

Characterization and performance of high power iron(VI) ferrate batteries

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Abstract

In this paper we report on the high power discharge performance and impedance characteristics of potassium ferrate (K₂FeO₄) and barium ferrate (BaFeO₄) cathodes in zinc alkaline dry cells. The results show that if ferrate materials can be packaged to maximize the cathode surface area, they may offer superior performance over electrolytic manganese dioxide at operating voltages exceeding 1.6 V and currents as high as 100 mA/g of active material.

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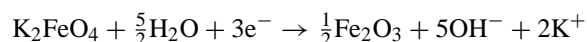
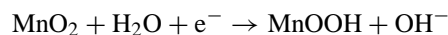
1. Introduction

The performance of portable electronic devices is typically limited by the energy density (per unit volume and per unit mass) of their battery power sources. Licht et al. [1] first suggested that salts of the ferrate anion (FeO₄²⁻) might offer significant advantages over conventional materials used as cathodes in alkaline dry cell batteries, because of the three electron transfer associated with the reduction of Fe(VI) to Fe(III). However, despite the potential superior performance of ferrate based batteries, numerous chemical and materials science hurdles remain before they can be fully implemented for use in commercial applications. In this paper, we report on the synthesis of ferrate cathode materials as well as their impedance characteristics and performance in high power zinc alkaline dry cells.

The ferrate anion, FeO₄²⁻, is unique from other polyatomic ions because it contains iron in a +6 oxidation state. Historical records attribute the first recorded observation of the ferrate anion to G.E. Stahl in 1702. This discovery and

other early ferrate investigations were summarized by Rosell [2]. Schryer et al. first succeeded in producing sizeable quantities of solid ferrate material using a wet chemical synthesis technique employing saturated solutions of potassium hydroxide to precipitate solid potassium ferrate [3,4]. The basic techniques described by Schryer et al. have since been modified to enhance product yield and purity [5,6]. A titrimetric method was also developed involving oxidation of chromite to determine the valence state of the iron and assay the purity of the product obtained [7]. The chromite method remains one of the most straightforward ways to determine the purity of K₂FeO₄ materials.

In the late 1990s, ferrate materials received major attention for their potential use as cathode materials in advanced battery designs. A typical alkaline dry cell uses a zinc anode, an aqueous potassium hydroxide (KOH) electrolyte, and a manganese dioxide (MnO₂) cathode. In an iron(VI) battery the manganese dioxide cathode is replaced with a ferrate material. The advantage is readily apparent when comparing the reduction of manganese dioxide with that of a typical iron(VI) cathode such as potassium ferrate. The respective half reactions are:



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Note that manganese dioxide participates in the transfer of only a single electron, whereas the potassium ferrate reaction is a three electron transfer. Licht et al. have successfully created batteries from both potassium ferrate (K_2FeO_4) and barium ferrate ($BaFeO_4$) compounds that have higher charge capacities than traditional cells employing manganese dioxide as a cathode material [8]. In this study, we constructed both potassium and barium ferrate cells to investigate the factors affecting iron(VI) battery performance. This paper reports on the effects of ferrate purity and cell construction on discharge performance measured using chronopotentiometry and electrochemical impedance spectroscopy techniques.

2. Experimental

Potassium ferrate was synthesized using the wet chemical method of Delaude and Laszlo [9]. High purity analytical grade KOH and $Fe(NO_3)_3$ (Acros Organics) were used as reagents to avoid potential contamination with nickel or cobalt that might catalyze reduction of Fe(VI) to Fe(III) [10]. Inductively coupled plasma atomic emission spectroscopy (ICPAES) analysis verified that the presence of these contaminants was below the detection limits of 0.05 ppm. Batch syntheses generated between 30 and 40 g of solid potassium ferrate, at 40–50% experimental yield. Barium ferrate was obtained via a double replacement reaction between barium hydroxide and a potassium ferrate precursor. Although this reaction can be completed in aqueous solution, it was found that the dry powder trituration technique [11] was simpler and generated $BaFeO_4$ product of similar purity to the solution method.

