



High Energy Capacity TiB₂/VB₂ Composite Metal Boride Air Battery

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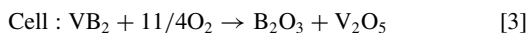
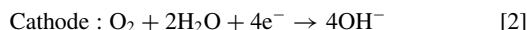
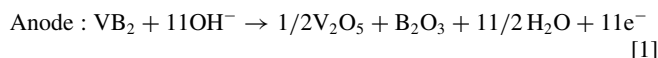
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Transition metal borides, such as VB₂ and TiB₂, are studied as battery anode materials both individually and as a composite anode for an air cathode battery. The combination of VB₂ and TiB₂ is shown to enhance anodic battery performance. In alkaline media, VB₂ and TiB₂ anodically discharge to yield respectively 11 and 6 electrons per molecule with VB₂ intrinsic gravimetric charge capacity of 4,060 mAh/g and 2,314 mAh/g for TiB₂, 3 to 5 fold higher than a conventional zinc anode. With an air cathode using external O₂, these boride/air batteries discharge at ~1 V, and exhibit unusually high, primary battery energy capacities. We show that the coulombic efficiency attained by the TiB₂ anode in boride/air batteries is not a strong function of the anode capacity per unit area (cm²) of anode, while the efficiency of the VB₂ anode decreases with increasing anode capacity. The discharge of VB₂ shows a unique singular voltage plateau, indicating that the 11 electrons discharge at a similar potential. Two voltage plateaus are observed during the TiB₂ discharge indicating the possibility of a two-step anodic oxidation. The combination of VB₂ and TiB₂ exhibits evidence of a synergistic increase of the capacity and discharge voltage of boride/air batteries.

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The development of improved energy density battery systems is driven by emerging technological demands of longer operational time and lighter weight for medical, military and consumer electronic devices. A principal focus of battery research in the past decade has been the advancement of the energy capacity of rechargeable Li-ion batteries, which have a capacity of 100 to 200 Wh/kg. Despite this, the capacity of rechargeable batteries remains approximately 5-fold lower than that of primary batteries. The highest commercial primary battery energy capacity is exhibited by zinc/air batteries.¹ Replacement of the air battery's zinc electrode by a higher capacity anode material has the potential to further increase the energy capacity. New materials, such as metal borides, have been studied due to their demonstrated high capacities as anodes for primary alkaline batteries. Of the large number of borides that have been investigated as anodes in alkaline media, TiB₂ and VB₂ exhibit the highest stability and demonstrated anodic capacity.²⁻⁹ Although Zn, TiB₂, and VB₂ have similar formula weights (65.39, 69.49, 72.56 g/mol), the Zn oxidative discharge releases only two electrons, whereas TiB₂ and VB₂ are observed to discharge up to 6 and 11 electrons, respectively. While the conventional Zn anode has an intrinsic capacity of 820 mAh/g (2*FW/Faraday*mAh), TiB₂ and VB₂ have respective intrinsic capacities of 2,314 and 4,060 mAh/g. Coupled with an air cathode, vanadium diboride has been reported to have among the highest energy density of any primary battery (5,300 kWh/kg).⁹ The 11 electron discharge reaction of the VB₂/air battery is given by the following half cell and full cell reactions:⁹



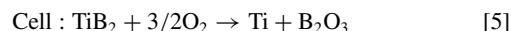
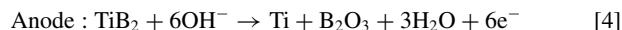
It is interesting to note that VB₂ discharges each of its 11 electrons at a singular discharge voltage plateau.⁹

Self-discharge is also of paramount important for the practical operation of a battery, and similar to Zn anodes, the VB₂ anode can react with the electrolyte under open circuit potential. In Zn/air batteries, the self-discharge loss was until recently mitigated by the addition of several percent mercuric oxide. More recently, the mercury additives have been replaced with compounds such as polyacrylic acid

