

Rapid chemical synthesis of the barium ferrate super-iron Fe(VI) compound, BaFeO₄

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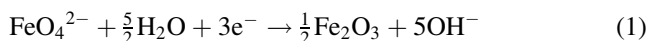
Abstract

An alternate rapid synthesis of BaFeO₄ is demonstrated. Fe(VI) salts, including BaFeO₄, are energetic cathode materials in super-iron batteries ranging from primary to secondary, and including aqueous and non-aqueous cells. Of the Fe(VI) salts, BaFeO₄ sustains unusually facile charge transfer, of importance to the high power domain of alkaline batteries. Unlike previous syntheses, BaFeO₄ preparation is demonstrated from all solid state room temperature reactants. This eliminates several synthetic procedural steps and improves stability to approach that of the rigorously stable chemically synthesized K₂FeO₄ salt. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: BaFeO₄; Super-iron; Fe(VI) cathode; Ferrate; Alkaline battery

1. Introduction

We recently introduced aqueous and non-aqueous batteries with several energy and environmental advantages based on Fe(VI) species whose chemistry had been relatively unexplored, and utilizing the three electron reduction of Fe(VI), such as [1–11]:



The term “ferrate” has been variously applied to both Fe(II) and Fe(III) compounds. Due to their highly oxidized iron basis, multiple electron transfer, and high intrinsic energy, we refer to cathodes containing Fe(VI) compounds as “super-iron” cathodes. Of the Fe(VI) salts, BaFeO₄ sustains unusually facile alkaline charge transfer [1–4,6–9] in the problematic high power domain of alkaline batteries. We have previously detailed the syntheses and analyses of K₂FeO₄, BaFeO₄ [7,8] and recently SrFeO₄ salts [9], and their use as a cathode.

In this technical update, we present an alternate rapid chemical synthesis of BaFeO₄.

2. Results and discussion

2.1. Solution versus solid reactant BaFeO₄ synthesis

The conventional synthesis of pure BaFeO₄ utilizes the precipitation of (soluble, dissolved) potassium ferrate(VI)

and a (soluble, dissolved) barium salt. For example, both K₂FeO₄ and Ba(OH)₂ are reacted in the solution phase, and BaFeO₄ is generated due to the higher alkaline insolubility of barium ferrate(VI) compared to that of potassium ferrate(VI). With this synthetic approach, we have observed effective BaFeO₄ precipitates occur starting with barium nitrate, chloride, acetate or hydroxide salt solutions. This conventional synthesis utilizing solution phase reactants is generalized on the left side of Fig. 1. The right side of this figure presents a schematic for an alternative synthesis using only solid state reactants. In principle, the restriction to solid state reactants has several advantages. Fewer preparatory steps should reduce requisite synthesis time and can increase the yield of the BaFeO₄ preparation. Fe(VI) solutions are susceptible to degradation to Fe(III) due to trace Ni(II) and Co(II) catalysis [1]. This may be avoided during Fe(VI) salt preparation, by strict control over solution impurities [7], but it is less complex to avoid this issue by utilizing solid reactants to minimize any solution contact time. Finally, the solid reactant synthesis may further stabilize BaFeO₄. K₂FeO₄, as chemically synthesized [7], is rigorously stable, no significant decomposition is observed for K₂FeO₄ stored dry for 1 month at 71 °C, temperatures of 150 °C are insufficient to induce any decomposition in 30 min, and only at 400° were we able to induce in the open air the rapid (30 min) full reduction of K₂FeO₄ from Fe(VI) to the Fe(III) salt (as observed by FTIR). The less soluble BaFeO₄ salt may be expected to be intrinsically more stable than K₂FeO₄. However, we have observed the solution phase chemically synthesized BaFeO₄ is less stable than K₂FeO₄,

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BaFeO₄ preparation, alternate synthetic modes

Each approach utilizes K₂FeO₄ and reactive barium salts such as barium hydroxide, oxide, acetate, halides, etc. exemplified by: K₂FeO₄ + Ba(OH)₂ → BaFeO₄ + 2KOH

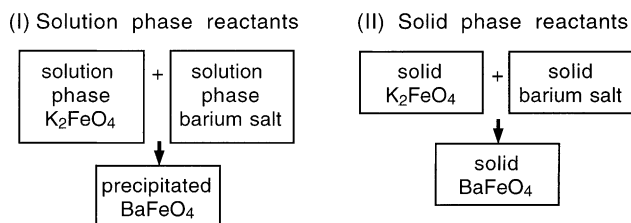


Fig. 1. Schematic representation of chemical syntheses for BaFeO₄ utilizing either solution phase (left side) or a solid phase reactants (right side).

although we had found that a 5% coating of KMnO₄ improves the BaFeO₄ robustness [7,11].

