# High power BaFe(VI)O$_4$/MnO$_2$ composite cathode alkaline super-iron batteries

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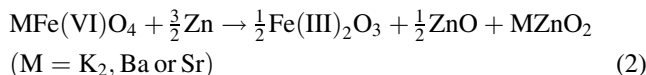
## Abstract

This short communication demonstrates that not only pure Fe(VI) cathodes, but also MnO$_2$/Fe(VI) composite cathodes can substantially enhance the high power discharge of alkaline batteries. The 2.8 Ω and 0.7 W high power discharge of alkaline cells are investigated for 3:1 and 1:1 composite MnO$_2$/BaFeO$_4$ cathode cells, provide discharge energies intermediate to that found in the (non-composite) BaFeO$_4$ cathode cell. At a constant 2.8 Ω load, the 1:1 composite MnO$_2$/BaFeO$_4$ cell delivers up to 40% higher energy capacity than the MnO$_2$ pure cathode alkaline cell, and up to three-fold the capacity of the constant 0.7 W power MnO$_2$ discharge. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* BaFeO$_4$; MnO$_2$; Super-iron; Fe(VI) cathode; Ferrate; Alkaline battery

We recently introduced aqueous and nonaqueous batteries with several energy and environmental advantages based on Fe(VI) species, and utilizing the three electron reduction of Fe(VI), such as [1–9]:

$$FeO_4^{2-} + \tfrac{5}{2}H_2O + 3e^- \rightarrow \tfrac{1}{2}Fe_2O_3 + 5OH^- \qquad (1)$$
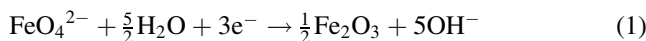
We have previously detailed the syntheses and analyses of K$_2$FeO$_4$, BaFeO$_4$ [5,6,9] and recently SrFeO$_4$ salts [7], and their use as a cathode. Of the Fe(VI) salts, BaFeO$_4$ sustains unusually facile alkaline charge transfer [1,2,4–7] in the problematic high power domain of alkaline batteries. As with a conventional MnO$_2$ alkaline cathodes, little electrolyte is required to support effective cathode discharge, indicating that KOH is not consumed during the cathodic reduction, and the general discharge of alkaline electrolyte cells utilizing a Zn anode and either a K$_2$FeO$_4$, a BaFeO$_4$ or a SrFeO$_4$ cathode, is expressed as:

$$MFe(VI)O_4 + \tfrac{3}{2}Zn \rightarrow \tfrac{1}{2}Fe(III)_2O_3 + \tfrac{1}{2}ZnO + MZnO_2$$
$$(M = K_2, Ba\ or\ Sr) \qquad (2)$$

As shown in Fig. 1, we initially demonstrated that the alkaline BaFeO$_4$ cathode can provide substantially longer discharges and greater energy in the problematic high power discharge domain, compared to both standard and "high power" alkaline MnO$_2$ cathode batteries, and as shown in

the Fig. 2 capacity versus discharge rate comparison, we have since demonstrated that an Mn(VII/VI)/Fe(VI) can lead to further increase in discharge energy in composite electrodes containing BaFeO$_4$ with AgMnO$_4$, KMnO$_4$ or other related manganate or permanganate salts [2,5,7,8]. MnO$_2$ is a widely distributed, highly optimized, and cost-effective cathode technology. The alkaline Fe(VI) storage cathode was only recently introduced [1], and at this time, mass produced super-iron salts are not yet available. Cost comparison between a mature and alternative new technology are a challenge, although it may be noted that the synthetic components of K$_2$FeO$_4$ and BaFeO$_4$ salts [5] are cost-effective, and that new synthetic routes are continuously being introduced [9].

In this short communication, we demonstrate that composite cathodes simultaneously containing both BaFeO$_4$ and MnO$_2$ can also improve the high power discharge domain compared to conventional alkaline batteries containing Fe(VI) free, MnO$_2$ cathodes.

