [10] V. H. Krebs, "The structure of the potassium ferrate and barium ferrats with 2 figures," *Z. Anorg. Chem.*, vol. 263, pp. 175, 1950, 1950.
- [11] S. Licht, V. Naschitz, L. Halperin, N. Halperin, L. Lin, J. Chen, S. Ghosh, and B. Liu, "Analysis of ferrate (VI) compounds and super-iron Fe (VI) battery cathodes: FTIR, ICP, titrimetric, XRD, UV/VIS, and electrochemical characterization," *J. Power Sources*, vol. 101, pp. 167-176, 2001.
- [12] J. P. Deininger, "Process for preparing potassium ferrate K<sub>2</sub>FeO<sub>4</sub>, European Patent, No.0082590, date of publication, June 29, 1983," 1983.
- [13] W. Foster, "The action of alkaline hypobromite on oxamide ,urea and potassium ferrocyanide," *J. Chem. Soc.*, vol. 35, p. 119, 1879.
- [14] Blattner, "Action des oxydes métalliques sur les hypochlorites alcalins et alcalino-terreux," *Bull. Soc. Chim. Mémoires, Paris*, vol. 7, pp. 700-708, 1892.
- [15] J. C. Poggendorf, "Giebt es galvanische Ketten ohne primitive chemische action," *Pogg. Ann.*, vol. 54, pp. 161, 1841, 1841.
- [16] K. Bouzek, M. J. Schmidt, and A. A. Wragg, "Influence of anode material composition on the stability of electrochemically-prepared ferrate VI solutions," *J. Chem. Tech. Biotech.*, vol. 74, pp. 1188-1194, 1999-a.
- [17] K. Bouzek, M. J. Schmidt, A. A. Wragg, and H. Bergmann, "Electrochemical ferrate VI production- anode material aspects," *Institution of Chemical Engineers Symposium Series*, vol. 145, pp. 153-160, 1999-b.
- [18] K. Bouzek, M. J. Schmidt, and A. A. Wragg, "Influence of electrolyte composition on current yield during ferrate VI production by anodic iron dissolution," *Electrochem. Commun.*, vol. 1, pp. 370-374, 1999-c.
- [19] K. Bouzek and Z. Macova, "Anode material aspects of the electrochemical ferrate VI synthesis," in *Procced. Int. Symp. Prague, edited by sharma V.K,jiang J.Q,Bouzek K*, 2004, pp. 9-18.

- [20] A. Denvir and D. Pletcher, "Electrochemical generation of ferrate. Part I: Dissolution of an iron wool bed anode," *J. Appl. Electrochem.*, vol. 26, pp. 815 - 822, 1996-a.
- [21] A. Denvir and D. Pletcher, "Electrochemical generation of ferrate. Part II: Influence of anode composition," *J. Appl. Electrochem.*, vol. 26, pp. 823-827, 1996-b.
- [22] K. Bouzek and I. Rousar, "Influence of anode material on current yield during ferrate VI production by anodic iron dissolution part I: Current efficiency during anodic dissolution of grey cast iron to ferrate (VI) in concentrated alkali hydroxide solutions," *J. Appl. Electrochem.*, vol. 26, pp. 919-923, 1996.
- [23] K. Bouzek and I. Rousar, "Influence of anode material on current yield during ferrate VI production by anodic iron dissolution part III: Current efficiency during anodic dissolution of grey cast iron to ferrate (VI) in concentrated alkali hydroxide solutions," *J. Appl. Electrochem.*, vol. 27, pp. 679-684, 1997.
- [24] K. Bouzek, I. Rousar, and M. A. Taylor, "Influence of anode material on current yield during ferrate VI production by anodic iron dissolution part II: Current efficiency during anodic dissolution of white cast iron to ferrate (VI) in concentrated alkali hydroxide solutions," *J. Appl. Electrochem.*, vol. 26, pp. 925 - 931, 1996.
- [25] A. I. Tsapin, M. G. Goldfeld, G. D. McDonald, K. H. Neelson, B. Moskovitz, P. Solheid, W. Klemner, S. D. Kelly, and K. A. Orlandini, "Iron (VI): Hypothetical candidate for the martian oxidant, Icarus," vol. 147, pp. 68-78, 2000.
- [26] G. Grube and H. G. Melin, "The influence of the AC ripple current to the anodic formation ferrate," *Z. Elektrochem.*, vol. 26, p. 153, 1920.
- [27] G. Grube, "The passivity of metals during anodic polarization," *Z. Elektrochem.*, vol. 33, p. 389, 1927.

*Views and opinions expressed in this article are the views and opinions of the author(s), International Journal of Chemistry and Materials Research shall not be responsible or answerable for any loss, damage or liability etc. caused in relation to/arising out of the use of the content.*