Cathodic chemistry of high performance Zr coated alkaline materials†

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A low level zirconia modification significantly stabilizes alternative higher energy cathodes under consideration to improve the energy storage capacity of alkaline batteries, and is demonstrated on materials including periodate, Fe(VI) "super-iron", manganese, nickel, bismuthate and silver oxide cathodes.

Significant metal hydride chemistry advances by Ovshinsky and co-workers pioneered its utilization as an energy storage anode.[1] The metal hydride alkaline (MH) battery stores approximately three fold higher energy than its Ni/Cad predecessor, and has set the stage for today's successful MH hybrid vehicles. Further improvements in energy density and cost effectiveness are urgently needed to diminish the global reliance of transportation on fossil fuels. Unlike the revolutionary anode, the cell's cathode utilizes the same fundamental chemistry as the Ni/Cad battery. This nickel oxyhydroxide cathode chemistry was introduced by Edison in the late 19th century.[2] The mass per unit of stored charge is several fold heavier for an NiOOH cathode than for the MH anode. NiOOH has intrinsic maximum 290 mAh g^{-1} based on a $1e^-$ alkaline reduction:

$$\begin{gathered}\mathrm{NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-;}\\ E = 0.55\ \mathrm{V^*}\ (* = \mathrm{vs\ SHE})\end{gathered} \tag{1}$$

Further energy storage improvements for the MH battery will be based on energetic, clean alternatives to the NiOOH cathode. Increases in cathodic energy can come from multiple e^- transfer and more positive redox potentials. However, the requisite higher energy tends to destabilize these alternative cathodes, which often tend to passivate when stored in alkaline media. The most common primary alkaline battery cathode material is MnO_2 with an intrinsic 1 e^- capacity of up to 308 mAh g^{-1}. A new primary cathode has high capacity based on the $2e^-$ reduction of Bi(V), bismuthate compounds.[3,4] Another new cathode is based on a class of Fe(VI) or "super-iron" oxides with a $3e^-$ intrinsic capacity (*e.g.* K_2FeO_4: 406 mAh g^{-1}), higher than MnO_2 and NiOOH.[5–8] Both Fe(VI),[9–11] and another new cathode, periodate, I(VII), we are studying, sustain rechargeable (secondary) battery performance. Redox reactions for these 1, 2 and 3 e^- alkaline cathodes may be generalized as:

$$\begin{gathered}\mathrm{MnO_2 + \tfrac{1}{2}H_2O + e^- \rightarrow}\\ \mathrm{\tfrac{1}{2}Mn_2O_3 + OH^-};\ E = 0.35\ \mathrm{V^*}\end{gathered} \tag{2}$$

$$\begin{gathered}\mathrm{BiO_3^- + \tfrac{1}{2}H_2O + 2e^- \rightarrow}\\ \mathrm{\tfrac{1}{2}Bi_2O_3 + 2OH^-};\ E = 0.3\text{–}0.5\ \mathrm{V^*}\end{gathered} \tag{3}$$

$$\mathrm{IO_4^- + H_2O + 2e^- \rightarrow IO_3^- + 2OH^-};\ E = 0.3\text{–}0.5\ \mathrm{V^*} \tag{4}$$

$$\begin{gathered}\mathrm{FeO_4^{2-} + H_2O + 3e^- \rightarrow}\\ \mathrm{\tfrac{1}{2}Fe_2O_3 + 5OH^-};\ E = 0.72\ \mathrm{V^*}\end{gathered} \tag{5}$$

Due to its extreme stability over a wide temperature and environmental range, zirconia has been used as a protective coating for a variety of materials.[12,13] It has been explored to a lesser extent to protect in aqueous alkaline media, as typical zirconia deposition methods such as spray pyrolysis, plasma deposition, and colloidal deposition tend to deactivate or only partially cover electroactive surfaces.[12–14] However, in aqueous alkaline media, zirconia is practically insoluble ($K_{sp} = 8 \times 10^{-52}$) and stable.[15] We introduce a novel zirconia coating, derived from an organic soluble zirconium salt. The formation/protection mechanism for zirconia coated alkaline cathodes is demonstrated.

Transition metal cathode materials are generally insoluble in a wide range of organic solvents. Whereas, the zirconia coating methodology is based on our experience (and surprise), that various possible transitional metal coating materials can be highly soluble in such solvents (such as our previous case of a $KMnO_4$ coating[6]). A variety of coating solvents were studied, and of these, ether was chosen due to its facile evaporation (bp = 34 °C), $ZrCl_4$ solubility, and no reaction or solubility with the cathode materials. A 1 wt% zirconia coating, prepared with 30 min coating time, is observed to have the best effect on charge retention of a coated cathode. 0.3 to 5% zirconia coatings were prepared. Excess coating is observed to the cathode overpotential, whereas, a lesser coating is insufficient for maximum charge retention.

