HIGHER CAPACITY, IMPROVED CONDUCTIVE MATRIX VB2/AIR BATTERIES (POSTPRINT)

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14. ABSTRACT *(Maximum 200 words)*
Transition metal borides, such as VB2, have been investigated as alternative, higher capacity anode materials. The VB2 high capacity is due to the capability to undergo a 4060 mAh/g formula weight multiple electron (11 e−) alkaline oxidative discharge at a singular discharge potential plateau. With a comparable formula weight (10% higher) to zinc, VB2 has an intrinsic gravimetric capacity five-fold higher than the 2 e− oxidation of the widely used zinc alkaline anode. One challenge to the implementation of VB2/air batteries is that resistive oxide products impede the discharge depth, and only thin anode batteries (for example 10 mAh in a 1 cm diameter cell) had been demonstrated to discharge effectively. This study demonstrates that (i) smaller particle size (nano-VB2, as opposed to macroscopic VB2) helps to alleviate this effect and (ii) a stacked anode compartment configurations improve the anode conductive matrix significantly, resulting in an increase in the coulombic efficiency of high capacity, thicker anodes in VB2/air batteries. Combined, these effects provide a 50% relative increase in the coulombic efficiency (from 50% to 75% at a 0.4 V discharge cutoff) of a 30 mAh coin cell, and increase the coulombic efficiency of the 100 mAh cell to 50%.

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Higher Capacity, Improved Conductive Matrix VB₂/Air Batteries

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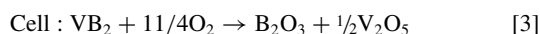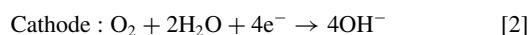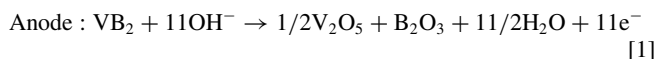*bLynntech, College Station, Texas 77845, USA*

Transition metal borides, such as VB₂, have been investigated as alternative, higher capacity anode materials. The VB₂ high capacity is due to the capability to undergo a 4060 mAh/g formula weight multiple electron (11 e⁻) alkaline oxidative discharge at a singular discharge potential plateau. With a comparable formula weight (10% higher) to zinc, VB₂ has an intrinsic gravimetric capacity five fold higher than the 2 e⁻ oxidation of the widely used zinc alkaline anode. One challenge to the implementation of VB₂/air batteries is that resistive oxide products impede the discharge depth, and only thin anode batteries (for example 10 mAh in a 1 cm diameter cell) had been demonstrated to discharge effectively. This study demonstrates that (i) smaller particle size (nano-VB₂, as opposed to macroscopic VB₂) helps to alleviate this effect and (ii) a stacked anode compartment configurations improve the anode conductive matrix significantly, resulting in an increase in the coulombic efficiency of high capacity, thicker anodes in VB₂/air batteries. Combined, these effects provide a 50% relative increase in the coulombic efficiency (from 50% to 75% at an 0.4 V discharge cutoff) of a 30 mAh coin cell, and increase the coulombic efficiency of the 100 mAh cell to 50%.

Higher energy density portable power is needed for consumer electronic, medical, and military devices, and drives the need for increased energy density batteries. Zinc-air batteries are primary batteries with the highest commercial energy capacity. They provide a practical capacity of up to 1,756 Wh/L, which is 5-fold higher than that of rechargeable Li-ion batteries and 10-fold higher than conventional alkaline primary (zinc anode/manganese dioxide cathode) batteries.[1,2] The capacity of zinc is limited by its oxidative discharge, which releases two electrons per zinc, leading to an intrinsic capacity of 820 mAh/g (=2*FW/Faraday*mAh). Transition metal borides have been investigated as alternative, potentially higher capacity anode materials due to their ability to undergo oxidative discharge processes that release multiple electrons per molecule. The highest capacity of these materials, vanadium diboride, has an alkaline capacity per VB₂ (FW 72.561 g/mol) intrinsic capacity of 4060 mAh/g (charge/FW), approximately five times that of zinc.[3–9] As with the zinc anode, the borides can chemically react to generate hydrogen, and this causes a parasitic loss of battery capacity. In 2007, we noted that a zirconia overlayer impedes this parasitic reaction and promotes the battery discharge reaction.[3,8] VB₂ coupled with an air cathode results in a battery material that is among the highest energy density of any primary battery (5,300 kWh/kg).[8] The VB₂ anode discharges all 11 of its electrons at a singular voltage plateau, in accordance with:[8–10]

