A novel alkaline redox couple: chemistry of the Fe^{6+}/B^{2-} super-iron boride battery

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A high capacity alkaline redox storage chemistry is explored based on a novel, environmentally benign zirconia stabilized Fe^{6+}/B^{2-} chemistry, which sustains an electrochemical potential matched to the pervasive, conventional MnO_2–Zn battery chemistry, however with a much higher electrochemical capacity.

Aqueous Zn–MnO_2 redox charge storage chemsity has been established for over a century and continues as the dominant mechanism of primary electrochemical storage. Capacity, power, cost, and safety factors have led to the annual global use on the order of 10^{10} primary Zn–MnO_2 batteries.[1] This chemistry is increasingly limited in meeting the growing energy and power demands of contemporary optical, electromechanical, electronic, and medical consumer devices. Therefore, the search for new energy storage chemistry systems with higher capacity and energy density has been increasingly emphasized.[1–6]

In 1999, we introduced a novel cathodic chemistry,[1] which 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 (308 mAh g^{-1}). In 2004 it was reported that metal borides could be used as anodic alkaline charge storage materials.[7,8] Representative transition metal borides include TiB_2 and VB_2 which can store several fold more charge than a zinc anode through multi-electron charge transfer:[7]

$$TiB_2 + 12OH^- \rightarrow Ti(amorphous) + 2BO_3^{3-} + 6H_2O + 6e^- \quad (1)$$

$$VB_2 + 20OH^- \rightarrow VO_4^{3-} + 2BO_3^{3-} + 10H_2O + 11e^- \quad (2)$$

However, two obstacles were evident towards implementation of this alkaline boride (MB_2, M = Ti or V) anodic chemistry. There is a significant domain in which the boride anode materials corroded spontaneously generating hydrogen gas, and the electrochemical potential of the boride anodes was more positive than that of zinc. Therefore a boride MnO_2 cell was subject to decomposition, and secondly the voltage of this cell was low compared to the electrochemical potential of the pervasive Zn–MnO_2 redox chemistry. In this paper, we introduce a novel battery chemistry system Fe(VI)–MB_2, and both obstacles of the boride anode are overcome. The super-iron cathode provides the requisite additional electrochemical potential, and our recently demonstrated zirconia hydroxide-shuttle overlayer, which stabilizes alkaline cathodic charge transfer chemistry,[6] also is demonstrated to prevent corrosion of the boride anode. This Fe(VI)–MB_2 alkaline battery chemistry system sustains much higher (two fold) electrochemical capacity than conventional MnO_2–Zn battery.

The alkaline redox couples studied in this paper are prepared in an electrochemical coin cell configuration, and utilize the zirconia coating procedure as detailed in ref. 6.

The alkaline thermodynamic potential of the three electron reduction of super iron cathodes Fe(VI ⇒ III) *via* eqn (3), is approximately 250 mV higher than the one electron reduction of MnO_2 *via* eqn (4), with potentials reported *versus* SHE (the standard H_2 electrode):

$$FeO_4^{2-} + H_2O + 3e^- \rightarrow \tfrac{1}{2}Fe_2O_3 + 5OH^-;\ E = 0.60\ V \quad (3)$$

$$MnO_2 + \tfrac{1}{2}H_2O + e^- \rightarrow \tfrac{1}{2}Mn_2O_3 + OH^-;\ E = 0.35\ V \quad (4)$$

Fig. 1 compares the discharge of alkaline electrolyte cells containing various anode and cathode couples. It is evident that the MnO_2/boride cell generates a low discharge potential, while the super-iron/zinc cell generates a potential that is too high compared to the conventional MnO_2/Zn cell. One driving force for the continued societal use of MnO_2/Zn chemistry is the several generations of devices, which have been designed for the normative 1.0–1.5 V optimal operative domain of the MnO_2/Zn battery. As

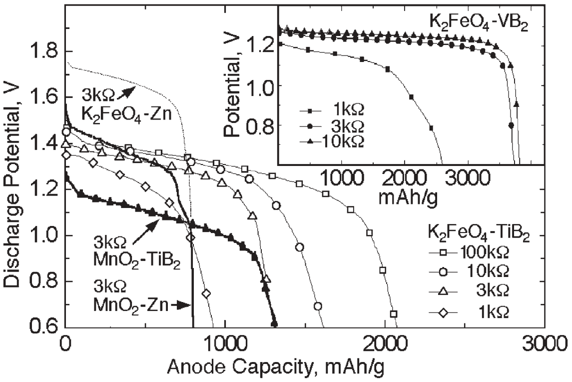

Fig. 1 Comparative discharge of conventional, super-iron cathode, and boride anode, alkaline batteries. Anodes are studied in cells with excess intrinsic cathode capacity, in a "button" cell containing 1 cm diameter electrodes in an adjacent anode/alkali separator/cathode configuration, discharged under the indicated constant ohmic load conditions. Cells contain a (conventional) MnO_2 cathode/Zn anode, or a K_2FeO_4 cathode, and/or a boride anode, and a KOH electrolyte. The boride anode is either TiB_2 (Aldrich 10 μm powder) or VB_2 (Aldrich 325 mesh powder), and contains 75% of the boride salt, 20% 1 μm graphite (Leico), 4.5% KOH and 0.5% binder (T-30, 30% teflon).