Potassium and barium ferrate products were both assayed using the chromite method to determine the percent iron(VI) content prior to assembly and testing of electrochemical cells. In order to insure accuracy of the chromite assay, triple replicate titrations were performed simultaneously for each ferrate sample, and a mean purity value was recorded. Standard deviations using the triple replicate technique were typically less than 0.5%. X-ray diffraction spectra were measured for both the potassium and barium ferrate materials using a Scintag PadV X-ray diffractometer. Spectra were measured using $Cu K\alpha$ radiation while scanning 2θ from 15° to 75° .

Test cells were assembled using either 1.0 cm diameter “button” or 2.0 cm diameter “coin” style stainless steel canisters. All cells were prepared using two layers of standard alkaline separator paper and an excess of Zn/ZnO anode paste obtained from disassembled commercial D-cell batteries. The electrolyte was 14 M KOH. The cathode layer was prepared by mixing 70% Fe(VI) material with 15% acetylene black (Cabot Chemical) and 15% SFG-6 graphite (Pimcao). The cathode mix was ground with a mortar and pestle to produce a homogeneous mixture, which was formed into a pellet using a hydraulic press held at 69 MPa for 10 s. Cell discharge and impedance spectroscopy measurements

were made using a CH Instruments model 660 Electrochemical Workstation and a Princeton Applied Research model 6310 Electrochemical Impedance Spectrometer. Chronopotentiometry discharge tests were performed at a constant current of 100 mA/g of active ferrate material. Impedance spectra were measured over a frequency range of 0.01 to 100,000 Hz.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction spectra for the K_2FeO_4 and $BaFeO_4$ samples. Comparisons between various batches of material yielded spectra that were similar to one another and those reported by other authors [12,13]. Interestingly, the K_2FeO_4 spectra exhibited a minor peak at a Bragg angle of $2\theta = 25.8^\circ$ which is consistent with the results of Audette et al. [12], but was not reported by Licht et al. [13] for this compound. Likewise Licht et al. report a minor peak at $2\theta = 28.4^\circ$ which we did not observe. These minor discrepancies may be due to differences in sample preparation and calibration procedures to subtract background noise.

To examine the effect of ferrate purity on discharge performance, a series of cells containing varying grades of potassium ferrate were assembled and discharged at a rate of 100 mA/g of active material. Fig. 2 shows the discharge curves obtained for 200 mg K_2FeO_4 cathodes having

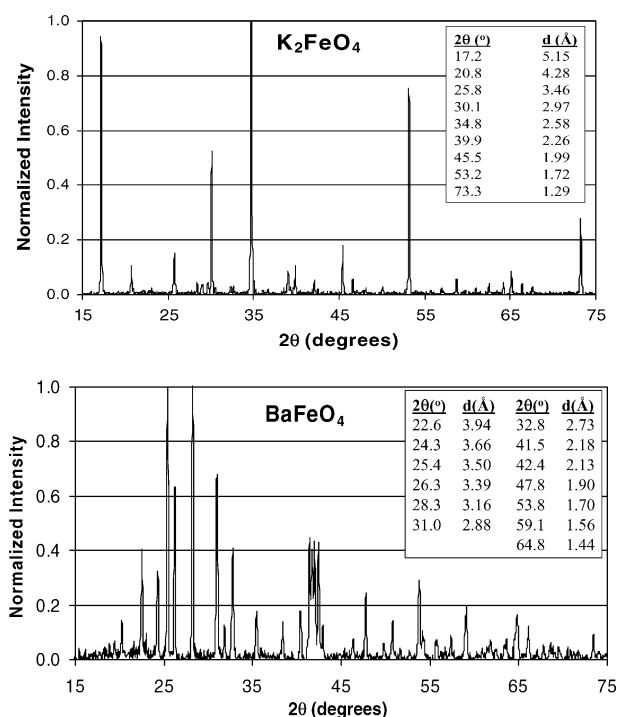


Fig. 1. Typical X-ray diffraction spectra obtained from potassium and barium ferrate samples. Specimens tested were 98% K_2FeO_4 and 96% $BaFeO_4$. The vertical intensity values are normalized by setting the value of the largest peak equal to 1.0.