Both the solution and solid phase pathways of BaFeO₄ preparation use a K₂FeO₄ reactant. The preparation of this K₂FeO₄ reactant, as used in this study, and as prepared by hypochlorite addition to ferric salts has been recently detailed [7]. The K₂FeO₄, as analyzed by chromite, has a purity of ~97%, and is stable (the purity remains constant to within ±0.1% per year as analyzed by chromite analysis). Details of the chromite titrimetric analysis, FTIR analysis, and inductively coupled plasma (ICP) analysis of ferrate salts used in the determination of Fe(VI) salt purity have recently been detailed [8].

2.2. Conventional solution phase reaction preparation of BaFeO₄

In this specific synthesis, an aqueous 0.42 M Ba(OH)₂ solution is prepared, by the dissolution at 0 °C of 210 g of Ba(OH)₂·8H₂O (98%, Riedel-de-Haen) in 5 l CO₂ free deionized water, and the solution is filtered through GF/A filter paper (Whatman 1820-915 glass microfibre paper) (solution A). A second solution is also prepared from CO₂ free deionized water, of 0.5 M K₂FeO₄, by the dissolution at 0 °C of 37.6 g K₂FeO₄ in 1.6 l of 2% KOH solution (solution B). Solution B is then filtered through GF/A filter paper into solution A with stirring at 0 °C (using an ice bath). Stirring is continued in the mixture for 30 min. The mixture obtained is filtered on a single funnel with 230 mm diameter GF/A glass microfibre paper, and then BaFeO₄, while on the filter, was washed with 10 l of cold CO₂ free deionized water, until the BaFeO₄ reached pH = 7. The resultant BaFeO₄ is dried for 16–24 h under room temperature vacuum (at 2–3 mbar), and yields 90–93 g of 96–98% purity BaFeO₄ as determined by chromite analysis.

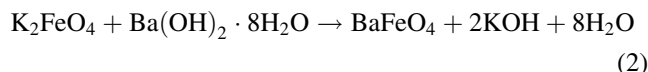
2.3. Solid phase reaction preparation of BaFeO₄

One equivalent (45.6 wt.%) of solid K₂FeO₄ are mixed per 0.5 eq. (36.5 wt.%) of solid Ba(OH)₂·8H₂O and 0.5 eq.

(17.8 wt.%) of solid BaO. The mix is ground for 15 min in a Fritsch Pulversette 0, yielding a viscous dough-like paste. The paste is transferred to a GF/A filter paper under suction, and washed with CO₂ free water until the wash decreases to pH = 7; then transferred to a drying flask, reaching a constant mass, under vacuum (at 2–3 mbar) for 4–5 h, to yield the product BaFeO₄. The 12 g of K₂FeO₄ yields 13 g of 97% Fe(VI) purity salt containing 96% BaFeO₄ and 3% K₂FeO₄. Three-fold larger syntheses proceed to similar purity, and with improved relative yield due to smaller transfer losses.

Probing and optimizing the above solid phase reaction, as a replacement for the solution phase reaction, was accomplished in several steps. Solid K₂FeO₄ reacts with a suspension (a supersaturated aqueous solution) of Ba(OH)₂ to yield a mixture of pure BaFeO₄ and pure K₂FeO₄. For example, a suspension is prepared of 81.2 g (0.26 mol) of Ba(OH)₂ in 2 l of 10 M KOH. To this suspension solid 51.0 g K₂FeO₄ (0.26 mol) is added, and stirred for 30 min. The K₂FeO₄ is highly insoluble in the solution, and is converted towards BaFeO₄. The resultant powder, still undissolved, is removed by filtration, and the precipitate washed with organic solvents, as previously described for similar purification step in K₂FeO₄ preparation [7]. The reaction yields a pure mixture of Fe(VI) salts (as determined by chromite, FTIR and ICP analysis) containing approximately a 4:1 ratio of BaFeO₄ to K₂FeO₄.

