

Chemical synthesis of battery grade super-iron barium and potassium Fe(VI) ferrate compounds

Stuart Licht^{*}, Vera Naschitz, Bing Liu, Susanta Ghosh, Nadezhda Halperin, Leonid Halperin, Dmitri Rozen

Department of Chemistry, Institute of Catalysis, Technion Israel Institute of Technology, Haifa, 32000 Israel

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Abstract

The chemical preparation of high purity potassium and barium ferrates for alkaline electrochemical storage are presented. The synthesized salts are used to demonstrate a variety of high capacity super-iron (Zn anode) alkaline AAA cell configurations which utilize these Fe(VI) salts. Results of 500 days, full stability, of the synthesized K_2FeO_4 are presented. Synthetic pathways yielding 80–100 g of 96.5–99.5% pure K_2FeO_4 and $BaFeO_4$ are presented, and the products of these syntheses are demonstrated to provide a high energy electrochemical discharge in a variety of AAA alkaline cells. $BaFeO_4$ super-iron alkaline AAA cells provide over 0.8 W h during 2.8 Ω discharge, yielding over 200% higher capacity than conventional alkaline batteries. The barium super-iron cell configurations studied provide higher capacity than the potassium super-iron alkaline cell configurations studied. © 2001 Elsevier Science B.V. All rights reserved.

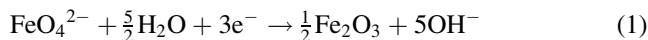
Keywords: Super-iron; Fe(VI) cathode; Ferrate; Primary battery; Alkaline battery

1. Introduction

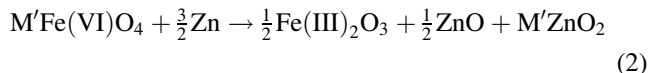
Recently, we introduced a new class of batteries termed super-iron batteries with several energy and environmental advantages [1–5]. Alkaline primary, metal hydride rechargeable, and lithium non-aqueous examples of super-iron batteries have been presented. This paper summarizes the chemical synthesis of potassium and barium Fe(VI) compounds for super-iron alkaline batteries, and the high discharge energies associated with these cells in a conventional cylindrical battery configuration.

Iron typically occurs as a metal, or in the valence states Fe(II) or Fe(III). Fe(VI) species have been known for over a century, although its chemistry remains relatively unexplored [6]. The term “ferrate” has been variously applied to both Fe(II) and Fe(III) compounds. Instead, due to their highly oxidized iron basis, multiple electron transfers, and high intrinsic energy, we refer to cells containing iron compounds in a greater than three valence state as super-iron batteries. The charge insertion or reduction of Fe(VI) represents an energetic and high capacity source of cathodic

charge. In the aqueous phase, we have demonstrated that the full 406 mA h/g K_2FeO_4 three electron cathodic charge capacity has been realized, as summarized by reactions such as [1–4]



In a zinc alkaline battery, the zinc anode generates a distribution of zinc oxide and zincate products. The situation for Fe(VI) is similar; the final Fe(VI) product will depend on the depth of discharge. Alkaline cells utilizing a Zn anode and K_2FeO_4 , or $BaFeO_4$ cathode, discharge in accord with $M' = K_2$ or Ba as

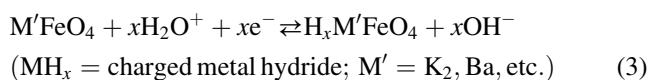


As in the case of the alkaline MnO_2 cathode, it is notable in Eq. (2) that hydroxide generated in the process of cathode reduction closely balances that consumed by a zinc oxidation anode, and therefore little excess electrolyte is required in the full storage cell. A capacity advantage of the alkaline (Zn | KOH | MnO_2) cell was the need for less electrolyte because the oxide/hydroxide for zinc discharge product is internal generated by the MnO_2 cathode during discharge.

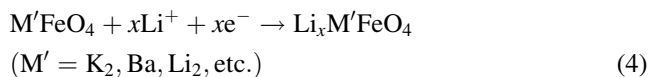
^{*} Corresponding author. +972-4-829-2963; fax: +972-4-829-3015.
E-mail address: chrlicht@technion.technion.ac.il (S. Licht).

Traditional LeClanché (Zn|NH₄Cl|MnO₂) have lower capacity due to the need for an external source of chloride (as provided with sufficient electrolyte) to generate their zinc chloride discharge product.

The unusually high discharge power densities observed in super-iron cells are compatible with the high power density sustainable in alkali electrolytes. From the environmental perspective, ferric oxide is a relatively benign discharge product. The observed 1.7–1.8 V open circuit potential of the cell described by Eq. (2), may be further increased or decreased by 0.15–0.2 V through the addition of a few percent of one of several electrocatalysts [3]. In aqueous KOH electrolyte, the observed extended reversibility (400 charge/discharge cycles) of the Fe(VI) cathode in a super-iron metal hydride cell suggests a complimentary proton insertion mechanism such as [1,3]



In non-aqueous electrolytes, Fe(VI) cell discharges in Li containing non-aqueous have been observed in accord with up to $x = 3$ [5]



The preparation of Fe(VI) salts has not been detailed for the new field of Fe(VI) batteries. Fe(VI) salts have a high oxidizing power, and have been prepared as an environmentally benign (due to the ferric oxide product) alternative to the chlorination, purification of water [7–10], and has also been recently suggested for the oxidative preparation of a variety of organic compounds [6,11,12].