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seen in the figure, the new super-iron/boride couple generates an open circuit voltage of 1.5 V, and an average discharge potential similar to the conventional alkaline MnO_2/Zn cell.

As seen in Fig. 1, a significant advantage of the boride anodes is the higher capacity compared to the conventional alkaline zinc anode (820 mAh g^{-1}). The TiB_2 anode discharge is in excess of 2000 mAh g^{-1}. In accord with eqn (1), and a formula weight, W = 69.5 g mol^{-1}, TiB_2, has a net intrinsic 6 electron anodic capacity of $6F/W$ = 2314 mAh g^{-1} (F = the faraday constant). Unlike TiB_2, the alkaline VB_2 anode undergoes an oxidation of both the boron and the tetravalent transition metal ion, with a net 11 electron process. In accord with eqn (2), VB_2, will have an intrinsic anodic capacity of $11F/(W = 72.6\ g\ mol^{-1}) = 4060$ mAh g^{-1}, rivaling the high anodic capacity of lithium (3860 mAh g^{-1}). As evident in the inset of Fig. 1 this substantial capacity of VB_2 is experimentally realized (3800 mAh g^{-1}) in the discharge of the alkaline super-iron VB_2 cell.

TiB_2 visibly reacts on contact with KOH electrolyte (evolving H_2 gas). This is not only a chemical loss of the electrochemical capacity, but is flammable. In addition due to the evolved gas, a sealed battery will swell or even crack during storage. Zirconia is extremely stable in aqueous alkaline media,[9,10] and based on our previous experience (Mn coating[11]), we recently developed a novel zirconia overlayer, which is derived from an organic soluble zirconium salt ($ZrCl_4$) *via* an organic medium.[6] In this study, high capacity boride anodes are modified with this novel zirconia coating methodology. ATR/FT-IR (attenuated total reflectance Fourier transform infrared) analysis results of uncoated and coated VB_2, TiB_2 anodes are shown in Fig. 2. Pure ZrO_2 is prepared (as a colloid) for comparison. Similar to the coated cathode materials,[6] the 1396 and 1548 cm^{-1} peaks on the coated TiB_2 and VB_2 coincides with the absorption spectra of pure ZrO_2/$Zr(OH)_4$ depending on the extent of hydration:[6,12]

$$ZrCl_4 + 2O_2 \rightarrow ZrO_2 + 2Cl_2;\ ZrO_2 + 2H_2O \Leftrightarrow Zr(OH)_4 \quad (5)$$

As recently demonstrated, this zirconia overlayer provides an ionic conductive, alkaline stable coating which is capable of mediating hydroxide transport from the electrolyte to the electrode.[8] A zirconia modified K_2FeO_4/AgO composite cathode exhibits longevity and high charge storage capacity.[6]

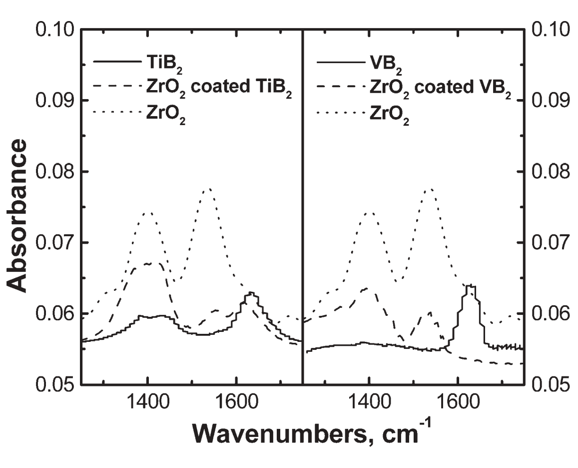

Fig. 2 ATR/FT-IR spectra of zirconia coated and uncoated TiB_2 and VB_2. Spectra of 5% coating included for emphasis; a 1% zirconia coating exhibits evident, but proportionally smaller, 1396 and 1548 cm^{-1} peaks.