Using solid state reactants instead, no room temperature reaction was observed for a 1:1 mole ratio of BaO to K₂FeO₄, when ground together for 3 h. However, spontaneous conversion to BaFeO₄ is achieved by replacing the BaO with conventional solid Ba(OH)₂·8H₂O. In this case, a 1:1 mole ratio of Ba(OH)₂·8H₂O to K₂FeO₄ yields upon grinding an immediate reaction to BaFeO₄. Hence, FTIR analysis of the ground solid BaO/K₂FeO₄ mixture yields the spectra of pure K₂FeO₄ (a single absorption at 807 cm⁻¹), without any of the three BaFeO₄ identifying absorptions which occur in the same region. The FTIR spectra of pure BaFeO₄ and pure K₂FeO₄, with inclusion of an BaSO₄ internal standard, are provided in Fig. 2. At room temperature, the presence of bound water, included within the hydrated solid Ba(OH)₂ salt, clearly facilitates the reaction of the ground mixture, yielding pure BaFeO₄ with the properly proportioned absorption peaks at 780, 812 and 870 cm⁻¹ as presented in the left side of Fig. 2. However, this solid K₂FeO₄/solid Ba(OH)₂·8H₂O reaction yields a wet paste, a suspension of solid BaFeO₄ in 13.9 M aqueous KOH, due to the dissolution product of 2 mol of KOH per 8 mol (0.14 kg) H₂O generated, in accordance with:



Intermediate syntheses demonstrated solid BaO could drive the reaction to BaFeO₄, when combined with as little as 50 mol% of Ba(OH)₂·8H₂O. The resultant mix, equivalent to the tetrahydrate Ba(OH)₂·4H₂O, are sufficient to support a

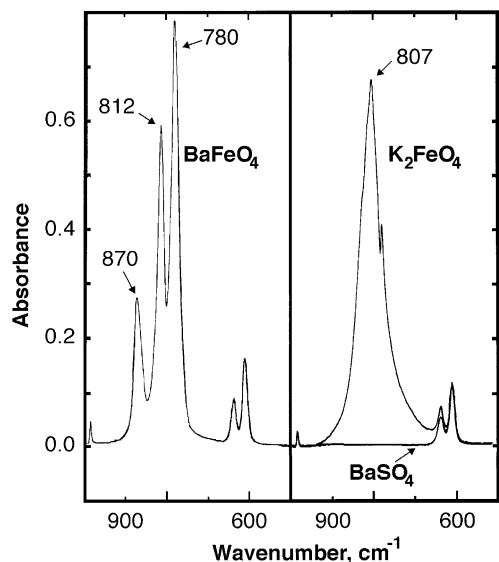


Fig. 2. IR absorption of solid spectra K_2FeO_4 , and $BaFeO_4$, $SrFeO_4$, mixed with a $BaSO_4$ standard. Overlaid over the K_2FeO_4 spectra, is the pure $BaSO_4$ IR spectra.

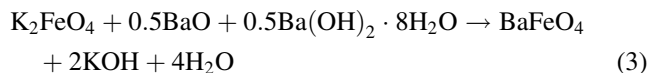
substantially complete (96–97%) room temperature conversion of the K_2FeO_4 to $BaFeO_4$, and generate a viscous dough-like blend of solid $BaFeO_4$ mixed with supersaturated KOH in accord with generation of only 4 mol of H_2O

Table 1
ICP, determined elemental constituents, chromite Fe(VI) content determination, and FTIR $BaFeO_4$ purity determination measured in $BaFeO_4$ samples

$BaFeO_4$ sample	ICP mole ratio		Fe(VI) purity chromite analysis (%)	$BaFeO_4$ purity FTIR analysis (%)
	Ba/Fe	2K/Fe		
Solution reactants	0.997	0.003	98.1	98.0
Solid reactants #1	0.947	0.035	99.2	98.2
Solid reactants #2	0.955	0.040	97.2	96.5
Solid reactants #3	0.948	0.030	99.4	97.8

From the ICP mass constituents are determined the mole ratio of principal cations. Solution reactant samples are prepared from aqueous solutions of K_2FeO_4 and $Ba(OH)_2$. Solid reactant samples are prepared by grinding a 1:0.5:0.5 equivalent mix of K_2FeO_4 , $Ba(OH)_2 \cdot 8H_2O$ and BaO .

for 2 mol of KOH.



2.4. $BaFeO_4$ analysis

ICP analysis of K_2FeO_4 and $BaFeO_4$ samples was conducted with an ICP Perkin-Elmer Optima 3000 DV to determine the relative weight percent, and mol% compositions