(i.e. Carbolpol), and other Zn/air self-discharge mitigation strategies include alloying, coating with Al₂O₃ and various organic corrosion inhibitors.¹⁰ Our prior efforts to stabilize VB₂ have involved using a zirconia overlayer to prevent corrosion of the boride surface while also allowing charge transfer during the anodic discharge process. Using this approach for macroscopic VB₂, we have been able to largely mitigate the VB₂ self-discharge through using a zirconia overlayer.^{3,9} Stored at 45 °C for one week, an uncoated VB₂ alkaline anode loses 10% of its original charge capacity, however with a 1% ZrO₂ coating the anode retains 100% of that capacity.⁹

Preparation of nanoscopic VB₂ has been investigated,¹¹⁻¹⁶ and the straightforward synthesis of anodically active nanoscopic VB₂ from elemental vanadium and boron in a planetary ball mill using a mechanochemical process has been reported.¹³⁻¹⁶ The voltage and rate advantages of nanoscopic compared to macroscopic VB₂ anodes in VB₂/air batteries has been characterized, providing 10 to 20% higher voltage as well as higher coulombic efficiency under low and moderate discharge loads.¹⁵

While there have been few prior characterizations of the anodic properties of TiB₂, the high conductivity of the material makes it a strong candidate for a potential anodic active material.² The 6 electron discharge reaction of the TiB₂/air battery is in accord with following half cell anodic (eq. 4) and full cell reactions (eq. 5), with the half cell cathodic reaction of eq. 2:



Room temperature measurements of the resistivity of TiB₂ 9–28 μΩ cm have been reported to be lower than the 16–38 μΩ cm range reported for VB₂.¹⁷ In comparison to vanadium diboride, TiB₂ has a lower theoretic capacity of 2,314 mAh/g, nonetheless this capacity is three fold greater than the commercially established alkaline zinc anode. In addition to examining TiB₂ or VB₂ anodes individually, composites of TiB₂ and VB₂ were examined to determine if the combination of these materials would provide improved electrochemical properties.

Experimental

Anodes were prepared using commercially available TiB₂ (Alfa Aesar, 325 mesh powder), macroscopic VB₂ (American Elements Organo-Metallics), and carbon black (TIMCAL C-ENERGY SUPER C65). Nanoscopic VB₂ was synthesized via ball milling using

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vanadium powder (Alfa Aesar) and boron powder (Alfa Aesar) as previously reported detailed.¹⁴ In a controlled argon atmosphere glove box system (Vacuum Atmospheres, Nexus-II), vanadium and boron powders were measured and transferred into a tungsten carbide milling chamber along with ten tungsten carbide balls, ten millimeters in diameter. The milling vessel was sealed, removed from the glove box, and placed into a Retsch PM 100 planetary ball mill, which was set to 600 rpm and allowed to run for four hours. After the vanadium diboride cooled to room temperature, the material was then collected in the glove box into a round bottom flask, and the mass was measured.

Panasonic PR675H batteries were used as a test bed for electrode fabrication to perform electrochemical tests as previously reported.¹⁵ In brief, the Panasonic cell was opened (the anode cap was removed from the cathode bottom), and the Zn anode material was cleaned out of both parts. We have recently detailed cell fabrication of composite anodes of Zn and VB_2 which demonstrate that zinc has been removed from the commercial (Panasonic PR675H) Zn/air battery shells.¹⁵ The Zn/ VB_2 composite clearly demonstrates two distinguishable plateaus at the normal Zn discharge voltage of 1.4 V and the lower VB_2 discharge voltage. Therefore based on the lack of a Zn plateau, we conclude that that all Zn has been effectively removed from the anode compartment.

