Global Scientific JOURNALS

GSJ: Volume 8, Issue 10, October 2020, Online: ISSN 2320-9186
www.globalscientificjournal.com

Ambient-stable $CuFeO_4$ synthesis process Wet

Abdellatif EL MAGHRAOUI, Abdelaziz ZEROUALE, Mustapha IJJAALI, Ahmed HARRACH

Laboratory of Chemistry of Condensed Mater (LCMC), Sciences and Technology Faculty, Sidi Mohammed Ben Abdellah University. P. O. Box 2202 Fez (Morocco).

Correspondance :

E-mail : E-mail : elmaghraabdellatif@yahoo.fr

Abstract

Cathodes made of Fe (VI) salts are capable of multiple electron reduction and are useful for the formation of energetic super-iron batteries. $CuFeO_4$ is of compelling interest, capable not only of 3e− cathodic storage like Fe (VI → III), but with an intrinsic availability of additional Cu (I) sites, for a total of a 5e− alkaline earth reduction:

$$CuFeO_4 \ + 5/2H_2O + 5\ é \quad \rightarrow \quad Cu \ \ + 1/2Fe_2O_3 \ + 5\ OH^-$$

Thanks to the interest of the cathodes made up of Fe (VI) salts, we can achieve the process of synthesizing copper ferrate which consists of substituting the Barium ions with the ferrate VI obtained by copper by mixing them with a solution of copper nitrate $Cu(NO_3)_2$, 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 around [15°C - 45 °C] and 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.

Keywords: Ferrate, oxidant, electrochemical, cathode, copper ferrate (VI), Purity, Stability.

Introduction

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 FeO_4^{2-}/ Fe^{3+}= 2.2 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 the 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 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, 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 the literature [16, 17, 18, 19]. The solubility of $BaFeO_4$, a salt more commonly studied in connection with super oxidant iron [20].

Recently, Ag_2FeO_4, 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 [21]. Attempts to search for alternative ferrate (VI) salts with high intrinsic storage capacity, such as $CaFeO_4$ and $MgFeO_4$, 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 $CaFeO_4$ [22].

In 1925, Losana [23], 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^{+}.

In a similar study, Gump [24], described the preparation of metal salts (Li^{+} - Cs^{+}) and and La^{3+} ferrates.

Material and method

The synthesis of $CuFeO_4$ is done by dissolving the ferrate salt of $BaFeO_4$ prepared in an aqueous solution of copper nitrate $Cu(NO_3)_2$ at a pH around 11 and temperature of [15°C- 45°C], for 40 minutes in order to obtain a heterogeneous black precipitate which deposits spontaneously and immediately at the bottom of the tube of copper salt, according to the ion exchange reaction of the ferrate VI salt with copper nitrate:

$$BaFeO_4 + Cu(NO_3)_2 \rightarrow CuFeO_4 + Ba(NO_3)_2$$

The heterogeneous black precipitate was filtered through filter paper, and washed three times with deionized water. The resulting product $CuFeO_4$ was dried for 6 h under vacuum at room temperature to give the exact mass of $CuFeO_4$.

As well as the analysis of the purity of the product $CuFeO_4$ was determined by chromite analysis and spectrophotometry.

The material obtained contains less than 1% copper equivalent relative to barium as well as the 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 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 which can be generalized as a 4.3% ferric oxide impurity.

The preparation of $BaFeO_4$ is done by mixing $Ba_3(Fe(OH)_6)_2$, H_2O 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 [25].

The synthesis reaction is as follows:

$$Ba_3(Fe(OH)_6)_2, H_2O + 3Ba(OH)_2 + 3/2\ O_2 \rightarrow 2\ BaFeO_4 + 4BaO + 10\ H_2O$$

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 [26], 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.

$$Cr(OH)_4^- + FeO_4^{2-} + 3\ H_2O \rightarrow Fe(OH)_3.(H_2O)_3 + CrO_4^{2-} + HO^-$$

The resulting chromate is titrated with a solution of ferrous salt with sodium diphenylamine

sulfonate as an indicator [27].

