Fe(VI) Catalyzed Manganese Redox Chemistry: Permanganate and Super-Iron Alkaline Batteries

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In principle, alkali permanganates represent a substantial cathodic charge source for electrochemical storage, but high rate charge transfer has been inefficient. This study presents a novel Fe(VI) species (super-iron) and manganese redox chemistry synergism. Also presented is the high discharge energies from cathodes which utilize this phenomenon in a conventional cylindrical battery configuration. Batteries formed with a cathode combining BaFeO₄ and KMnO₄, and using a conventional zinc alkaline anode in an AAA cylindrical cell configuration, exhibit an unusually high discharge capacity of 2.2 Wh. The discharge efficiency of solid alkaline permanganate or manganate cathodes is probed, and improved charge transfer of Mn(VII) redox chemistry in the presence of Fe(VI) is demonstrated. In a reciprocal manner, enhancement of Fe(VI) charge transfer are demonstrated upon inclusion of manganese salts, and also that added cesium further improves the combined Fe(V)/Mn(VII) cathode.

1. Introduction

Solution phase alkaline permanganate provides a high power and capacity cathodic discharge.^{1,2} Yet for solid alkaline permanganate cathodes, effective reductive charge transfer has remained a challenge. Whereas variations of solid manganese dioxide salts have been of wide interest as commercial cathodes, this is not the case for the higher valence, higher intrinsic capacity, manganese salts such as the alkali or alkali earth permanganates or manganates.³⁻⁵

We recently introduced batteries with several energy and environmental advantages based on Fe(VI) species^{6–9} whose chemistry had been relatively unexplored,¹⁰ and in accord with⁶

$$\text{FeO}_4^{2-} + \frac{5}{2}\text{H}_2\text{O} + 3\text{e}^- \rightarrow \frac{1}{2}\text{Fe}_2\text{O}_3 + 5\text{OH}^-$$
 (1)

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. A low level (2-5 wt %) of permanganate or manganate salts when added to Fe(VI) salts, is sufficient to renew an Fe(VI) salt when blocked by a small presence of a passivating Fe(III) oxide, which we generalized for either permanganate or manganate with⁷

$$2MnO_{4}^{-} + Fe_{2}O_{3} + 2OH^{-} \rightarrow 2MnO_{2} + 2FeO_{4}^{2-} + H_{2}O$$
(2)
$$3MnO_{4}^{2-} + H_{2}O + Fe_{2}O_{3} \rightarrow 3MnO_{2} + 2OH^{-} + 2FeO_{4}^{2-}$$
(3)

This study presents a novel Fe(VI) species (super-iron) and manganese redox chemistry intercatalysis, and the high discharge energies from cathodes which utilize this phenomenon in a conventional alkaline cylindrical battery configuration.

2. Experimental Section

We have previously detailed the synthesis of K_2FeO_4 and $BaFeO_4$ salts and their use as a cathode.^{5–8} A cathode composite is formed by mixing an Fe(VI) salt (either K_2FeO_4 , $BaFeO_4$), and/or manganese salt, with graphite and electrolyte. CsMnO₄ is synthesized by precipitation from KMnO₄ with Cs₂(SO₄),¹¹ and other materials are commercial analytical grade.

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), and the outer MnO₂ mix, replaced with a pressed super-iron and/or (per)manganate salt 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 added graphite as a matrix to support the cathode reduction. Cells were discharged as indicated at a 2.8 Ω , a 75 Ω , or a 275 Ω , constant resistance load, or in one case 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.