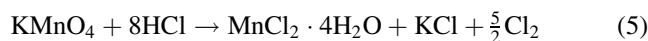
This study focuses on the chemical preparation of high purity potassium and barium ferrates for alkaline electrochemical storage. Synthetic pathways yielding 80–100 g of 96.5–99.5% pure K₂FeO₄ and BaFeO₄ are presented, and the products of these syntheses are demonstrated to provide a high energy electrochemical discharge in a variety of AAA alkaline cells.

2. Chemical synthesis

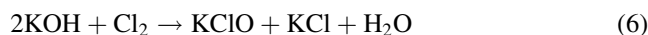
Fe(VI), or ferrate(VI), compounds may be chemically synthesized to a high degree of purity, from a variety of ferric salts, in a variety of alkaline hydroxide media. Hypochlorite is a particularly effective oxidizing agent in the synthesis. However, the synthesis can be a challenge: for example, small variations in the filtration, purification, and drying processes, can lead to decomposition and diminish purities. We have been stepwise scaling up the synthesis to the 0.5 kg range. This paper summarizes syntheses yielding 80–100 g of 96.5–99.5% pure K₂FeO₄ and BaFeO₄, and providing high energy electrochemical discharge in AAA alkaline cell configurations.

2.1. K₂FeO₄ synthesis

An amount of 1 liter of KOH concentrated solution is prepared with Barnstead model D4742 deionized water from 0.620 kg of KOH pellets from Frutarom, Haifa, Israel (analytical reagent KOH with ~14% water, <2% K₂CO₃, <0.05% Na, <0.03% NH₄OH, and 0.01% or less than of other components). The solution is converted to potassium hypochlorite by reaction with chlorine. The Cl₂ is generated in-house within a 2 liter Woulff (spherical) flask (made by Schott of Duran glass) with 3 necks. The glass connections are attached to a 1 liter dropping funnel with pressure equalizer inlet (with a burette controlled liquid inlet and another connection is to a gas-outlet. In the Woulff flask 0.25 kg KMnO₄ (99% CP grade, Frutarom), and from the dropping flask 1.13 liter of 37% HCl (AR grade, Carlo-Erba) is added dropwise to the KMnO₄ to generate chlorine in accord with

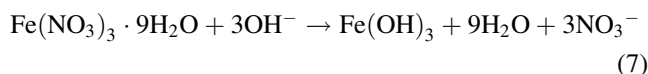


Droplets, HCl and water are removed from the evolved Cl₂, through a series of 2 liter Dreschel (gas washing) flasks connected in series. The first and third are empty (to prevent back flow); the second contains water (to remove HCl), the fourth contains 95–98% H₂SO₄ (to remove water), and the fifth flask contains glass wool (to remove droplets). The evolved, cleaned Cl₂ flows into a reaction chamber (a sixth Dreschel flask containing the concentrated KOH solution, and surrounded by an external ice–salt bath), where it is stirred into concentrated KOH solution. Excess gas is trapped within a final flask containing waste hydroxide solution. Chlorination of the KOH solution generates hypochlorite, which is continued until the weight of the concentrated KOH solution has increased by 0.25 kg, over a period of approximately 90 min, in accord with

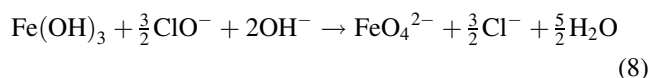


This hypochlorite solution is cooled to 10°C. Alkalinity of the solution is increased, and KCl removed, through the addition of 1.46 kg KOH pellets, added slowly with stirring, to permit the solution temperature to rise not more than 30°C. Stirring is continued for 15 min, and the solution is cooled to 20°C. The precipitated KCl is removed by filtration through a 230 mm diameter porcelain funnel using a glass microfiber filter (cut from Whatman 1820-915 GF/A paper).