III. Results

The yield of the reaction of the synthesis of the $CuFeO_4$ 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).

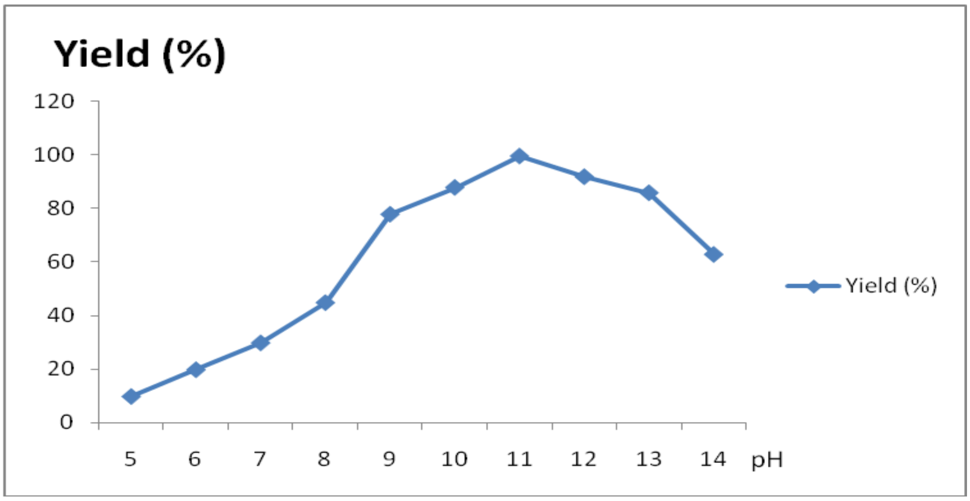

Figure 1: Reaction yield of the synthesis of ferrate (VI) $CuFeO_4$ as a function of the pH of the reaction medium.

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.

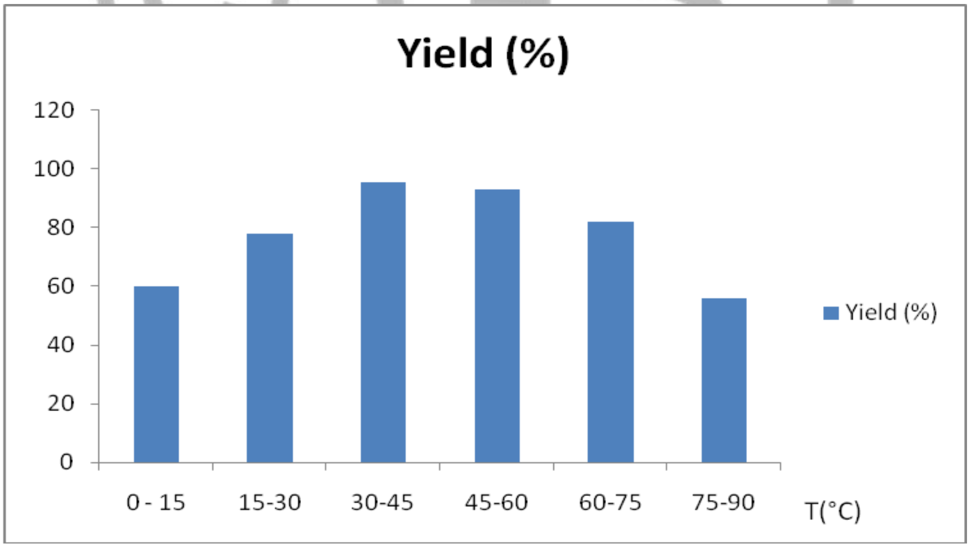

Figure 2: Yield of the reaction of the synthesis of ferrate (VI) $CuFeO_4$ as a function of the temperature of the reaction medium.