3. Results and Discussion

This study probes cathodic charge transfer through the preparation and use of sealed cylindrical alkaline cells. Although not isolating the cathode redox couple as effectively as in a galvanostatic, or potentiostatic, three-electrode configuration, this configuration has several advantages: the same type of anode was used throughout the study (as removed from the commercial Zn alkaline cell) and exhibits facile (low polarization, efficient) charge transfer. Hence, the charge-transfer attributes of the cathode are demonstrated, and which limit the observed discharge characteristics of these cells. Advantages of this two-electrode cell are its reproducibility and sealing (preventing competing oxygen reduction effects), that the cell requires a minimum of electrolyte, and that it provides a direct

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Figure 1. Cell potential and energy capacity of alkaline super-iron AAA cells. Cells contain various indicated weight fractions of Fe(VI), Mn(VII), and Mn(VI) salts, in the cathode mix, and use either a KOH or CsOH electrolyte. The "pure" cathode mix includes 3.5 g of KMnO₄, 4.9 g of CsMnO₄, or 4.1 g of BaMnO₄ in the 9 wt % graphite mix. The combined mass of a BaFeO₄/KMnO₄ cell cathode increases smoothly with the increasing fraction of BaFeO₄, from 3.5 g of KMnO₄ in the 0% BaFeO₄ cathode to 4.3 g in a pure BaFeO₄ cathode. The sodium permanganate mix also includes solid NaOH to avoid an over wet mix, as well as a higher graphite content (2.1 g of NaMnO₄·H₂O and NaOH in a 9:1 weight ratio) mixed with 32 wt % graphite. KMnO₄ or BaMnO₄ cathodes contain 9 wt % 18 *m* KOH electrolyte; while CsMnO₄ contains 9 wt % 18m CsOH, and the NaMnO₄·H₂O cathode uses no added electrolyte (water is inherent in the salt). Top and middle sections: cells discharged at low constant load rate using a constant load of 2.8 Ω or a constant power of 0.7 W.

electrochemical comparison to a well-characterized (widely distributed, commercial AAA alkaline) existing cell which provides ~ 0.3 Wh at high (0.7 W) discharge and ~ 1.4 Wh at low discharge rate.⁶

Composite alkaline BaFeO₄ cathodes exhibit high energy capacities.^{6,7,9} This "super-iron" battery energy is seen in the 95% BaFeO₄ curve in the top of Figure 1, exhibiting a capacity of 1.8 Wh to a 0.8V discharge. Included are this study's novel even higher discharge storage capacity, which may be derived in alkaline cells containing both Fe(VI) and Mn(VII) salts. The cells are prepared with identical zinc anodes and separators, as removed from commercial AAA alkaline cells. Under these conditions, and as seen in the figure's middle, a cathode

comprised of only KMnO₄, exhibits less than half of the capacity of the BaFeO₄ cathode. As previously noted,⁷ Fe(VI) discharge is blocked by a small presence of a passivating Fe(III) oxide. The 75 Ω energy capacity of pure BaFeO₄ is 1.75 Wh with a discharge profile highly similar to that of the 95% BaFeO₄/5% KMnO₄ composite cathode detailed in the top section of Figure 1. Cells containing high fractions of both BaFeO₄ and KMnO₄ discharge to a higher capacity than cathodes comprised of either salt alone. Hence, a cathode with either 50:50 or 75:25 relative weight percent of BaFeO₄ to KMnO₄ yields respective discharge capacities of 1.83 and 1.95 Wh. Finally as seen in the figure, utilization of a CsOH, rather than KOH electrolyte further enhanced the discharge energy to 2.1–2.2 Wh. The resultant



Figure 2. Measured and theoretical charge capacities of alkaline AAA cells containing various fractions of Fe(VI) and Mn(VI) salts. The K₂-FeO₄/KMnO₄ composite cathodes contain a fixed 3.5 g of K₂FeO₄ and/ or KMnO₄. Cathodes also contain 9 wt % graphite and 18 *m* KOH. Note, all measured capacities above 1.25 Ah approach intrinsic limitations of the \sim 1.4 maximum Ah packed zinc anode.

volumetric capacity of 600 Wh/cc is high compared a maximum 400 Wh/cc for a high performance MnO_2 cathode alkaline AAA cell.