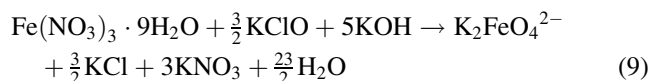
A ferric salt is added to the hypochlorite solution, reacting to Fe(VI), as a deep purple FeO₄²⁻ solution. An external ice–salt bath surrounds the solution to prevent overheating. Specifically, to the alkaline potassium hypochlorite solution at 10°C, is added 0.315 kg ground Fe(NO₃)₃·9H₂O (98% ACS grade, ACROS). In alkaline solution, the ferric nitrate constitutes hydrated ferric oxides or hydroxides, summarized as



which is oxidized by hypochlorite to form the solvated Fe(VI) anion, FeO_4^{2-}



During the ferric addition, a surrounding ice–salt bath is applied to maintain the solution temperature below 35°C. Following this addition, the solution is stirred for 60 min, with the solution temperature controlled at 20°C. For potassium salts, the overall reaction is summarized by Eqs. (7) and (8) as



Following this, the KOH concentration of the resultant Fe(VI) solution is increased to precipitate K_2FeO_4 . Specifically into this solution is stirred 1.25 liter of 0°C, 9.6 M KOH. After 5 min the suspension is (simultaneously) filtered onto two 120 mm P-1 sintered Duran glass filters (Schott).

The two precipitates are dissolved in 1.6 liter of 2.57 M KOH, and quickly filtered through a funnel with two layers of GF/A filter paper of 230 mm diameter, directly into 1.7 liter of 0°C, 12 M KOH. The solution is stirred for 15 min at 3°C, and then the solution is filtered onto a 90 mm P-2 sintered Duran glass filter (Schott). The wet K_2FeO_4 is dissolved in 0.850 liter of 0°C, 2.57 M KOH solution, and quickly filtered on two sheets of filter paper GF/A 150 mm diameter, in a filtering flask which contains 2.7 liter of a 12 M KOH solution.

From this point, two grades of K_2FeO_4 are produced. The first generates higher yield, 90 g K_2FeO_4 , at a purity of 96–97%. The second generates 80 g of K_2FeO_4 at even higher purity 97–98.5%. Both exhibit effective battery discharge. In both procedures, the wet K_2FeO_4 is redissolved in 0.850 liter of 0°C, 2.57 M KOH solution, and quickly filtered on two sheets of filter paper GF/A 150 mm diameter, into a filtering flask containing 2.7 liter, 12 M KOH solution. The resulting suspension is stirred for 15 min at 0°C and is filtered through a P-2 sintered glass filter. This redissolution/filtering step is repeated in the second (highest purity) procedure. In either procedure, on the same filter, the precipitate is successively rinsed: 4×0.16 liter *n*-hexane; 2×0.08 liter isopropyl alcohol; 8×0.15 liter methanol, and finally 3×0.080 liter diethyl ether. The K_2FeO_4 is dried for 30–60 min under room temperature vacuum (at 2–3 mbar).

2.2. BaFeO_4 synthesis

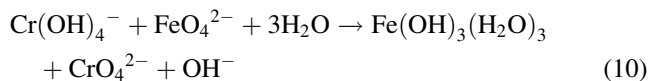
The dried K_2FeO_4 product has been found to be stable in time, and may be used for BaFeO_4 synthesis directly or after storage. BaFeO_4 was synthesized by utilizing the higher alkaline insolubility of barium ferrate(VI) compared to that of potassium ferrate(IV). We have observed effective Fe(VI) precipitates occur starting with barium nitrate, chloride, acetate or hydroxide salts. In this synthesis, 0.210 kg

$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (98%, Riedel-de-Haen) was dissolved in 5 l deionized water, with CO_2 removed by argon flow at 0°C, and the solution is filtered through GF/A filter paper (solution A). In a second solution, 0.08 kg K_2FeO_4 was dissolved at 0°C in 1.6 l, 2% KOH solution (37.6 g KOH in 1.6 l water, with CO_2 removed by argon flow through the solution), and then filtered through GF/A filter paper (150 mm) into the solution A with stirring at 0°C (using an ice bath). Stirring is continued in the mixture for 20 min. The mixture obtained was filtered on a single funnel with GF/A glass microfiber paper, diameter of 230 mm, and then, the residue of BaFeO_4 was washed with 10 l cold distilled water without CO_2 , until the BaFeO_4 reached $\text{pH} \cong 7$. The resultant BaFeO_4 is dried for 16–24 h under room temperature vacuum (at 2–3 mbar) and yields 90–93 g of 96–98% purity BaFeO_4 as determined by chromite analysis.

Both, K_2FeO_4 and BaFeO_4 are highly stable. K_2FeO_4 , prepared as described above, is particularly robust, and the long-term stability (over 1 year) is presented in Fig. 1. As shown in the figure inset, K_2FeO_4 appears to be stable, whether sealed under dry N_2 or sealed in air, and is also stable under acetonitrile (and a variety of other organic electrolytes [5]). K_2FeO_4 , chemically synthesized to a purity of over 97–99%, tends to fall to ~96.5% purity, at which point no further fall is observed for the duration of the experiment (over 1 year). The less soluble BaFeO_4 salt is expected to be intrinsically more stable than K_2FeO_4 , although our chemically synthesized BaFeO_4 is somewhat less stable. We have found that, a 5% coating of KMnO_4 improves the BaFeO_4 robustness. The coating is added as follows: 4.74 g KMnO_4 (30.0 mM) was dissolved by stirring in 0.33 l of acetonitrile. An amount of 90.0 g (0.348 M) BaFeO_4 powder is added. BaFeO_4 is insoluble in this solution and the suspension was stirred for 30 min. Acetonitrile is removed under vacuum, initially with stirring for 60 min to remove the majority of the acetonitrile. This is continued without stirring for 3 h to fully dry the 5% KMnO_4 coated BaFeO_4 .