$$Anode: VB_2 + 11OH^- \rightarrow 1/2V_2O_5 + B_2O_3 + 11/2H_2O + 11e^- \quad [1]$$

$$Cathode: O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad [2]$$

$$Cell: VB_2 + 11/4O_2 \rightarrow B_2O_3 + \frac{1}{2}V_2O_5 \quad [3]$$

The thermodynamic (intrinsic battery) potential of Equation 3 is 1.55 V.[8–10] The experimental VB₂/air battery is observed to discharge at a fraction of this intrinsic potential. An advance of the VB₂ anode has been the synthesis of active, nanoscopic (∼400 nm particle size) material compared to commercially available macroscopic (∼5,000 nm) material. Nanoscopic VB₂/air batteries discharge at over 1 V; this compares to 0.8 V for the macroscopic VB₂/air batteries.[11,12] The improved discharge voltage correlates with fewer surface oxides (as measured by XPS) in the nanoscopic compared to the macroscopic VB₂.[10] Nanoscopic VB₂ is readily synthesized by ball milling elemental vanadium and boron in a 1:2 molar ratio.[11–13]

One challenge to the implementation of VB₂/air batteries is that only thin anode batteries (for example 10 mAh in a 1 cm diameter coin cell) discharge effectively. The observed coulombic efficiency (the discharged mAh output of the cell relative to the intrinsic capacity of the material) decreases with increasing capacity as the resistive oxide discharge products impede the discharge depth. For example, under the same load, a 2.5, 5, 10 or 30 mAh VB₂/air cell discharged to 80%, 60%, 50% or 30 to 40% columbic efficiency respectively.[9,12,13] In this study, we provide a path to ameliorate this effect through advanced anode configurations with an improved conductive matrix.

Materials and Methods

Anodes were prepared using nanoscopic VB₂, synthesized in-lab as previously described,[11,13] or using commercially available macroscopic VB₂ (American Elements Organo-Metallics), carbon black (TIMCAL C-NERGY SUPER C65), and KOH pellets (Alfa Aesar). PowerOne P675 batteries were used as a test bed for electrode fabrication to perform electrochemical tests. The cell fabrication is as previously delineated.[9–13] In brief, the air electrode from the PowerOne P675 battery is kept intact and reused. The Zn anode of the PowerOne P675 cells was removed by opening the existing cell, removing the anode active material, and using the separator and cathode as received for the VB₂/air battery. VB₂ electrodes were prepared first by mixing 70 wt% active material (VB₂) and 30 wt% carbon black, then measuring the appropriate amount of dry material, and lastly spreading the mixture with isopropyl alcohol and allowing the working electrode to dry. An 8 M KOH electrolyte solution was used. The density of VB₂ is 5.1 g/cm³.[12] The tap density of the nano VB₂ powders is similar to that of the macro VB₂ powder, and the powder densities vary with compression. Electrostatics can be a challenge in transferring the nano VB₂ powder, and instead it is easier to uniformly spread the powder/isopropyl mixture. There is no noticeable difference with regards to amount of battery electrolyte necessary for the nano and macro VB₂ anodes. SEM and TEM respectively of the macroscopic and nanoscopic VB₂ used in this study are shown in Fig. 1, and related XPS, impedance and XRD characterization are provided in references 10 and 12. The cell was closed with the cap in reverse so that the anodic material was in contact with the electrolyte.