According to the curve (Fig. 2), it can be seen that the yield of ferrate (VI) decreases with increasing temperature from [40 °C- 60 °C], which implies that the optimum temperature of the medium of the synthesis reaction is around [15 °C - 45 °C], because in this temperature range the yield reaches its maximum.

IV. Monitoring of the degradation of ferrate as a function of time.

The results of $CuFeO_4$ degradation monitoring show that the storage period can reach 12 months with a degradation rate in the first six months is limited to 4.2%.

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:

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

$D.O_i$: Optical densities of iron (VI) respectively in the initial state

$D.O_f$: Optical densities of iron (VI) in the final state

Tableaux 1: Optical density of the solution of ferrates (VI) of the synthesized phase $CuFeO_4$ as a function of the rate of degradation between the initial state of production and different months of storage of ferrate VI (%) as well as as a function of the rate of degradation between months of ferrate VI storage (%).

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	**1.2**	**1.2**
2	**2.3**	**1.1**
3	**2.6**	**0.3**
4	**3.7**	**1.1**
5	**4**	**0.3**
6	**4.2**	**0.2**
7	**6.3**	**2.1**
8	**8.2**	**1.9**
9	**9.3**	**1.1**
10	**9.4**	**0.1**
11	**10**	**0.6**
12	**11**	**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).

V. DISCUSSION

The pH required 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 [22], [23], 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 $CuFeO_4$ by wet way is required.

The optimum temperature, which is around [15 °C- 45 °C], for the synthesis of $CuFeO_4$ (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 Zhihua Xu and col., 2007 [22], as the decrease in impurities leads to better stability and increases the discharge performance of the calcium ferrate (VI) sample with a higher intrinsic capacity. large and better flow capacity.

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

VI. Conclusion

This manuscript reviews the most suitable method for the synthesis of room-stable ferrate (VI) $CuFeO_4$ from the reaction of copper nitrate $Cu(NO_3)_2$ and $BaFeO_4$ whose pH is around 11, at a temperature around [15 °C- 45 °C] and a reaction time of around 40 minutes.

The process for the wet synthesis of ferrate (VI) of $CuFeO_4$ from $BaFeO_4$ is a very easy and very promising method, although there is still a need for further technical, economical improvement regarding industrial application.

VII. Références

[1] **Abdellatif EL MAGHRAOUI1, Abdelaziz ZEROUALE1, Mustapha IJJAALI1 and Kawtar FIKRI BENBRAHIM, 2013,** 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(28), pp.3690-3697, 12 July,2013.

[2] **Hrostowski H. J., Scott A.B., 1950,** The magnetic susceptibility of potassium ferrate, J. Chem. Phys., 18, pp. 105-107, 1950.

[3] **Ockerman L.T., Schreyer J.M., Thompson G.W. ,1951** ,Preparation and purification of potasuim ferrate VI , J.Am.chem.soc.,73,PP.1379-1381,1951.

[4] **Schreyer J.M., Thompson G.W., Ockerman,L.T.,1953**, Potasuim ferrate (VI), inorg. synthesis, 4, PP.164-169,1953.

[5] **Hooker. A., 1920,** Chem. and Met. eng., 23, p. 961, 1920.

[6] **Thompson G. W., Ockerman L.T., Schreyer J. M., 1951**, Preparation and purification of potassuim ferrate VI, J. Am. Chem. Soc., 73, pp. 1379-1381, 1951.

[7] **R. Scholder, H. Bunsen, F. Kin, W. Zeiss and Z. Anorg, 1955,** "Zur Kenntnis der Ferrate(VI)," Zeitschrift für Anorga- nische und Allgemeine Chemie, Vol. 282, No. 1-6, 1955, pp. 268-279, 1955. doi:10.1002/zaac.19552820129.