2.3. Purity

The percentage of the original iron containing material which is converted to solid Fe(VI) salt was determined by the chromite method [13] to probe the iron valence state, measured through Fe(VI) redissolution as FeO_4^{2-} to oxidize chromite, and in which the chromate generated is titrated with a standard ferrous ammonium sulfate solution, using a sodium diphenylamine sulfonate indicator



3. Electrochemical discharges

Barium and potassium, as synthesized according to the previous section, yield an effective discharge in a variety of cell configurations. This will be exemplified through cells

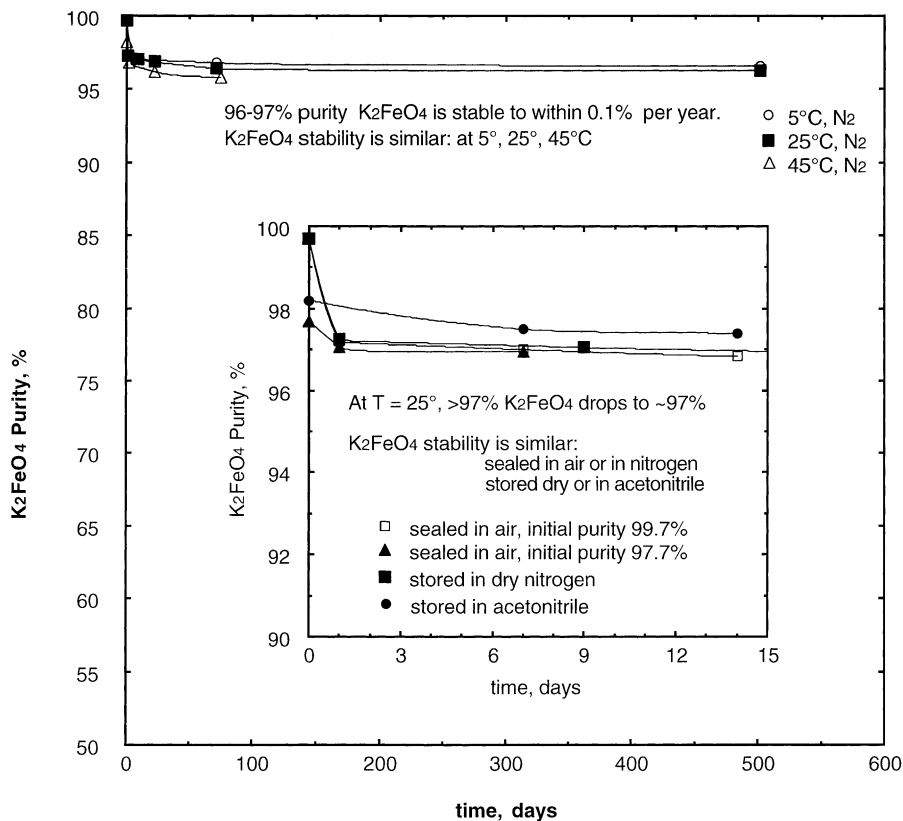


Fig. 1. The long term stability of K_2FeO_4 , measured after sealing in a variety of conditions.

prepared with a conventional alkaline anode, and a super-iron cathode, in a conventional AAA cell configuration.

3.1. Experimental AAA details

A cathode composite was formed by mixing a specified mass of Fe(VI) salt (either K_2FeO_4 or $BaFeO_4$) with an indicated weight percent of various carbon or other additives. With the exception of the $1\ \mu\text{m}$ graphite (Leico Industries), each of the additives is from Aldrich or ALFA-AESAR Chemical. In the experiments, components are removed from standard commercial AAA alkaline cells (a cylindrical cell configuration with diameter 10.1 mm, and a 42 mm cathode current collector case height), and the outer MnO_2 mix, replaced with a pressed K_2FeO_4 or $BaFeO_4$ mix; followed by reinsertion of the separator, Zn anode mix, gasket, and anode collector and resealing of the cell. The cathode composites contain various cathode salts with different carbons added as a matrix to support the cathode reduction. Cells were discharged at various constant resistance loads. Cell potential variation over time was measured via LabView Data Acquisition on a PC, and cumulative discharge, as ampere hours, determined by subsequent integration. The theoretical charge capacity is calculated by the (three Faraday per mole, converted to ampere hours) measured cathode mass of the Fe(VI) salt. The three electron Fe(VI) faradaic efficiency is determined by comparison of

the measured cumulative ampere hours of discharge to the theoretical charge capacity.

A variety of high energy capacity discharges using both the synthesized barium and potassium Fe(VI) salts are presented in Figs. 2–7.