1% ZrO_2 coating on K_2FeO_4: 8 mg $ZrCl_4$ (AR grade, ACROS®) is dissolved in 8 ml ether (Fisher®), and stirred with 0.8 g solid (insoluble) K_2FeO_4 in air for 30 min, followed by vertex suction, then vacuum removal of the remaining solvent, and drying overnight. K_2FeO_4 of 97–98.5% purity was prepared as detailed elsewhere by alkaline reaction of $Fe(NO_3)_3$ with KClO.[6] AgO, was prepared by the 85 °C alkaline reaction of $AgNO_3$ with $K_2S_2O_8$, as detailed elsewhere.[7] Other cathode materials MnO_2 (EraChem K60), NiOOH (from Powerstream® Ni-MH button cell), $NaBiO_3$ (ACROS®) and KIO_4 (ACROS®), and AgO are effectively coated with the same methodology. Analysis of the coating is performed with Attenuated Total Reflectance Fourier Transform Infrared (ATR/FT-IR) Spectrometry (Nicolet 4700), in which the powder sample is compressed to a thin pellet and pressed firmly onto a Smart Orbit (Thermo Electron Corporation) diamond crystal. ATR/FT-IR spectra of several uncoated and coated cathode materials are shown in Fig. 1. Pure ZrO_2 is prepared (as a colloid without the cathode salt) for comparison.

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† The HTML version of this article has been enhanced with colour images.

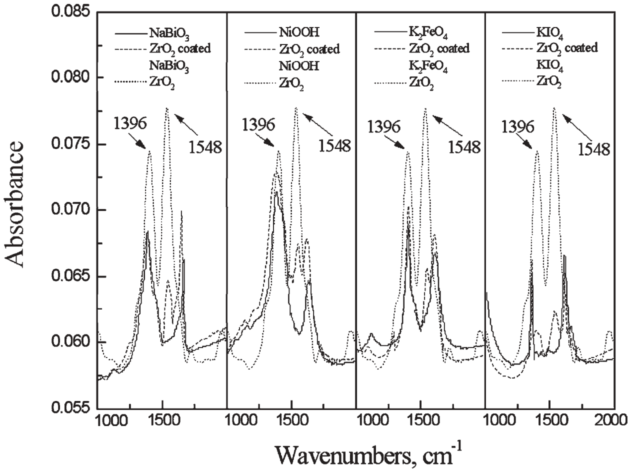


Fig. 1 ATR/FT-IR spectra of zirconia coated and uncoated cathode materials $NaBiO_3$, NiOOH, K_2FeO_4 and KIO_4. Spectra of 5% coating included for emphasis; a 1% zirconia coating exhibits evident, but proportionally smaller, 1.35 and 1.55 μm peaks.

The prominent 1608 cm^{-1} peak of the commercial $ZrCl_2$ fully disappears (not shown), and as seen in Fig. 1, new 1396 and 1548 cm^{-1} peaks on the coated material coincides with the absorption spectra of pure $ZrO_2/Zr(OH)_4$ depending on extent of hydration:[16]

$$ZrCl_4 + 2O_2 \rightarrow ZrO_2 + 2Cl_2; \quad ZrO_2 + 2H_2O \Leftrightarrow Zr(OH)_4 \tag{6}$$

The effect of the 1% zirconia coating on alkaline cathodes can be dramatic. Electrochemical enhancement of the zirconia coating is probed through the preparation of alkaline (metal hydride anode) button cells with coated, or uncoated, cathodes. Cathodes shown are composed of 20 mAh of KIO_4 or K_2FeO_4 (coated or uncoated), with graphite as a conductor (1μ graphite, Leico Industries Inc.). Saturated KOH is used as the electrolyte, and the metal hydride anode is as removed from a Powerstream® Ni-MH button cell. Cells are discharged at constant load of 3000 Ω; the potential variation over time is recorded *via* LabView Acquisition on a PC, and the cumulative discharge determined by subsequent integration.

Alkaline periodate represents a new reversible I(VII) cathode, based on the unexpected low solubility of KIO_4 in concentrated KOH (rising with increasing KOH, then drops from 3 to 0.0001 M KIO_4 as KOH increases from 6 to 10 M). Fig. 2 presents the discharge of KIO_4. Typical of other multiple e^- alkaline cathodes, the cathode passivates, and after 7 days storage the discharge is only a small fraction of its initial capacity. However, as seen with a 1% zirconia coating the initial discharge capacity is retained. Stabilized zirconia was introduced as a pH sensor for high temperature aqueous systems,[17] and $Zr(OH)_4$ has long been known as a hydroxide ion conductor which will readily exchange between solution phase hydroxide, phosphate, fluoride, and sulfate.[18–21] The insoluble Zr centers provide an intact shield, as represented in Scheme 1, and with eqn (6) right, a necessary hydroxide shuttle to sustain alkaline cathode redox chemistry.