Once the fabrication process had been completed, cells were discharged at constant loads as indicated in the results and discussion. The change in voltage with time during discharge was measured using NI LabVIEW 2010 and NI USB-6210 multifunction data acquisition. The electrochemical performance of the sandwich cells was investigated and reported as coulombic efficiency, defined as the measured capacity compared to the theoretical (intrinsic, 4060 mAh/g) anode discharge capacity as a percentage. The theoretical capacities were determined from the relative mass of VB₂ in the cells.
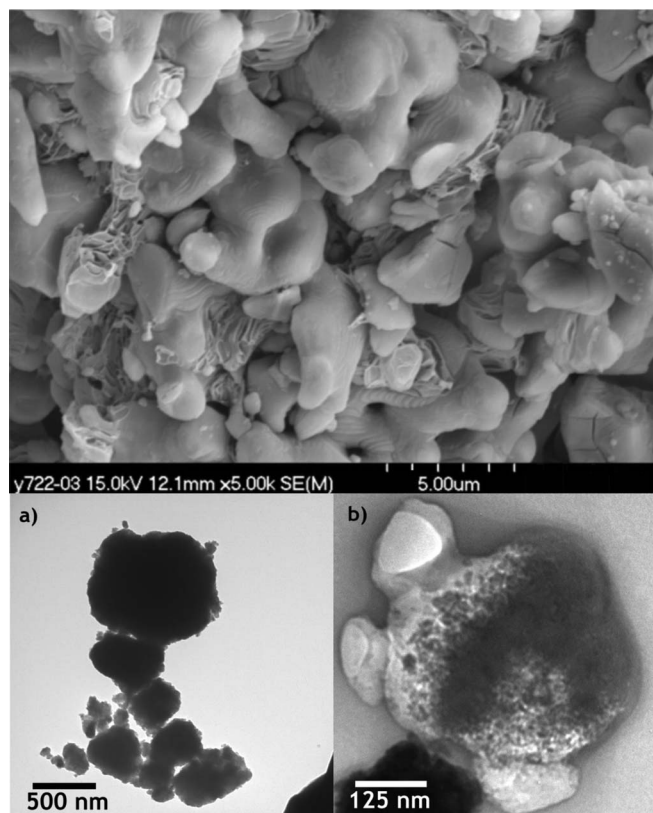
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Figure 1. SEM of macroscopic[14] VB$_2$ and TEM of nanoscopic VB$_2$.[11]

Results and Discussion

Capacity effect and nano- versus macro- material.—The effect of capacity fade with increased cell capacity is seen in Fig. 2, which compares macroscopic VB$_2$/air batteries of various capacities. Each cell is discharged over the same load (3,000 ohm), and, as in our prior studies, each anode contains a mix of VB$_2$ and 30 wt% Timcal carbon. The addition of further carbon (not shown) diminishes cell capacity and does not substantially improve the observed coulombic efficiency. It is seen that while a 2.5 mAh VB$_2$/air cell can reach high efficiencies (as measured to a discharge cutoff of 0.4 V), the 5 mAh and 10 mAh
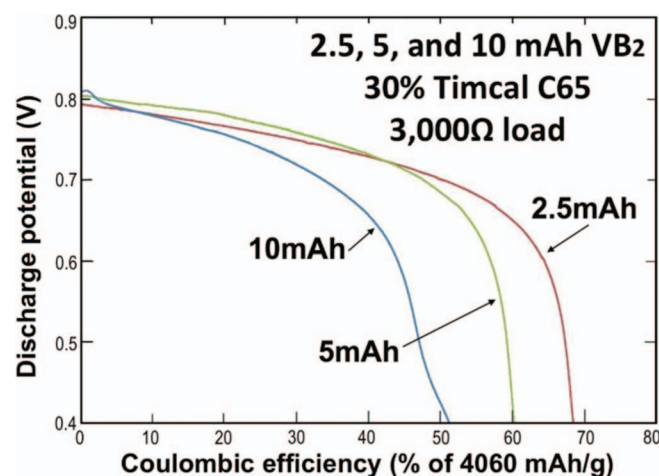

Figure 2. Discharge showing the capacity effect on 2.5, 5, and 10 mAh macroscopic-VB$_2$/air battery anodes containing 30% Timcal C65 and 70% active material. The capacity effect on the nanoscopic material is comparable to that of the macroscopic VB$_2$ material.
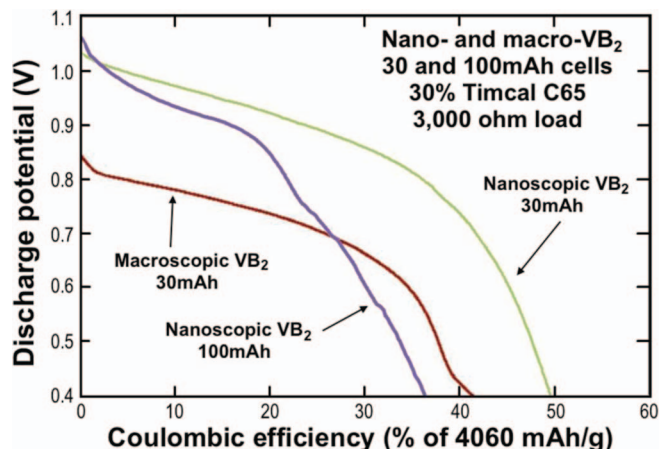