TiB_2 and VB_2 electrodes were prepared first by mixing 70 wt% active material (TiB_2 , VB_2 , or a composite as described in the text) and 30 wt% carbon black, then measuring the appropriate amount of dry material onto the top of the anode cap, and lastly spreading the mixture with isopropyl alcohol and allowing the working electrode to dry under ambient conditions. An 8 M KOH (Alfa Aesar) electrolyte solution was used. The cell was then closed with the cap in reverse so that the anodic material was in contact with the electrolyte, and glued shut with a fast-drying epoxy. Once the fabrication process was completed, cells were placed on a holder and 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 individual VB_2 or TiB_2 anodes, as well as the composite anode, was investigated and reported as specific capacity (mAh/g) and coulombic efficiency, the percentage of the measured capacity was compared to the theoretical (intrinsic) anode discharge capacity of the TiB_2 or VB_2 or composite mixture anodes. The theoretical capacities for the composites were determined from the theoretical capacities from each individual component and the relative mass.

Scanning electron microscopy is conducted with a PHENOM Pro-X SEM.

Results and Discussion

TiB_2 /air battery discharge.— The incorporation of an appropriate conducting material into the electrode matrix is needed to provide continuous electron-conducting pathways to the active boride material. We had previously found that Timcal C65 carbon black powder provides an effective conductive matrix for the VB_2 anode.^{15,16} Discharges of the TiB_2 /air cell were studied to determine a preferred Timcal C65 composition for the anode mix by studying the discharge of cells with various weight ratios of TiB_2 compared to the Timcal carbon additive. Figure 1 compares four sets of 10 mAh cells containing various amounts of carbon black to determine which composition would be used for further testing. The TiB_2 /air battery discharges at an initial plateau at ~ 1 V followed by a minor shorter duration secondary plateau at ~ 0.85 V for anodes with capacities ranging from 2.5–10 mAh. The extent of this smaller, secondary, lower voltage plateau varies from 0 to 30% of the observed total discharge. The presence of two distinct voltage plateaus suggests that the discharge of TiB_2 may occur in stages, and the discharge voltage is related to a different local chemical potential for the reaction over these voltage ranges. Changes in the conductivity of the material during discharge may also contribute to the presence of two voltage plateaus. While the emphasis of this effort was on the effect of combining TiB_2 and VB_2 , the

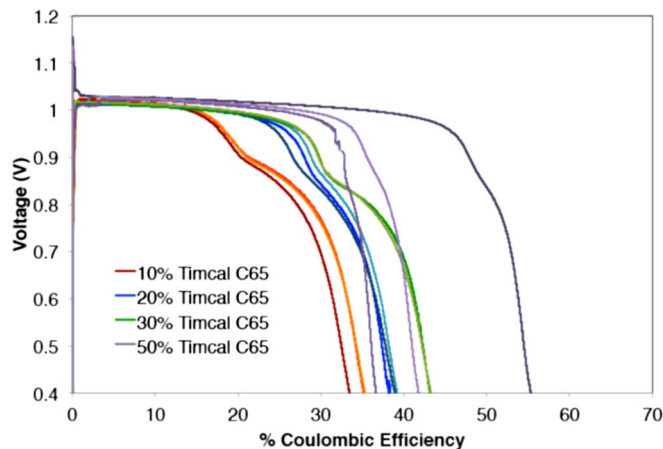


Figure 1. The effect of various carbon ratios (the weight percent of Timcal C65) in the TiB_2 anode mix on the discharge efficiency of the TiB_2 /air cell; 10 mAh capacity TiB_2 cells, 3000 Ω load.

further investigation of the discharge process of TiB_2 is needed. Our recent study of the discharge mechanism of VB_2 determined specific discharge products and provided an updated reaction for the anodic discharge process.¹⁸

From the data in Figure 1, it is evident in the figure that the specific capacity of the TiB_2 /air cell improves with increasing carbon content in the anode mix. Using the 30 wt% carbon mixture, a coulombic efficiency (experimental specific capacity/theoretical specific capacity) of $\sim 40\%$ was obtained. However, the highest examined anode composition of 50 wt% TiB_2 and Timcal was not used in subsequent measurements due to (i) the large variation observed between multiple samples of the same composition as observed from the data in Figure 1, and (ii) the large fraction of anodically inactive (carbon) material in the anode mix, which diminishes the total capacity, despite the higher coulombic efficiency. The anode composition of 70 wt% TiB_2 with 30 wt% carbon black was selected for further analysis of this anode candidate due to the relatively high observed reproducibility and specific capacity, as well as to maintain the same percentage of carbon black also used in our prior measurements with the analogous VB_2 anode.^{8,14,18}