3.2. Electrochemical $BaFeO_4$ super-iron AAA discharge

Fig. 2 presents, load and temperature effects on the discharge storage capacity of alkaline barium super-iron AAA cells. The synthesis, and cylindrical AAA cell configuration and experimental conditions are as described in the above sections, and the cathode mix is comprised of 90 wt.% $BaFeO_4$, 4% $1\ \mu\text{m}$ graphite, 3% carbon black, 3% $KMnO_4$. The choice of conductors in the Fe(VI) cathode mix [4], and the use of a low level permanganate additive [3] have been previously described. Also as previously described, the cell generates $\sim 200\%$ higher capacity than a conventional alkaline Zn/ MnO_2 in the high power ($0.7\ \text{W} \cong 2.8\ \Omega$) domain [1], and displays a flatter voltage profile during discharge than conventional cells. As expected from the flat voltage profile, in addition to the AAA $2.8\ \Omega$ discharges shown in Fig. 2, highly similarly discharges are obtained during constant current, 0.5 A discharge (not shown), or constant power, 0.7 W discharge (not shown) of this super-iron AAA cell configuration. The percent storage capacity in Fig. 2 is determined by the

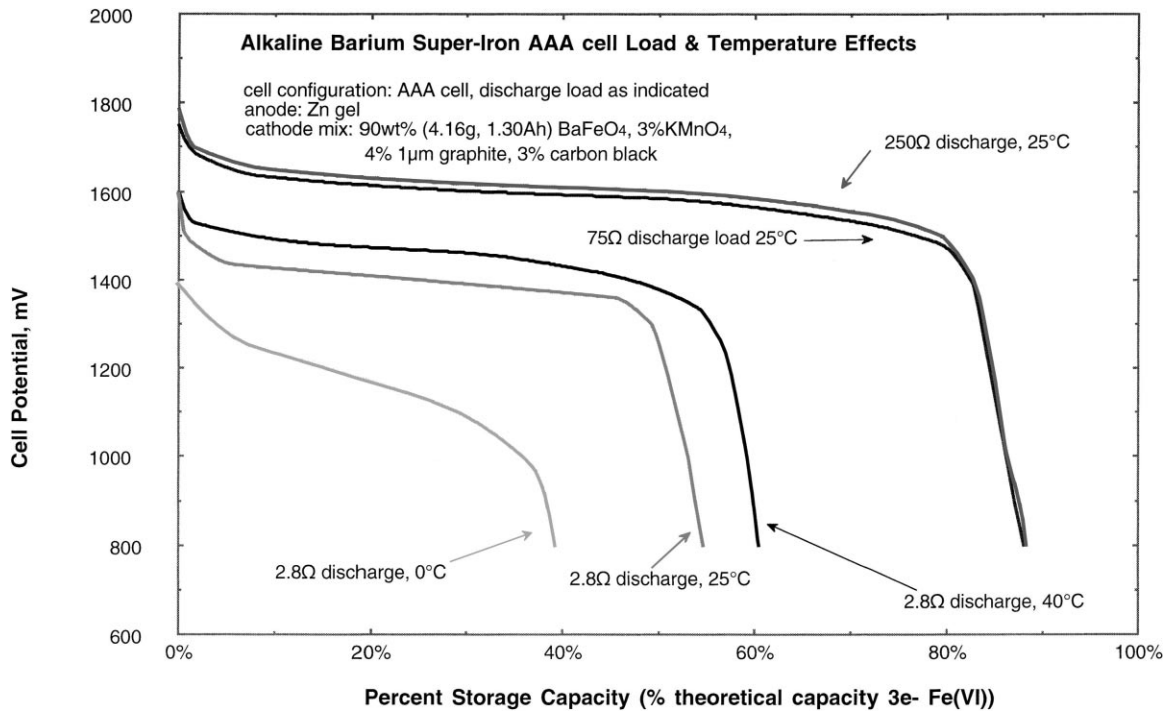


Fig. 2. Load and temperature effects on the discharge storage capacity of alkaline barium super-iron AAA cells. The cylindrical AAA cell configuration and experimental conditions are as described in the text. The percent storage capacity is determined by the measured cumulative ampere hours, compared to the theoretical capacity.