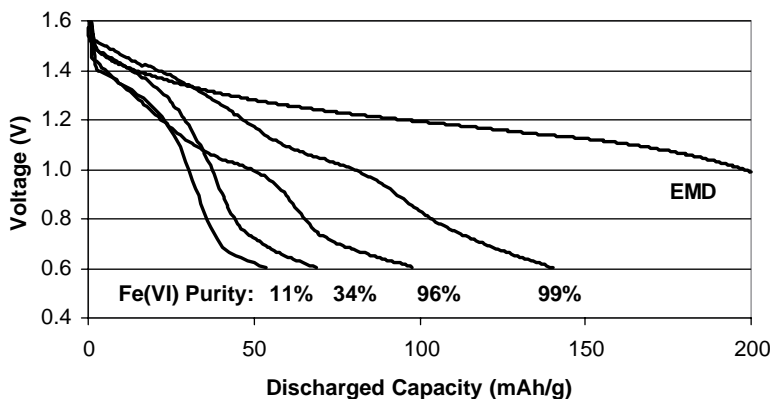


Fig. 2. Effect of ferrate purity on discharge performance. Purity is reported as percent Fe(VI) content measured by the chromite oxidation method. All cells were discharged at a mass specific rate of 100 mA/g of active ferrate material. The discharge curve for electrolytic manganese dioxide (EMD) is included for comparison.

purities of 11, 34, 96 and 99% Fe(VI) content. Potassium ferrate batteries typically exhibited open circuit potentials between 1.6 and 1.7 V, with an overpotential of approximately 0.1 V that appeared once discharge began. The performance of the 99% pure sample exceeded that of the lower purity ferrate cells, but was still easily outperformed by the industry standard electrolytic manganese dioxide (EMD). Soon after the load was applied, the potential for all the ferrate cells dropped rapidly and a stable region of operating voltage was never obtained.

The major impurity present in the potassium ferrate samples consisted of Fe(III) material in the form of iron oxide. It was hypothesized that the presence of a passive layer of Fe_2O_3 on the cathode surface prevented charge transfer and electrolyte access to the interior of the cathode and thereby prohibited utilizing the full charge capacity of the test cells. When cells were disassembled following the initial discharge, it was observed that a rusty orange layer had been produced on the outside of the cathode pellet. When these cathodes were broken open, the interior revealed a significant amount of what appeared to be un-reacted black colored K_2FeO_4 . Some of the cathodes were broken up and dissolved in water, producing a dark purple solution characteristic of the aqueous FeO_4^{2-} anion. Alternatively, if the partially spent cathode was physically mixed to homogenize the material, the cell could be reconstructed and placed back on the test unit at which point the cell potential returned to the initial open circuit value of approximately 1.6 V. These two methods confirmed that even the poorly performing cells still contained active (but inaccessible) ferrate material after the discharge tests had been completed.

To further investigate the formation of the passive Fe(III) layer, cells using a pellet cathode formed from 200 mg of ferrate material were compared with cells using a thin disc cathode formed from 20 mg of ferrate material. Thus, the thickness of the 20 mg disc was one-tenth that of the 200 mg pellet, thereby greatly increasing the surface area to volume ratio of the cathode. Fig. 3 shows the discharge curves of both potassium ferrate and electrolytic manganese diox-

ide (EMD) for the two cathode geometries. While the EMD was not greatly affected by modifying to the surface area to volume ratio, the potassium ferrate performed remarkably better in the thin disc configuration. Potassium ferrate cells constructed in this fashion demonstrated a stable operating region, maintaining a near constant cell potential of approximately 1.6 V well into the discharge cycle. As shown in Fig. 3, the potential of the 20 mg potassium ferrate cell did not drop below 1.0 V until nearly 250 mAh of charge had been removed for each gram of active ferrate material. When compared with the 20 mg disc EMD cell, the potassium ferrate provided both a higher discharge capacity, as well as a higher and more stable operating voltage, resulting in a much greater mass specific energy density.