The effect of the capacity of the anode (either 2.5, 5, or 10 mAh) on the specific capacity (mAh/g) and coulombic efficiency of the active TiB_2 anode material was determined by measuring the discharge of the TiB_2 /air battery with 70% TiB_2 and 30% Timcal C65 as presented in Figure 2 and Table I. As observed from the data in Figure 2 (bottom), the observed specific capacities of the TiB_2 /air battery are largely unrelated to the cell capacity. This is particularly important since higher capacity anodes are needed for practical commercial cells.

In comparison, for macroscopic VB_2 anodes as the cell capacity increases, the specific capacity and percent coulombic efficiency rapidly diminishes. For example, discharged under the same 3,000 Ω load, a 2.5 mAh VB_2 anode air cells discharges to over 80% coulombic efficiency, while 5, 10 or 30 mAh VB_2 anode cells discharge to only $\sim 60\%$, 50% or 40% coulombic efficiency respectively.^{16,18} In contrast to VB_2 , the experimental capacity of TiB_2 anodes is maintained at higher material loadings which is significant since obtaining thicker electrodes that maintain high coulombic efficiencies is needed for developing practical cells.

The performance of the TiB_2 anode was also evaluated at various rates using constant resistive loads ranging from 1,000 to 10,000 ohms in order to evaluate the anode performance under various discharge rates. Typically, as seen in Figure 3, there is an onset time to full discharge voltage that increases at higher initial discharge currents (at smaller resistive discharge loads). This onset time diminishes (not shown) when the cell sits for a day or more prior to discharge, allowing the electrolyte to more fully permeate throughout the cell. The results of these tests, shown in Figure 3, exhibit a substantial decrease in

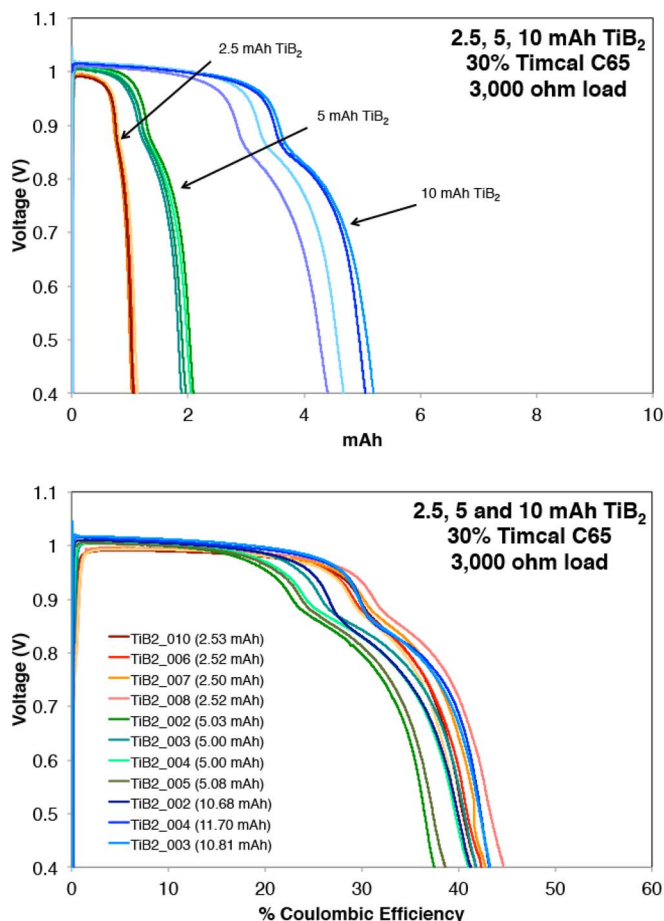


Figure 2. Top: Discharge capacity of 2.5, 5, and 10 mAh TiB_2 /air battery anodes containing 30% Timcal C65 and 70% active material. Bottom: Specific capacity of TiB_2 anodes with different cell capacities.