Unlike uncoated titanium boride, a 1% zirconia coated (a 0.1 μm ZrO_2 overlayer on 30 μm diameter) TiB_2 does not evolve hydrogen. Stability of, not only the K_2FeO_4 cathode but also, the TiB_2 anode, dramatically improves with this zirconia coating. As seen in Fig. 3, after storage, the uncoated super-iron titanium boride cell generates only 10–15% of the 3 kΩ load (~0.5 mA cm^{-2}) discharge capacity of the fresh cell. One hundred percent of the charge capacity is retained, when zirconia coated boride is utilized. In lieu of the uncoated electrodes, if either anode or cathode (but not both) is coated, then a fraction, but not all, of the charge capacity is lost. Also evident in the figure, the zirconia coated super-iron vanadium boride cell also retains its substantial charge capacity after storage. The fundamental chemistry of conventional alkaline primary[4] and metal hydride rechargeable[2] batteries are understood, and continue to be of widespread interest. The charge retention for these super-iron boride cells is already comparable to that observed in early alkaline primary cells, and is better than that of contemporary alkaline rechargeable cells. We observe that the vanadium boride anode exhibits higher stability than the titanium boride anode. Accelerated long-term stability is measured at higher temperature. Without the zirconia overlayer, after one week storage the vanadium boride anode retains 90% of the original charge capacity at 45 °C (100% after one week with the zirconia coating), and 65% of the charge capacity at 70 °C (85% with zirconia).

The range from maximum experimental (<160 mA g^{-1}) to theoretical ($2F$ per Zn + $2MnO_2$ = 222 mAh g^{-1}) charge storage capacities of the conventional alkaline Zn–MnO_2 cell are shown as dashed vertical lines in Fig. 3. The theoretical capacities for the complete super-iron TiB_2 (6F per TiB_2 + $2K_2FeO_4$) and super-iron VB_2 ($11F$ per VB_2 + $11/3K_2FeO_4$) are higher respectively at 345 and 369 mAh g^{-1}. The discharge of the complete super-iron boride redox chemistry is investigated in Fig. 3 using cells with balanced anode and cathode capacity (based on the intrinsic capacity of the

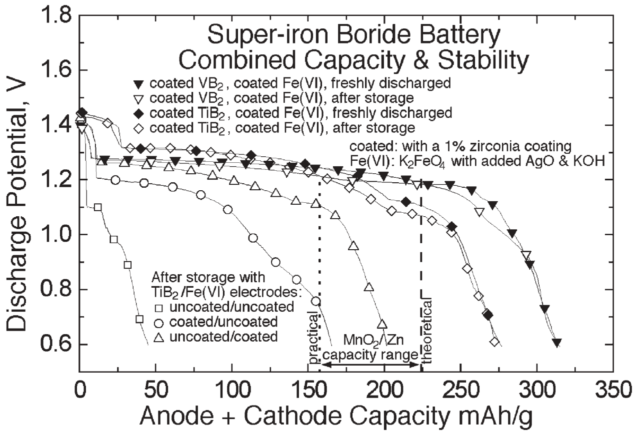

Fig. 3 Capacity (anode + cathode) of the super-iron boride alkaline battery to the conventional (manganese dioxide/zinc) alkaline battery. The super-iron boride cell contains either a TiB_2, or a VB_2 anode, as indicated in the figure. The cathode is 76.5% K_2FeO_4, 8.5% AgO, 5% KOH and 10% 1 μm graphite. Charge retention (stability) of the cells are compared freshly discharged, and after 1 week storage, with, or without, a 1% zirconia coating applied to the Fe(VI) or boride salts.

anode and cathode components). The reaction products will depend on the depth of discharge, pH and the degree of dehydration of the boric and ferric products, and the cell may be generalized in the representative deep discharge reaction (according to eqn (1), (2) and (3)):

$$TiB_2 + 2FeO_4^{2-} + 2OH^- \rightarrow Ti + Fe_2O_3 + 2BO_3^{2-} + H_2O \quad (6)$$

$$6VB_2 + 22FeO_4^{2-} + 10OH^- \rightarrow 6VO_4^{3-} + 11Fe_2O_3 + 12BO_3^{2-} + 5H_2O \quad (7)$$

As seen in Fig. 3, the super-iron titanium boride cell combined anode and cathode capacity is experimentally in excess of 250 mAh g^{-1}, and that of the super-iron VB_2 cell is over 310 mAh g^{-1}, which is two fold higher than that of the conventional alkaline battery chemistry (MnO_2/Zn). The super-iron VB_2 is diagrammatically represented in the graphical abstract.

The super-iron boride chemistry exhibits significantly higher charge storage than conventional alkaline primary storage chemistry. A further optimization of both the boride and super-iron salt particle size, coupled with study and variation of the zirconia coating, should further enhance cell performance. Alternate metal borides, as well as alternate super-irons will also affect characteristics of the super-iron boride cell capacity. Expected high intrinsic alkaline capacities of alternate borides include that for ZrB_2, MgB_2, CrB_2, CoB_2, NiB_2, TaB, TaB_2, and LaB_6. In addition to K_2FeO_4, the cathodic behavior of a variety of super-iron salts has been studied including Ag_2FeO_4, and other alkali (lithium, sodium, rubidium and cesium) and alkali earth (strontium and barium) Fe(VI) salts,[13–17] and further understanding of the charge transfer of these, and other, novel super-iron salts will also impact charge transfer, retention, capacity of the new super-iron boride chemistry. This work was supported in part by the US Department of Energy. Authors Licht and Yu conducted this boride battery study and acknowledge a prior borohydride collaboration with D. Qu.

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