While the performance of thin disc ferrate cells appeared promising, it is also clear the full advantage of the ferrate material was not achieved under these conditions. K_2FeO_4 has a theoretical charge capacity of 406 mAh/g, yet cell potentials still dropped well below 0.60 V before discharging even 300 mAh/g. We suspected that even in the thin disc

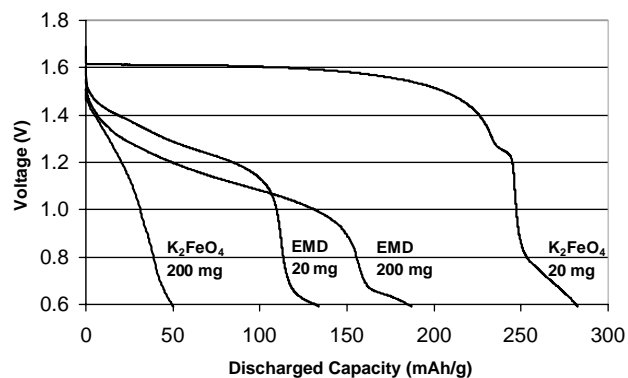


Fig. 3. Effect of surface area on ferrate cathode performance. Cathodes were pressed either into a low surface area cylindrical pellet (200 mg) or a high surface area thin disc (20 mg), with the thickness of the discs being roughly one-tenth that of the pellets. Cells were created using 1.0 cm diameter button cells and 98% pure K_2FeO_4 . Cells were discharged at a mass specific rate of 100 mA/g of active ferrate material.

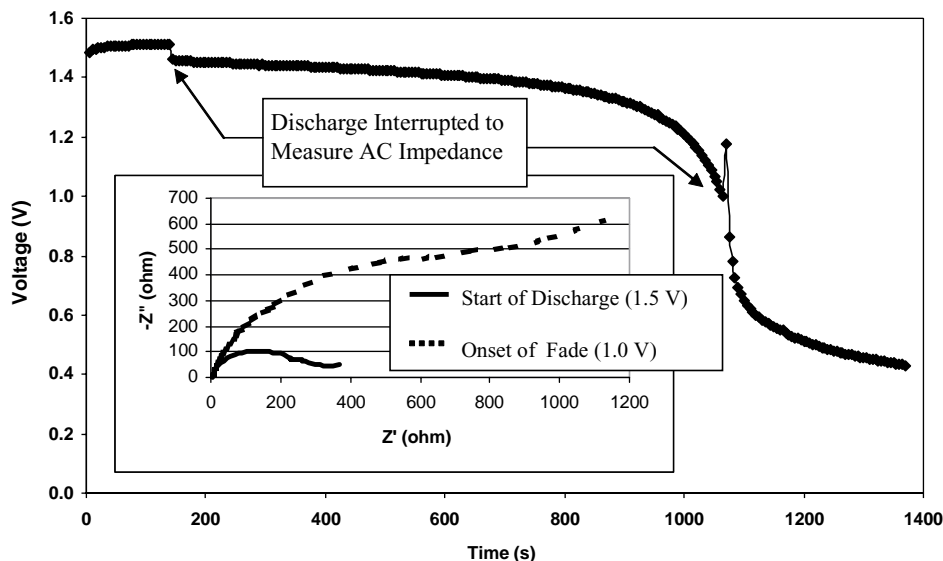


Fig. 4. Change in AC impedance upon discharge of a potassium ferrate cell. The inset Nyquist plot shows the real and imaginary impedance components measured at two points in the discharge cycle. The solid Nyquist curve was obtained at a cell potential of 1.5 V in the stable operating region, and the dashed curve was obtained at 1.0 V, the onset of the voltage fade.