[8] **Scholder R., 1965,** Uber alkali-oxo-metallate (V) der elemente chrom, mangan, eisen und kobalt, Bull. Soc. Chem. Fr., 7, pp.1112-1114, 1965.

[9] **W. F. Wagner, J. R. Gump and E. N. Hurt, , 1952** "Factors Af-fecting Stability of Aqueous Potassium Ferrate(VI) Solu-tions," Analytical Chemistry, Vol. 24, No. 9, pp. 1497-1498, 1952. doi:10.1021/ac60069a037

[10] **Audette R.J., Quail J.W., 1972**, Potassium, Rubidium, Césium, and barium ferrates VI: préparations, infrared spectra, and magnetic susceptibilities, Inorg. Chem., 11, pp. 1904 -1908, 1972.

[11] **Scholder R., Kindervater F., Zeiss W., 1956-b,** Uber orthoferrate IV, Z. Anorg. Allg. Chem., 283, pp.330-337, 1956.

[12] **Kopelev N.S., Perfiliev Y.D., Kiselev Y.M., 1992**, Mossbauer study of soduim ferrates (IV) and (VI), J. Radioanal. Nucl. Chem., 162 (2), pp. 239 - 251, 1992.

[13]**Kisselev Y.M., Kopelev N.S., Zav'yalova N.A., perfiliev Y.D., Kazin P.E., 1989,** The preparation of alkali métal ferrates VI, Russ. J. Inorg. Chem., 34, pp. 1250-1253, 1989.

[14] Cici M., Cuci Y., 1997, production of some coagulant materials from galvanizing workshop waste, Waste manage., 17,7, pp. 407 – 410, 1997.

[15] Lee Y.H., M. Cho., Kim J.Y., Yoon J., 2004, Chemistry of ferrate Fe (VI) in aqueous solution and its application as a green chemical, J. Ind. Eng. Chem., 10, pp. 161-171, 2004.

[16] S. Licht, S. Ghosh, journal of power sources 109, 465, 2002.

[17] K .E. Ayers, N. C. White, 2005, journal of the electrochemical society 152A467,2005.

[18] S.Licht, V.Naschitz, S.Ghosh, L.Lin, 2001, Electrochemical communication. 3, 340, 2001.

[19] S.Licht, R.Tel-reded, 2004, Chemical communications 628, 2004.

[20] S.Licht, V.Naschitz, B.Wang, 2002, J. Power sources 109,1(67), 2002.

[21] S. Licht, L. Yang, B. Wang , 2005, Electrochemistry Communications, 7 , p. 931, 2005.

[22] Zhihua Xu a,b, Jianming Wang a,*, Haibo Shao a, Zheng Tang a, Jianqing Zhanga,2007, Preliminary investigation on the physicochemical properties of calcium ferrate(VI), Electrochemistry Communications,9,pp. 371–377, 2007.

[23] L. Losana, 1925, Gazz. Chim. Ital, vol. 55, pages 468-97,1925**.**

[24] J. Gump., E. Hart, W. Wagner. 1952, Analyt. Chem. Vol. 24, pages 1497-1498, 1952.

[25] Abdellatif EL MAGHRAOUI, Abdelaziz ZEROUALE1, Mustapha IJJAALI1,2015, SYNTHESIS PROCESS OF STABLE $BaFeO_4$ BY DRY METHOD, International Journal of Chemistry and Materials Research, 3(4): 100-106, 2015. ISSN(e): 2311-763X/ISSN(p): 2312-0991.

[26] Tsapin A. I., Goldfeld M. G., Mcdonald G.D., Nealson K.H., Moskovitz B., Solheid p., Klemner W., Kelly S.D., Orlandini K.A., 2000, iron (VI): Hypothetical candidate fort he Martian Oxidant Icarus 147, pp. 68-78, 2000.

[27] J. Q. Jiang, B. Lloyd, 2002, « Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and waste water treatment» Water Research, 36, pp 1397-1408, 2002.