The permanganate to manganate reduction, or direct reduction to MnO_2 , in aqueous alkaline media are

 $MnO_4^{-} + 1e^{-} \rightarrow MnO_4^{2-}$ E = 0.56 V vs SHE (4)

$$MnO_4^{-} + 2H_2O + 3e^{-} \rightarrow MnO_2 + 4OH^{-}$$

E = 0.58 V vs SHE (5)

The MnO₂ product can undergo a further 1e⁻ reduction, as utilized in the conventional commercial alkaline cell:

$$2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$$
$$E = 0.35 \text{ V vs SHE} (6)$$

As seen in Figure 2, inclusion of even small amounts of the Fe(VI) salts, such as 5% BaFeO₄ or K₂FeO₄, dramatically enhances charge transfer, yielding higher measured cathodic capacities for KMnO₄. At 75 Ω load in the AAA cell configuration, KMnO₄ or K₂FeO₄ alone discharge to 160 mA/ g, whereas a 40% KMnO₄/60% K₂FeO₄ composite cathode discharges to 300 mAh/g. In principle, permanganate can undergo an eq 5 and 6 total of a 4e⁻ alkaline cathodic reduction. KMnO₄ has a large theoretical discharge capacity, but exhibits inefficient charge transfer, measured as a low experimental capacity in the figure, which also includes the theoretical (intrinsic) storage capacity of cells containing a variety of relative compositions of BaFeO4 and KMnO4. The intrinsic capacities are calculated from the mass of KMnO₄ and BaFeO₄ in the cell, assuming a 4 faradays mole⁻¹ Mn(VI \rightarrow III), and 3 F mol⁻¹ Fe(VI \rightarrow III), reduction, and subsequently converted to ampere hours. Experimentally, Fe(VI) salts can attain the complete 3e⁻ faradaic capacity of eq 1, although K₂FeO₄ is less charge efficient at higher current densities than BaFeO₄.⁶⁻⁹ As evident in the figure, a wide BaFeO₄/KMnO₄ composition range, including cells varying from 20% to 80% BaFeO4 (and 20% to 80% KMnO₄), each exhibits a high discharge capacity. Charge capacity increases from 160 mAh/g with the pure KMnO₄ cathode to 340 or 290 mAh/g, respectively, in 30%/70% or 3%/97% KMnO₄ /BaFeO₄ composite cathodes.

In the storage cell, low solubility, or insolubility is preferred to minimize parasitic cathode/anode interactions. As we have previously summarized, the lighter alkali permanganate salts have a high aqueous solubility, e.g., 4 m ($m \equiv$ molal) for LiMnO₄, and 0.5 m for KMnO₄, whereas the respective solubility of 0.07 and 0.01 m for RbMnO₄ and CsMnO₄ is very low. Whereas the solubility of the alkali earth magnesium, calcium, strontium and barium permanganates, is very high (e.g.. 9, 8, and 2 m respectively for Ca(MnO₄)₂, Sr(MnO₄)₂ and Ba-(MnO₄)₂), the solubility of barium manganate, BaMnO₄, is very low.⁷ BaFeO₄ is insoluble in water. As with other Fe(VI) salts, the permanganate salts also generally exhibit a rapid decrease in solubility with increases in hydroxide concentration.^{6,7}

Figure 1, middle, summarizes the measured discharge of several pure permanganate or manganate cathode alkaline AAA cells. Despite the lower intrinsic $Mn(VI \rightarrow IV)$ capacity of the barium manganate salt, this salt's cathode approaches 1.0 Wh, yielding a higher discharge capacity than the sodium or potassium permanganate cathode cells. As is evident in the figure, the measured discharge capacity is higher, despite the lower intrinsic $4e^-$ capacities, for the heavier alkali cation permanganate cathodes is ~0.45, 0.8, and 1.3 Wh. Note, the sodium permanganate discharge required a higher fraction (32 wt %) of graphite to generate a discharge.