configuration the formation of a passive Fe(III) layer still limited the discharge of ferrate material. To quantify this effect, AC impedance spectroscopy was used to examine cells in the early stages of discharge and in the midst of the voltage fade after the knee of the discharge curve. Fig. 4 shows the discharge curve of a potassium ferrate cell that was interrupted to measure the AC impedance. As shown in the inset Nyquist plot, the impedance is low in the early stages of discharge. This is logical since the discharge of the cell is occurring largely on the surface of the cathode that is immediately exposed to the electrolyte. However, once the outer surface of the cathode has been depleted, further discharge requires charge transport into the interior regions of the cathode. As reduced Fe(III) accumulates on the surface, charge transport is hindered. This is evident in the impedance spectrum obtained at the onset of the voltage fade of the cell. Although the cell potential at this point is still reasonably high (1.0 V), the impedance of the cell has risen dramatically, and as a result the voltage drops precipitously upon further discharge. In order to create a commercially viable ferrate battery, it will be necessary to minimize the impedance problem while retaining the great advantage in charge capacity afforded by the Fe(VI) oxidation state.

Solubility is a second challenge to the development of potassium ferrate cathodes. K_2FeO_4 is extremely soluble in water, and slightly soluble in all but saturated KOH electrolytes. To address this issue, several ferrate salts such as barium ferrate have been explored having more favorable solubility characteristics [14]. While barium ferrate has a lower theoretical charge capacity ($BaFeO_4 = 311 \text{ mAh/g}$ versus $K_2FeO_4 = 406 \text{ mAh/g}$), our initial tests with this material seem promising. Fig. 5 shows the discharge curves for 20 mg thin disc cells constructed from both K_2FeO_4 and $BaFeO_4$. The barium ferrate provides stable operating

potentials that are 0.1–0.2 V higher than those of potassium ferrate, and typically discharges to a greater extent of its theoretical capacity before experiencing the rapid drop in cell potential. As shown in Fig. 6, $BaFeO_4$ clearly outperformed

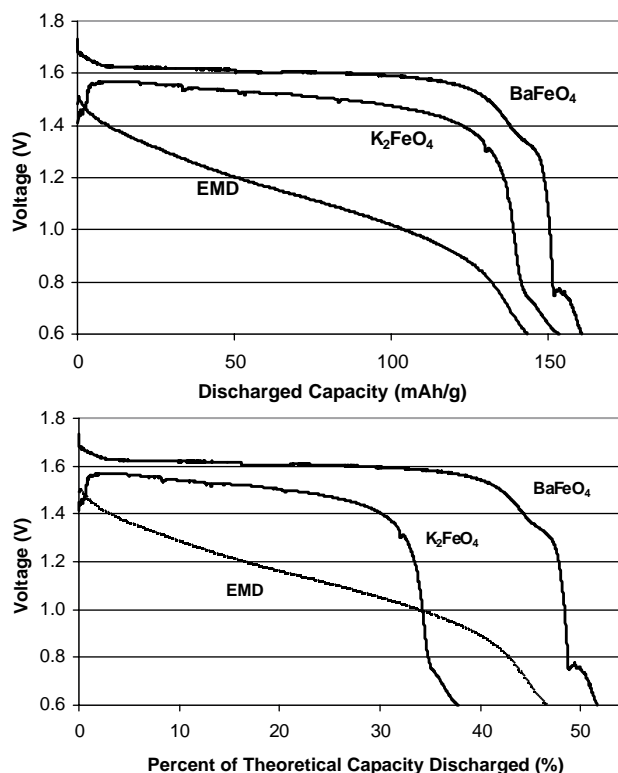


Fig. 5. Discharge comparison of potassium ferrate (98% pure), barium ferrate (96% pure), and electrolytic manganese dioxide cells. The figures show the same cell discharge events plotted with different horizontal axes to allow comparison of cathode materials on a per gram basis and as percent of theoretical charge capacity.