This study probes cathodic charge transfer through the preparation and discharge of sealed cylindrical alkaline cells. Although, not isolating the cathode redox couple as effectively as in a galvanostatic, or potentiostatic three electrode configuration, this (two electrode) configuration has several advantages; the same type of anode was used throughout the study (as removed from the commercial Zn alkaline cell). As this anode exhibits facile (low polarization, efficient) oxidation, the charge transfer attributes of the cathode are effectively demonstrated. It is the cathode which

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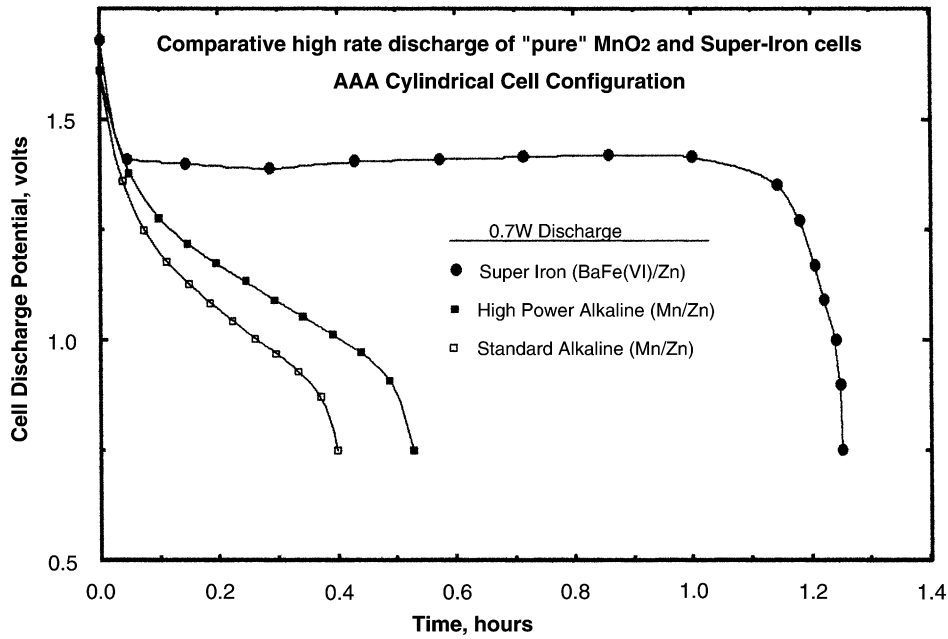*E-mail address:* chrlicht@techunix.technion.ac.il (S. Licht).

Fig. 1. Comparative discharge in time of the $MnO_2$ and super-iron alkaline batteries (figure adapted from [1]).

limits the observed discharge characteristics of these cells. Advantages of this two electrode cell, are it's reproducibility, sealing (preventing competing oxygen reduction effects), that the cell requires a minimum of electrolyte, and that it provides a direct comparison to a widely distributed commercial cell. In the experiments, components are removed from standard commercial AAA alkaline cells (a cylindrical cell configuration with diameter 10.4 mm, and a 42 mm cathode current collector case height). The outer $MnO_2$ mix is then replaced with a pressed super-iron and/or $MnO_2$ cathode mix. This is then 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 added graphite as a matrix to support the cathode reduction. Cells were discharged as indicated, either at a 2.8 $\Omega$ constant resistance load, or at a constant power of 0.7 W. Cell potential time variation was measured via PC/LabView Data Acquisition, and cumulative discharge, as ampere hours, determined by subsequent integration.
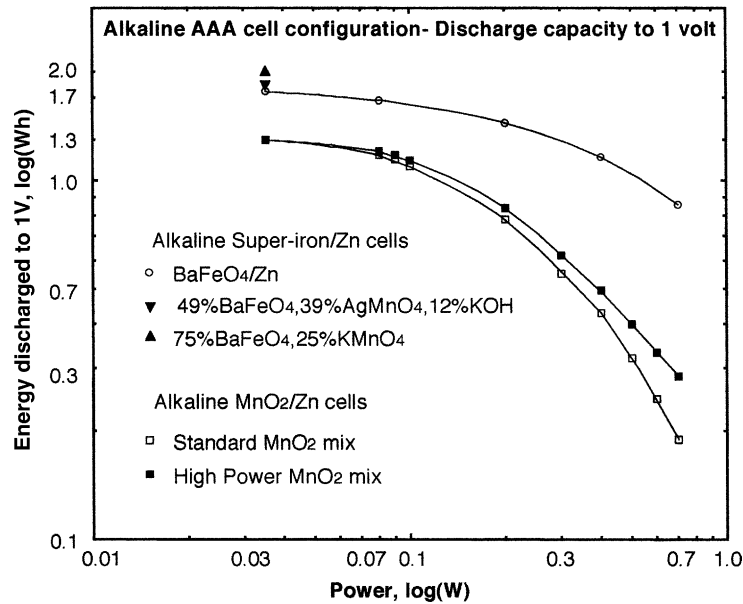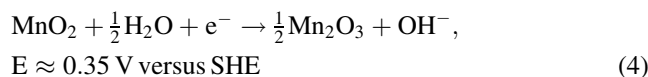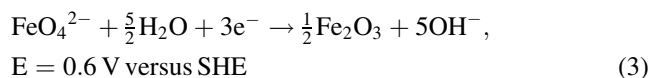