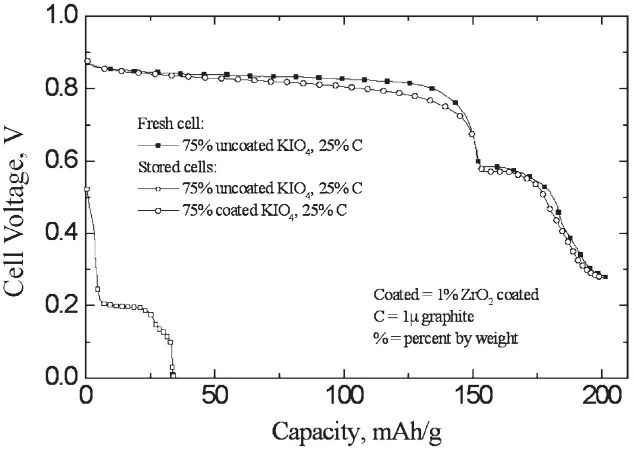
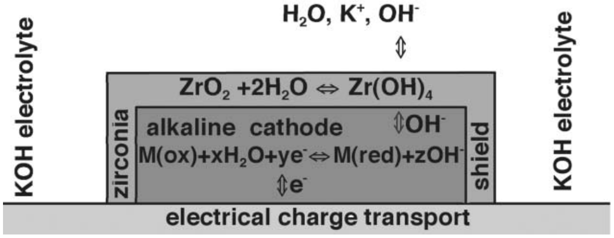


Fig. 2 Discharge capacity of KIO_4-MH button cells fresh and after 7 days storage, at a constant discharge load of 3000 Ω.



Scheme 1 Representation of zirconia alkaline cathode protection.

Among the super-iron cathodes, K_2FeO_4 exhibits higher solid state stability (<0.1% decomposition per year) and higher intrinsic $3e^-$ capacity than pure $BaFeO_4$, but the rate of charge transfer is higher in the latter. Charge transfer is enhanced manyfold in K_2FeO_4 by small additions of AgO or KOH, and at low current densities the cathode approaches the intrinsic, over 400 mAh g^{-1}, storage capacity.[7] However, the Fe(VI) forms a ferric overlayer,[9,11] upon storage the bulk Fe(VI) remains active,

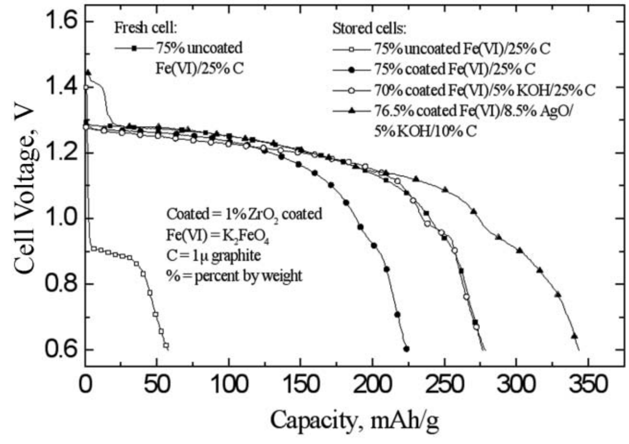


Fig. 3 Discharge capacity of K_2FeO_4 (and K_2FeO_4 composite) -MH button cells fresh and after 7 days storage, at a constant discharge load of 3000 Ω.

but the overlayer passivates the alkaline cathode towards further discharge. This is seen in Fig. 3, in which the fresh pure K_2FeO_4 discharges well, but requires a large fraction (25 wt%) of graphite as a supporting conductive matrix, and the capacity. which decreases by an order of magnitude after 7 days of storage. A 1% zirconia coating dramatically improves the capacity after storage, which is further improved with a 5% KOH additive. Interestingly, a low level AgO additive to the cathode, not only facilitates charge transfer, sustaining an effective discharge with a smaller conducting support (10%, rather than 25% graphite), but as seen in the figure yields an even greater discharge capacity than the uncoated, fresh K_2FeO_4. The initial small 1.4 V plateau in this discharge is consistent with the related added AgO reduction.[7]

Capacity retention requirements of contemporary commercial metal hydride batteries are rigorous. For example, they are also tested at higher temperature and over longer periods of time. The low level zirconia coating presented here, is environmentally benign, opens a new direction to the substantial stability of multiple e^- alkaline cathodes, and is likely to be further improved through variation of particle size and further optimization of the cathode coating process. In addition to Fe(VI) and I(VII) cathodes, the zirconia coating methodology is shown to be readily transferable to a variety of alkaline battery cathode materials including manganese, nickel, bismuthate and silver oxide cathodes, which will be examined in future studies. This work was supported in part by the US Department of Energy.

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