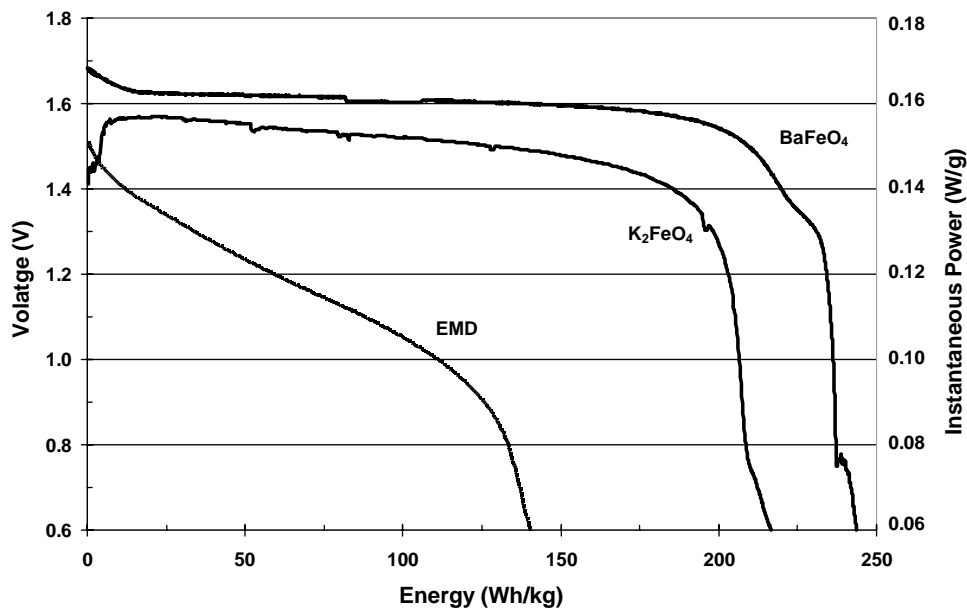


Fig. 6. Energy density and instantaneous power of potassium ferrate (98% pure), barium ferrate (96% pure), and electrolytic manganese dioxide cells. Cells were discharged at a mass specific rate of 100 mA/g of active ferrate material.

electrolytic manganese dioxide (EMD) both in terms of mass specific energy density and instantaneous power. The barium ferrate exhibited nearly twice the energy density of EMD (240 Wh/kg versus 120 Wh/kg) when discharged to 1.0 V, and did so while maintaining a steady mass specific instantaneous power supply of roughly 0.16 W/g. Finally, it should be noted that a constant 100 mA/g current was used to create these discharge curves rather than the less demanding constant resistive loads often employed in other studies. These tests show mass specific power densities considerably greater than many of those previously reported for ferrate materials [1,14], and are comparable to the power densities obtained for iron(VI) composite cathodes modified with other materials such as KMnO_4 , AgMnO_4 , and MnO_2 [15–17].

4. Conclusions

Ferrate materials have great promise as cathode materials because of their ability to accept three electrons in a reduction half reaction. However, based on these results it is clear that when Fe(VI) cathodes are reduced, the high impedance of the discharged Fe(III) material compromises cell performance. This presents a challenge that must be overcome if ferrate cathodes are to gain widespread use in battery applications. There are several possible approaches that might improve charge transfer in ferrate cathodes. Perhaps the simplest involves the bulk mixing of various conductive materials with the ferrate. However, this approach addresses the impedance issue by replacing some ferrate with a material that may have a lower charge capacity and/or higher cost. A more desirable alternative may be the formulation of com-

posite cathode materials that integrate other electrochemically active materials with the ferrate and provide the added benefit of supporting higher currents. Our data suggest that a third solution to the impedance problem is to maximize the surface area of ferrate cathodes, perhaps by integrating a spiral wound battery geometry with a thin film Fe(VI) cathode. We are currently conducting preliminary experiments in this area and hope to report on such a design in the near future.

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