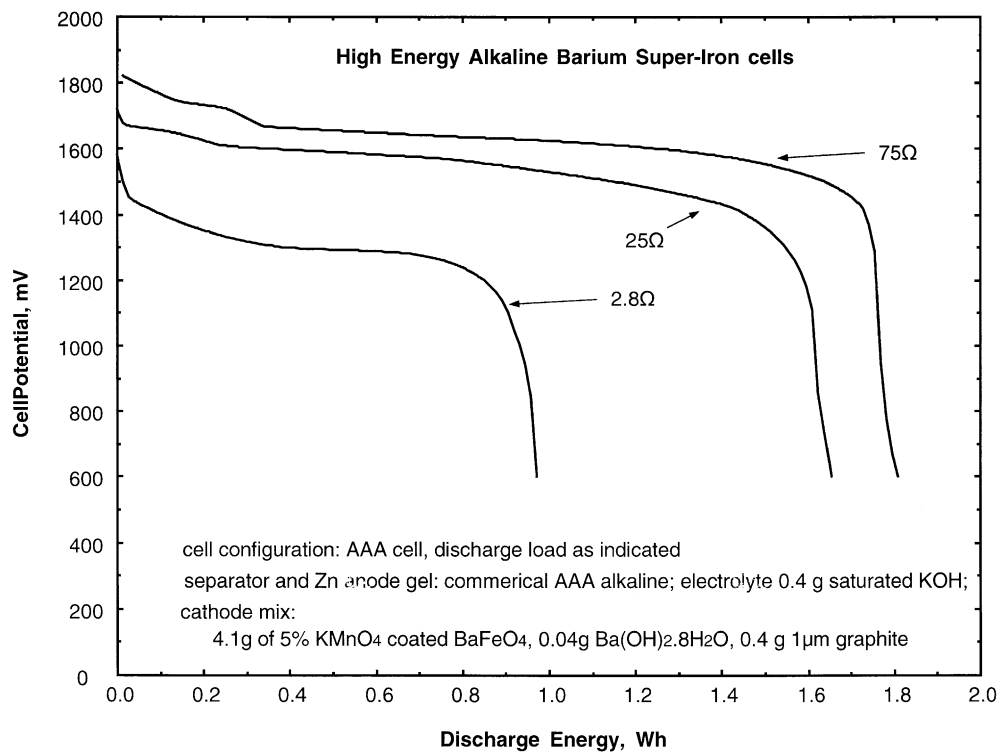


Fig. 3. High energy alkaline barium super-iron AAA cells: cell potential variation during high, medium, and low constant load discharge. The cylindrical AAA cell configuration and experimental conditions are as described in the text.

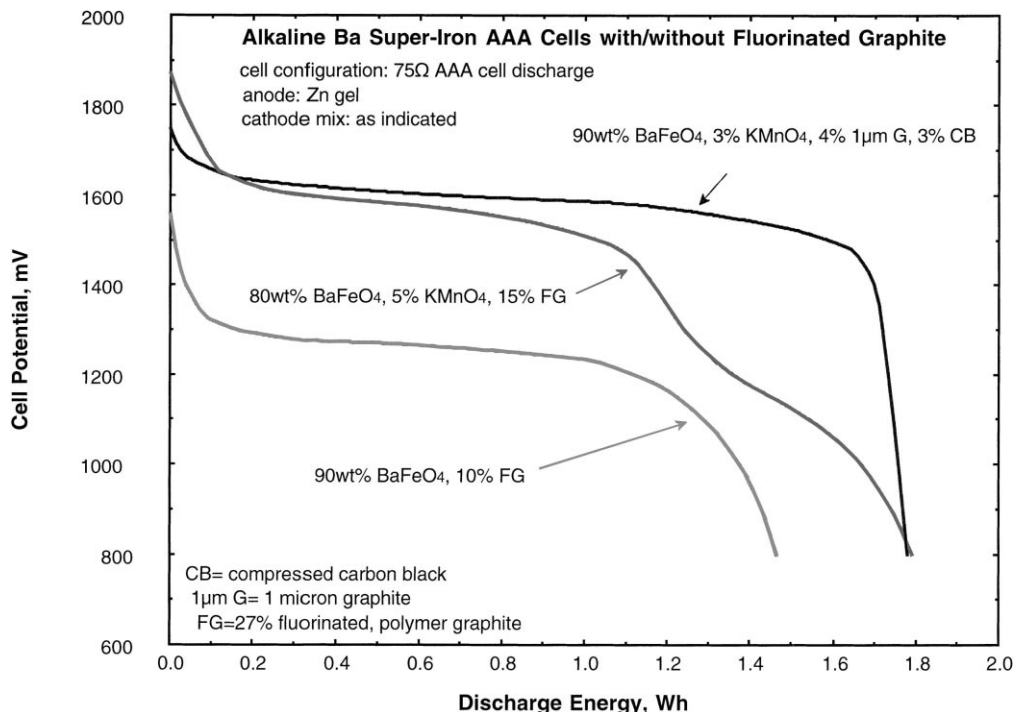


Fig. 4. Alkaline barium super-iron AAA cells containing either fluorinated graphite or containing conventional conductors in the cathode mix: cell potential and discharge energy. The cylindrical AAA cell configuration and experimental conditions are as described in the text.

measured cumulative ampere hours, compared to the theoretical capacity. Alternately, and as presented in Fig. 3, the KMnO_4 activator can be directly added as a coating to the BaFeO_4 , and this procedure is described in the previous BaFeO_4 synthesis section. Also as indicated in Fig. 3, the cathode mix can include a small amount of barium

hydroxide, which as previously described [2], further decreases the Fe(VI) salt solubility. These additives have relatively little effect on the discharge voltage profile as seen in comparing Figs. 2 and 3. Fig. 3 summarizes representative high energy alkaline barium super-iron AAA cells during high, medium, and low constant load discharge.