Figure 3. Characteristic discharge curves of VB$_2$/air batteries containing higher capacity anodes with either macroscopic or nanoscopic VB$_2$, mechanosynthesized from the elemental powders of vanadium and boron in a planetary ball mill.[9] Also included is the 100 mAh standard configuration cell, showing that at high capacity, the performance of the cell diminishes.

cells are limited by respectively diminishing higher capacities. This poses a significant problem as capacities reach 30 mAh and higher.

The capacity fade trend for the macro-anode VB$_2$/air continues with a larger 30 mAh anode VB$_2$/air cell, as seen as the red curve in Fig. 3. The 30 mAh cell achieves only ~40% coulombic efficiency (compared to 61% coulombic efficiency for the thinner, 5 mAh battery discharged in Fig. 2). One means to increase not only the cell voltage, but also the coulombic efficiency, shown in Fig. 3, is to replace the macroscopic VB$_2$ with in-house synthesized nanoscopic VB$_2$. Both the macro and nano-anode cells are mixed with the same (30%) carbon fraction and discharged at the same load. It is evident in the figure that the nano-cell exhibits not only higher discharge voltage (1.0 compared to 0.8 V), but also higher coulombic efficiency (49% for the nano-VB$_2$ compared to 40% for the macro VB$_2$). However, the columbic efficiency for the nano-VB$_2$, albeit higher, also experiences substantial capacity fade for higher capacity, increased thickness anodes. For example, the 5 mAh nano-VB$_2$ cell discharges to 73% coulombic efficiency (not shown), compared to 61% for the 10 mAh nano-VB2 cell.

As demonstrated in Fig. 3, the nanoscopic VB$_2$ yields higher coulombic efficiency for thicker, higher capacity VB$_2$. To date, further variations in the nano-VB$_2$ particle synthesis or variations in the carbon component of the conductive matrix of the anode have not yielded further improvements in the coulombic yield of thicker anode VB$_2$/air batteries. To approach capacities of commercial cells, we set as a minimum goal of this study 50% coulombic efficiency of a 100 mAh VB$_2$/air coin cell. However, as seen in Fig. 3, the 100 mAh nanoscopic-VB$_2$ anode/air battery provides only 36% coulombic efficiency with the optimized anode mix.