Fig. 2. Comparative power curves for various $MnO_2$ and super-iron alkaline Zn AAA configuration cells. $BaFeO_4$ data is from [1] and [5]. $BaFeO_4/AgMnO_4$ data is from [7]. $BaFeO_4/KMnO_4$ data is from [8]. High power and standard $MnO_2$ data are from the MX2400 Ultra AAA cell specifications on the Duracell® website.

Of relevance to both practical electronics and as a fundamental energy comparison, a constant power density, rather than constant load or constant current density, is a more stringent comparison of cathode capabilities. In this discharge, the lower average cathode potential of the $MnO_2$ cathode (Eq. (4)) compared to Fe(VI) (Eq. (3)), must be compensated by a higher average current density, and this will further impair the $MnO_2$ charge transfer.

$$FeO_4{}^{2-} + \tfrac{5}{2}H_2O + 3e^- \rightarrow \tfrac{1}{2}Fe_2O_3 + 5OH^-,$$
$$E = 0.6 \text{ V versus SHE} \tag{3}$$

$$MnO_2 + \tfrac{1}{2}H_2O + e^- \rightarrow \tfrac{1}{2}Mn_2O_3 + OH^-,$$
$$E \approx 0.35 \text{ V versus SHE} \tag{4}$$

Cathodes were prepared with 5.0 g of dry $MnO_2$ cathode mix, or 4.7 g of dry $BaFeO_4$ cathode mix (containing 4.3 g of 5% $KMnO_4$ coated $BaFeO_4$ and 0.4 g 1 μm graphite, the benefits and preparation of this light Mn(VII) coating have been discussed [5,8]). More of either cathode mix can be packed with grinding or added pressing, but is not observed to significantly improve the cathode discharge characteristics. Alternately, a 3:1 "$MnO_2$" to "Ba" composite cathode was prepared with 75% by mass of the dry $MnO_2$ cathode mix and 25% of the dry $BaFeO_4$ cathode mix, for a total dry mass of 4.9 g. Finally, a 1:1 "$MnO_2$" to "Ba" composite cathode was prepared with 50% by mass of the dry $MnO_2$ cathode mix and 50% of the dry $BaFeO_4$ cathode mix, for a

total dry mass of 4.8 g. A 0.4 g of saturated KOH is added to each of the various cathode mixes, which are then pressed and reinserted into the cell.

As previously observed, under conditions of constant, rapid 0.7 W discharge in an AAA cell configuration, the $MnO_2$ discharges to a maximum of 0.52 h, whereas a 5% $KMnO_4$, 95% $BaFeO_4$ cathode (containing 4.0 g $BaFeO_4$) discharges for 1.26 h [6]. As seen in Fig. 3, due to the lower average voltage discharge for the pure $MnO_2$ cathode, its 0.7 W discharge is diminished compared to the 2.8 Ω. In comparison, high capacities are shown for both a constant load (2.8 Ω) discharge and for a constant power (0.7 W) discharge, for the cell containing a cathode composed primarily of $BaFeO_4$. Equivalent results were measured with unopened and "reconstructed" cells. These demonstrate that the reinsertion of the anode components, separator and repacked cathode mix has no observable effect on the measured discharge characteristics. The latter case contains $MnO_2$ cathodes prepared from the extricated cathode, which is then washed, and dried (to remove electrolyte, but retain the original dry $MnO_2$/graphite cathode mix), which is then mixed with fresh electrolyte.