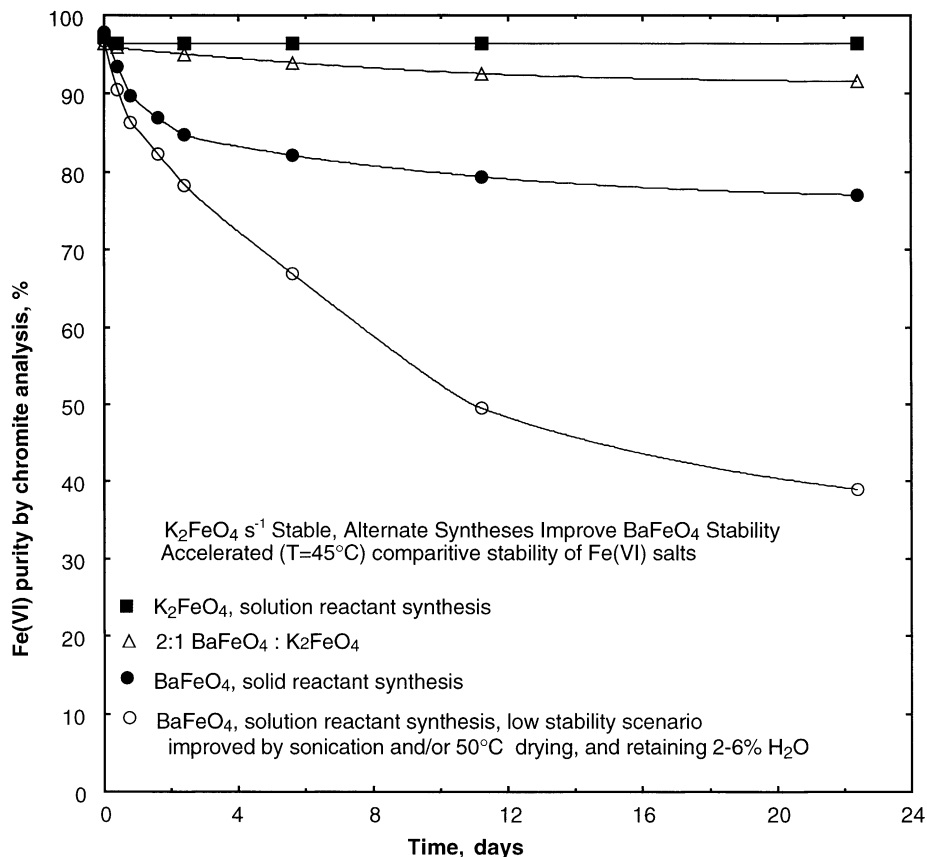
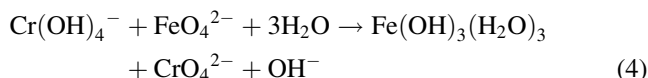


Fig. 3. The 45 °C stability after storage of K_2FeO_4 , $BaFeO_4$ and $K_2FeO_4/BaFeO_4$ mixed salts, as determined by chromite analysis.

of the principal cations in the sample. In addition, the synthesized BaFeO₄ samples were analyzed using a Bruker VECTOR 22 FTIR spectrometer and displayed a qualitative FTIR spectra identical to the left side of Fig. 2. The purity was also determined quantitatively by this FTIR measurement using the BaSO₄ standard, as previously detailed [8]. The percentage of the original iron containing material which is converted to solid Fe(VI) salt was also determined by the chromite method [8] to probe the iron valence state, measured through Fe(VI) redissolution as FeO₄²⁻ to oxidize chromite, and in which the chromate generated is titrated with a standard ferrous ammonium sulfate solution, using a sodium diphenylamine sulfonate indicator:



Summaries of the ICP, FTIR and chromite analysis results are presented in Table 1 for a typical solution phase reactant synthesized BaFeO₄, as well as for repeat syntheses of solid reactant synthesized BaFeO₄. The ICP suggests that the Fe(VI) content within the solid reactant synthesized BaFeO₄ contains 3–4% K₂FeO₄, and the complete analyses provide evidence that the solution reactant and solid reactant synthesized BaFeO₄ are of comparable high purity, averaging an Fe(VI) content of 97–98%.

Stability measurements of Fe(VI) purity, as determined by chromite analyses, were performed following elevated temperature (45 °C) storage to enhance observation of any material instability. As seen in Fig. 3, synthesized K₂FeO₄ is stable at this temperature. The observed 45 °C stability of the solution reactant synthesized BaFeO₄ is highly variable, varying strongly with small changes in synthesis conditions. A typical case of a less stable, solution reactant synthesized, BaFeO₄ is included in the figure. The solid reactant synthesized BaFeO₄ is consistently more stable, as exemplified in

the figure, and as shown is further stabilized when ground as a 2:1 mix with solid K₂FeO₄.

This paper summarizes an alternate rapid synthesis of BaFeO₄. Unlike previous syntheses, BaFeO₄ is prepared using all solid state room temperature reactants which eliminates synthetic procedural steps, and also generates a highly pure Fe(VI) salt. Alternate syntheses should be explored to investigate their effect on BaFeO₄ cost effectiveness, stability, yield and purity.

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