The "sandwich" configuration and its derivatives.—In addition to decreasing the VB$_2$ particle size to improve the efficacy of thicker anode discharge, we next explore alternatives to the standard planar steel anode current collector shown in Fig. 4a, which is a standard zinc air coin cell with the zinc anode replaced by VB$_2$. Instead, we utilize a high surface area porous 316 steel as a current collector; specifically, McMaster-Carr, 92315T101 Stainless Steel Perforated Sheet, hole diameter 0.006″. In this case, the VB$_2$/Timcal carbon mix is sandwiched between two disks of this porous steel sheet to improve the electrical contact between the current collector and the VB2/carbon anode mix; the "sandwich" anode configuration is shown in Fig. 4b. Constant pressure is maintained between the sandwich anode and the standard anode current collector with fine, conductive, 316 stainless steel wool, McMaster 7364T81 (not shown in the figure scheme). The 316 stainless is alloyed to be alkaline resistant, and is observed to be
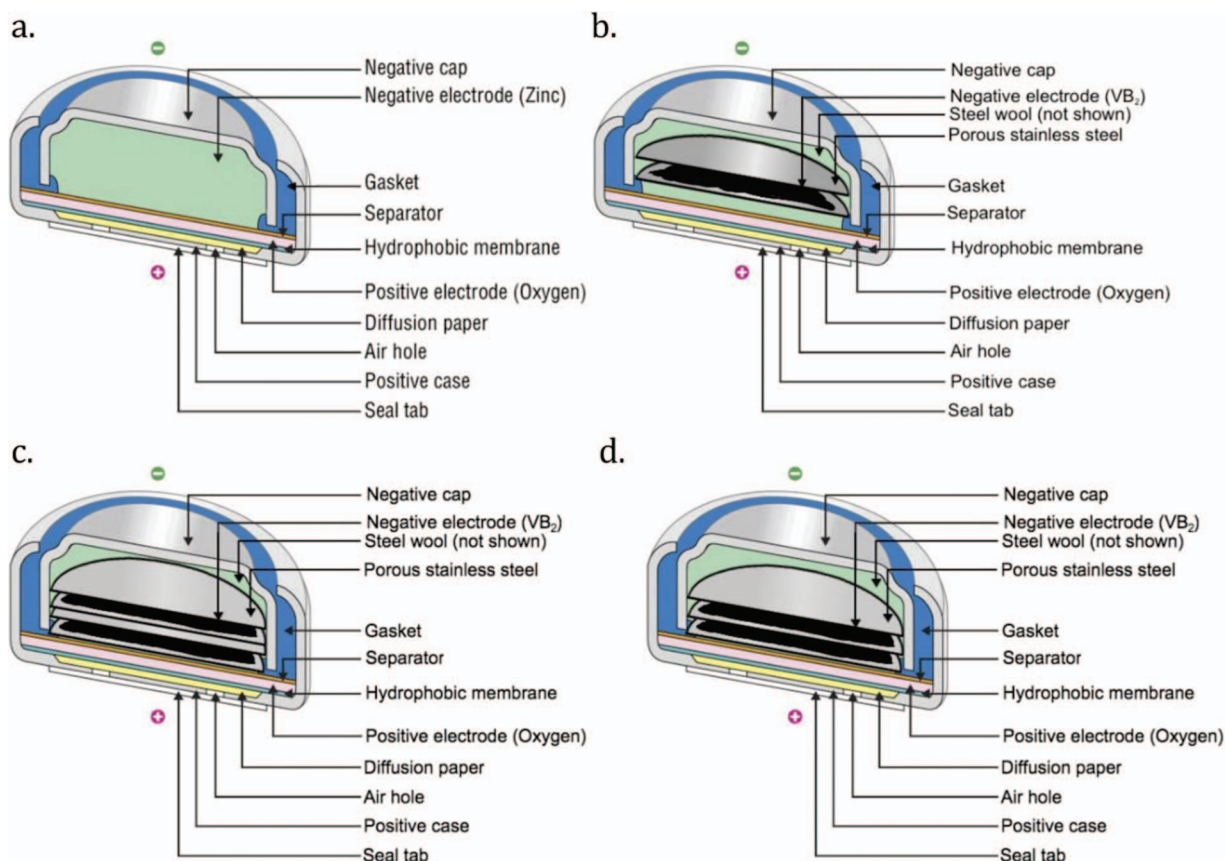
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Figure 4. a) Standard coin cell as used for zinc-air or VB$_2$-air batteries. b) The sandwich cell with only a single sandwich unit can be converted to the (c) stacked sandwich configuration by placing a second sandwich unit on top of the first. The (d) contiguous sandwich cell is made by removing one of the interfacial middle disks of porous stainless steel and simply having one disk that is in contact with the active anode material on both sides. Images are adapted from https://energyautonomoussystem.wordpress.com/2013/01/24/zinc-air-battery-the-revolution/

inert in the alkaline electrolyte environment, displaying zero capacity in control, blank experiments. That is, when the anode compartment is filled with only the 316 perforated sheet and wool (and not VB$_2$), the cell does not display any charge above the 0.4 cutoff voltage during discharge. Fig. 5 includes a comparison of the 30 mAh nano-VB$_2$/air

Figure 5. Discharge of the VB$_2$/air coin cell containing either standard, sandwich, stacked sandwich and contiguous stacked anode configurations. The 30 mAh anode is compared in the standard and sandwich configurations. Single (30 mAh), double (60 mAh) and triple (100 mAh) stacked sandwich configurations are compared, and 100 mAh triple stacked sandwich and triple contiguous sandwich anode configurations are compared.

battery discharged with the standard anode collector (49% coulombic efficiency) to that of the 30 mAh anode sandwich configuration nano-VB$_2$/air cell, and the improvement with the sandwich configuration in coulombic efficiency is substantial, to 75% coulombic efficiency.