Recently, as a general class barium salts have been restricted by the US EPA [10], and it is of interest to probe whether $MnO_2$/$BaFeO_4$ composite cathodes, containing reduced barium levels, will also exhibit enhanced discharge compared to the pure $MnO_2$ cathode. As also presented in
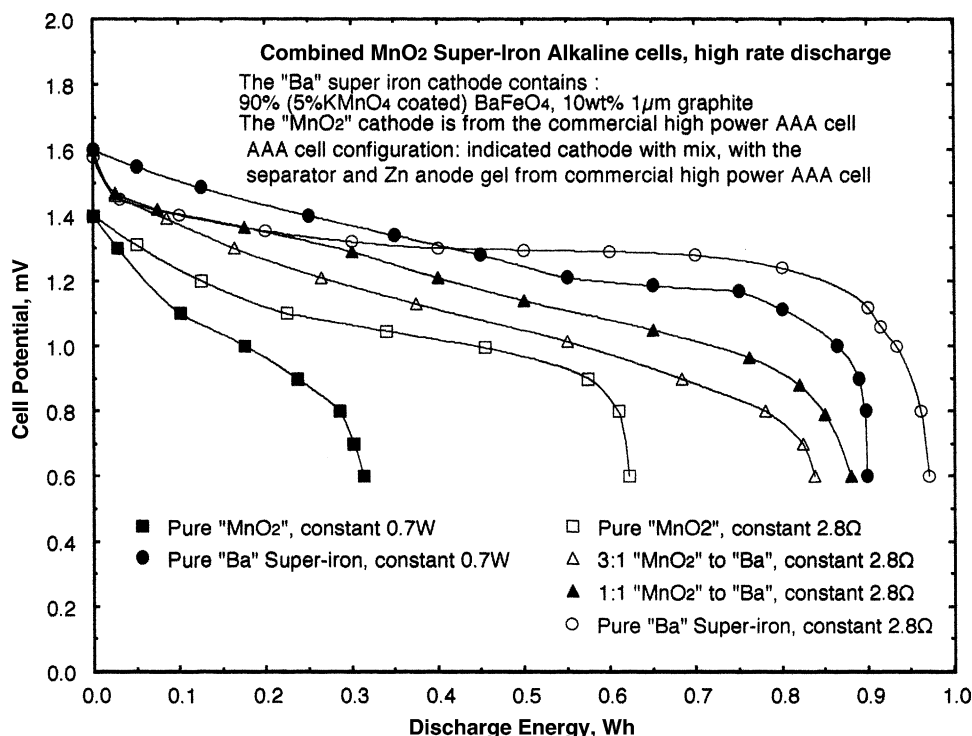


Fig. 3. The high power domain discharge of super-iron ($BaFeO_4$ and $BaFeO_4$/$MnO_2$ composites) compared to the discharge of $MnO_2$ cathode cells, each in a conventional cylindrical (AAA) alkaline cell configuration. In the super-iron AAA experiments, components are removed from the standard alkaline cell, and the outer $MnO_2$ mix, replaced with a pressed $BaFeO_4$ mix (containing 1 μm graphite and saturated KOH); followed by inclusion of the separator, Zn anode mix, and anode collector. As indicated on the figure, the cells are discharged with either a constant power (0.7 W) or a constant resistive (2.8 Ω) load.

Fig. 3, $BaFeO_4$ or $BaFeO_4/MnO_2$ composites, containing less barium, exhibit significantly higher discharge energy compared to the $MnO_2$ cathode in conventional alkaline cells, and intermediate to the values observed for the $MnO_2$ free, $BaFeO_4$ cathode. Under the same 2.8 Ω load, high rate conditions, the 3:1 composite $MnO_2/BaFeO_4$ cathode cells yields 0.78 Wh to an 0.8 V discharge cut-off, providing ∼30% additional capacity compared to the 2.8 Ω pure $MnO_2$ cell discharge, and more than double the capacity of the pure $MnO_2$ 0.7 W discharge. The 1:1 composite $MnO_2/BaFeO_4$ cathode cells yield 0.85 Wh to an 0.8 V discharge cut-off, providing ∼40% additional capacity compared to the 2.8 Ω pure $MnO_2$ cell discharge, and triple the capacity of the pure $MnO_2$ 0.7 W discharge. We have previously reported that the improvements in the high power discharge domain are intrinsic to the unusually facile charge transfer of $BaFeO_4$, which is better than that observed for either $MnO_2$ or $K_2FeO_4$ [8]. As with the AAA cells, our initial results with larger cross-section AA cells yield a proportional improvement in the high discharge domain when incorporating the new Fe(VI) cathode into this configuration compared to the conventional alkaline $MnO_2$ cathode. Although, beyond the scope of this short communication, the related enhanced power should result in proportionally improved high discharge domain results for larger cross-section (C or D) configuration alkaline cells.

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