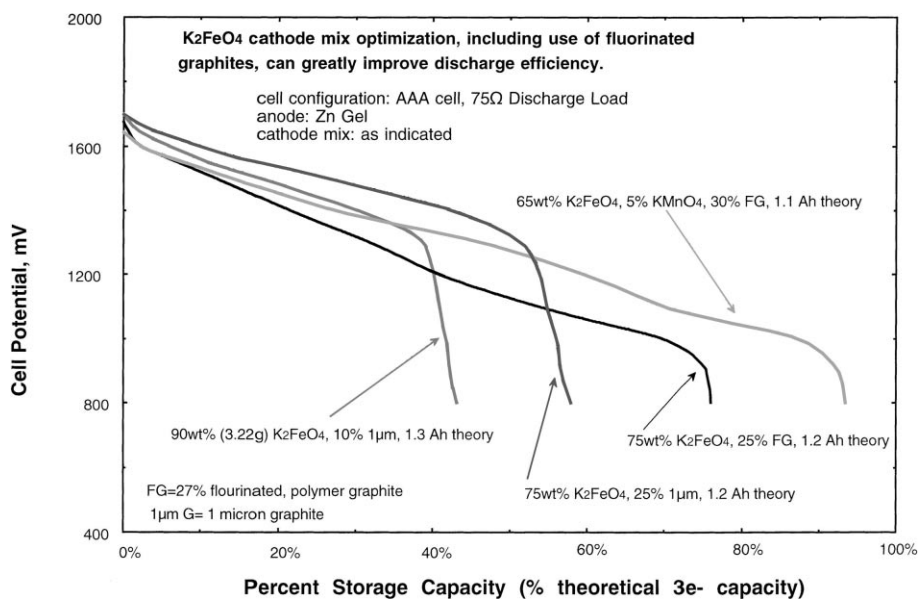


Fig. 5. Cathode optimization in potassium super-iron cells. The cylindrical AAA cell configuration used and experimental conditions are as described in the text. The percent storage capacity is determined by the measured cumulative ampere hours, compared to the theoretical capacity.

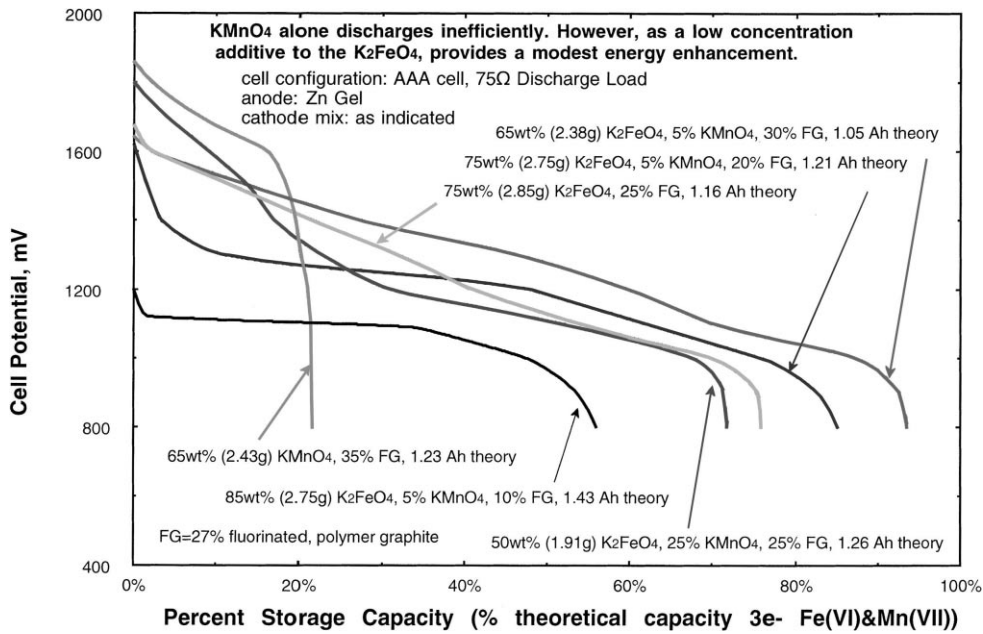


Fig. 6. Discharge variation in potassium super-iron cells containing fluorinated graphite and KMnO_4 . The cylindrical AAA cell configuration used and experimental conditions are as described in the text. The percent storage capacity is determined by the measured cumulative ampere hours, compared to the theoretical capacity.

Alternate conductors such as Fluorinated graphites can be used in the cathode mix [4] to also achieve high discharge energies. However, these alternate materials tend to be less conductive, requiring higher percentage composition within

the cathode mix, and can result in a more complex voltage discharge profile. Fig. 4 presents alkaline barium super-iron AAA cells containing either fluorinated graphite or containing conventional conductors in the cathode mix.