To scale up (construct higher capacity cells), the sandwich units, which individually achieve a high efficiency, can stack on top of one another to make larger capacity cells. The 60 mAh stacked sandwich cell, seen in Fig. 4c with two 30 mAh sandwich units, did not reach the individual sandwich cell 75% efficiency, though it still discharged with a relatively high coulombic efficiency of 61% (Fig. 5). Higher capacities were explored by the addition of yet another sandwich unit (the "stacked 3 sandwich" configuration) to achieve the desired 100 mAh capacity. While these cells performed with a greater coulombic efficiency than those constructed in the standard configuration (comparison can be seen in Fig. 5), the increased capacity still resulted in a loss of efficiency to ∼50%. Although capacity fade is significantly diminished with the sandwich anode configuration and the goal of 50% coulombic efficiency for discharge of the 100 mAh cell is attained, it is evident that electronic communication between individual stacks needs to be further improved to mitigate the efficiency decrease observed with multiple unit anode stacks.

The improvements achieved by the sandwich unit configuration spawned variations of the sandwich configuration, namely the "double contiguous" sandwich configuration (Fig. 4d) and the "triple contiguous" sandwich configuration (not shown). The advantage of these configurations is not seen in their efficiencies, which are observed to be on par with that of the stacked sandwich configurations (the triple contiguous sandwich and stacked 3 sandwich are comparable in terms of efficiency, ∼50%, seen in Fig. 5), but in the fact that the amount of porous stainless steel required for the cell is diminished. This reduces
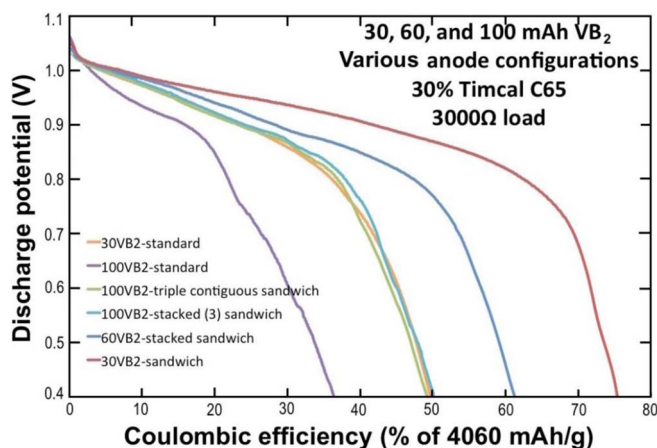
the overall weight and cost of materials of the cell. The higher anodic capacity of VB_2 compared to Zn (4,060 compared to 820 mA/g) is a distinct advantage. The coulombic efficiency of the 100 mAh hour VB_2 at 50% with the improved conductive matrix is the highest to date, yet clearly there is room for additional improvement. Commercial Zn air coin cell battery discharge variation with load is not widely available. In one case a 100 mAh Zn air cell is rated to deliver 91 mA hour at a 3,000 Ω load,[15] and in another case a 675 mAh cell is rated to deliver 518, 584, or 593 mAh respectively at 51, 150 or 620 Ω load.[16]

Conclusions

Stacked anode configurations improve upon the coulombic efficiencies of higher capacity VB_2/air cells. Vanadium diboride is intrinsically more energy dense than zinc (4060 mAh/g vs. 820 mAh/g, respectively), and its implementation in primary batteries has been impeded by its low coulombic efficiencies at high capacities. With the described porous stacked anode configurations providing a larger surface area for the current collector, the effects of the passivating layer (caused by the resistive oxide discharge products forming at the surface of the current collector) have been mitigated, allowing fabrication and verification of 100 mAh VB_2/air cells. While the enhanced performance is offset by the increase in the weight of materials needed for the cell, further optimization of the "stacked sandwich" anode configuration and its derivatives may provide a path to the replacement of zinc in commercial primary batteries by the more energy dense VB_2.

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