The cathode reduction is supported by a conductive matrix provided through inclusion of graphite in the cathode mix. As we have previously demonstrated, BaFeO₄ with as low as 3-10% added carbon is capable of sustaining high current densities with low polarization losses.^{6,7} In the presence of BaFeO₄, the enhanced Mn(VII) charge transfer indicated in Figure 2, is attributed in part to the improved conductive matrix that this Fe(VI) salt provides. Figure 3, probes the experimental 4e⁻ (for permanganate) or 3e⁻ (for manganate) efficiency, determined by comparison of the measured cumulative discharge ampere hours, as a fraction of the intrinsic charge determined from the mass of the salt. In Figure 3, utilization of higher weight fractions (cathodes employing 32 wt %, rather than 9 wt %) graphite greatly improves the percent storage capacity. Hence, in each case reductive charge transfer appears to be limited by an insufficient conductive matrix.

In Figure 3, it is observed that the CsMnO₄ cathode, with inclusion of 32 wt % graphite, approaches 100% of the theoretical 4 e⁻ capacity. Three voltage plateaus are visible in this CsMnO₄ discharge, and are evidently attributable to permanganate, manganate and MnO₂ reduction steps occurring at ~1.67, 1.3, and 0.9 V respectively during 0–25, 25–75, and 75–95 of the percent storage capacity. Also in Figure 3 as expected for the overall 3e⁻ reduction in the barium manganate discharge, when compared to a 4e⁻ permanganate reduction the lowest potential discharge step is accentuated (elongated), due to the larger relative contribution of the final Mn(IV \rightarrow III) reduction described in eq 6.

The CsMnO₄ cathode facilitates more efficient charge transfer, compared to KMnO₄, and has the additional previously discussed benefit of lower solubility than the potassium salt. However, the intrinsic capacity of CsMnO₄ is lower due to its heavier formula weight. Instead in the super-iron alkaline cell, cesium benefits may be incorporated, without the need to include the heavier cesium permanganate salt, by direct replacement of the KOH electrolyte with a CsOH electrolyte. In Figure 1, top,



Figure 3. Salt cation and conductance (wt % graphite variation) effects on the discharge storage capacity of permanganate and manganate alkaline AAA cells during discharge at low constant load rate (75 Ω). The percent storage capacity is determined by the measured cumulative ampere hours, compared to the theoretical capacity. The 9 wt % graphite cells are detailed in the Figure 1 legend. In the 32 wt % graphite cells, the mass of KMnO₄ is 2.3 and that of CsMnO₄ is 2.7 g. The potassium and barium cathodes contain 9 wt % 18 *m* KOH electrolyte, and the cesium cathode contains 9 wt % 18 *m* CsOH.

this adds more efficient reduction toward the end of the discharge, and further enhances total energy capacity.

Figure 1, bottom, demonstrates that the additional permanganate enhanced super-iron cell energy capacities realized at low discharge rate in Figure 1, top, do not substantially impair the high discharge rate performance of the cell. Under rapid discharge conditions the capacity of the alkaline MnO₂ cell falls to a small fraction of its energy capacity in the low rate domain. We had shown that the super-iron alkaline cell capacity advantage over conventional alkaline cells is particularly large in the high discharge rate domain, amounting to a severalfold increase in capacity.⁶ In the lower section of Figure 1 these 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 BaFeO₄. As seen in the left-most curve, under these 2.8 Ω discharge conditions, the KMnO₄ leads to not only a lower capacity but also due to the higher polarization, the lower cell potential generates a lower power of only ~ 0.4 W during the discharge. Significantly, it is also seen that a cathode comprised of equal KMnO₄ and BaFeO₄ weight fractions, retains the majority of the capacity advantage, approaching 0.8 Wh, when also discharged at the 2.8 Ω constant load (again, ~0.6-0.7 W).

4. Conclusions

Cathodes formed with a cathode combining $BaFeO_4$ and $KMnO_4$, in a cell using a conventional zinc alkaline anode in

an AAA cylindrical cell configuration, exhibit an unusually high discharge capacity of 2.2 Wh. The discharge efficiency of solid alkaline permanganate or manganate cathodes is probed, and improved charge transfer of Mn(VII) redox chemistry occurs in the presence of Fe(VI) is demonstrated. In a reciprocal manner, Fe(VI) electrochemistry is enhanced upon inclusion of manganese salts, and added cesium further improves the combined Fe(V)/Mn(VII) cathode.

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