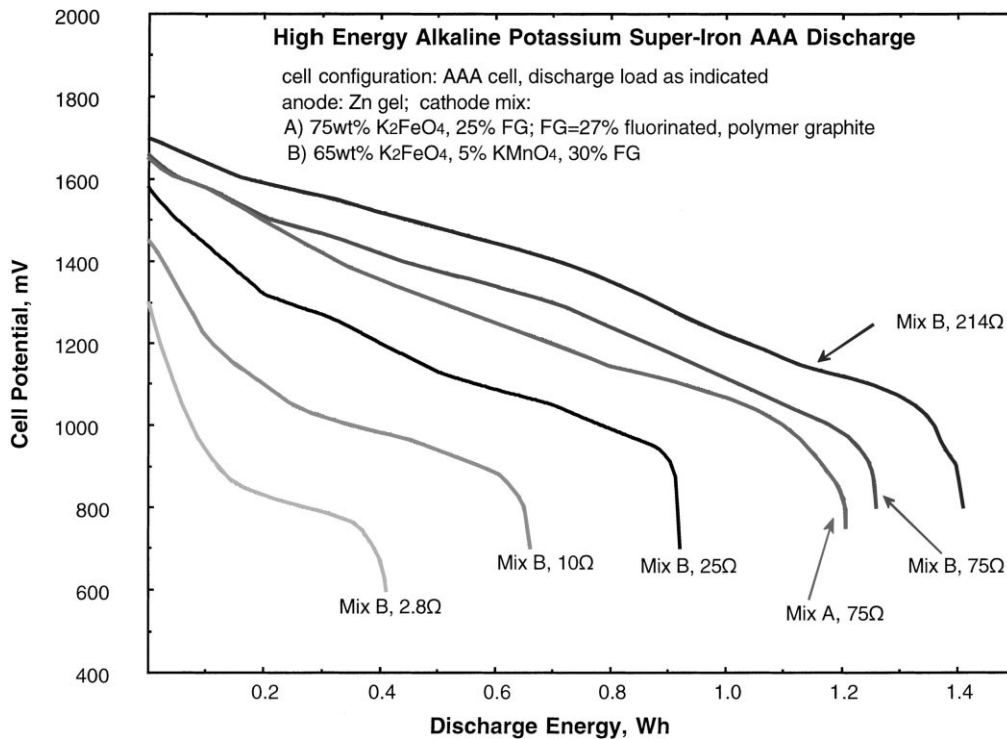


Fig. 7. High energy alkaline potassium super-iron AAA cells: cell potential variation and energy of discharge. The cylindrical AAA cell configuration and experimental conditions are as described in the text.

3.3. Electrochemical K_2FeO_4 super-iron AAA discharge

As previously discussed [1,3,4], alkaline K_2FeO_4 cells prepared with conventional graphites and discharged at moderate or high rates do not release as high a percentage of their intrinsic storage capacity as those in comparable $BaFeO_4$ cells. However, the K_2FeO_4 alkaline cell configuration can be improved in a series of optimization steps. As shown in Fig. 5, the use of higher weight fractions of regular (1 μm particle size) graphite greatly improves the K_2FeO_4 percent storage capacity. Also seen in the figure, a K_2FeO_4 cathode mix including use of fluorinated graphites can further substantially improve discharge efficiency. Further optimizing this cathode (Fig. 6) is probed with various K_2FeO_4 cathodes containing fluorinated graphites. It is seen that low concentrations of the fluorinated graphite are insufficient, and that $KMnO_4$ alone discharges inefficiently, however, as a low concentration additive to the K_2FeO_4 , provides a modest energy enhancement. Finally, Fig. 7 presents, the voltage profile during discharge of several high energy alkaline potassium super-iron AAA cells. Comparing Figs. 3 and 7, it is seen that the $BaFeO_4$ provides a flatter discharge profile and higher overall energy capacity, and it is seen that there is still considerable room for improvement in the potassium Fe(VI) alkaline cell configuration.

4. Conclusions

This paper summarizes the chemical preparation of high purity potassium and barium ferrates for alkaline

electrochemical storage, and demonstrates a variety of high capacity super-iron (Zn anode) alkaline AAA cell configurations which utilize these Fe(VI) salts. $BaFeO_4$ super-iron alkaline AAA cells provide over 0.8 Wh during 2.8 Ω discharge, yielding over 200% higher capacity than conventional alkaline batteries. The barium super-iron cell configurations studied provide higher capacity, than the potassium super-iron alkaline cell configurations studied. Results of 500 day full stability of the K_2FeO_4 are presented. Synthetic pathways yielding 80–100 g of 96.5–99.5% pure K_2FeO_4 and $BaFeO_4$ are presented, and the products of these syntheses are demonstrated to provide a high energy electrochemical discharge in a variety of AAA alkaline cells.

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