the specific capacity and voltage as the discharge rate increases, in a manner previously reported for the VB_2 anode.¹⁵

Composite TiB_2 - VB_2 /air discharge.— We investigated composite TiB_2 and VB_2 anodes to determine if the combination of these materials would result in a synergistic effect to improve (i) the coulombic efficiency of higher capacity (thicker) VB_2 -containing anodes, (ii) the TiB_2 coulombic efficiency, and (iii) the VB_2 discharge voltage. Figure 4 presents a scanning electron microscopy (SEM) image of the

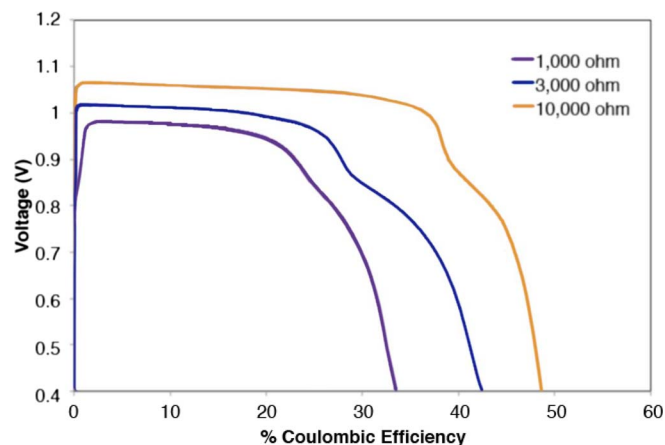


Figure 3. Discharge curves of 10 mAh TiB_2 cells over constant resistive loads ranging from 1,000 ohm to 10,000 ohm; 10 mAh TiB_2 anodes prepared with 30 wt% carbon.

composite anode (30 wt% VB_2 ; 70 wt% TiB_2) without the presence of Timcal C65. In the SEM the macroscopic VB_2 consists of the 1–5 μm particles, and the TiB_2 consists of particles primarily in the μm 5–25 range. As seen in the SEM the VB_2 is well dispersed and generally in contact with some TiB_2 .

In order to observe the discharge effects of the composite TiB_2 and VB_2 anode in the boride/air battery, a 10 mAh capacity anode was prepared that was comprised of 5 mAh of VB_2 (30 wt% VB_2 ; intrinsic capacity 4,060 mAh g^{-1}) and 5 mAh of TiB_2 (70 wt% TiB_2 ; intrinsic capacity 2,314 mAh g^{-1}). The resultant composite anode boride/air discharge curves and the comparison to pure VB_2 or TiB_2 anode air batteries is shown in Figure 5. In the batteries containing a composite anode, the voltage is substantially higher for the initial plateau region when compared to the VB_2 discharge curve, and is characteristic of the TiB_2 (alone) discharge effects.

Table I compares the experimental and theoretical capacities of the individual and composite electrodes. For the 10 mAh cells: the macroscopic VB_2 : TiB_2 (50:50) had a higher experimental specific capacity relative to the theoretical specific capacity (55% of theoretical) compared to the individual 10 mAh VB_2 (50% of theoretical) or TiB_2 electrodes (40% of theoretical). The effective higher specific capacity also results in a higher capacity for the composite, as shown in Figure 5. The higher ratio of the specific capacity to theoretical capacity for the VB_2 : TiB_2 composite compared to individual VB_2 and TiB_2 electrodes supports that there is a synergistic effect occurring between the materials which contributes to increasing the capacity. It is possible that one of the products of TiB_2 discharge may contribute to increased electrical connectivity to the VB_2 particles.

Table I. Comparison of theoretical and experimental capacities and specific capacities of VB_2 , TiB_2 , and composite VB_2 - TiB_2 /air cells.

Category	Sample ID	Wt% VB_2	Wt% TiB_2	Wt% Carbon	Ratio of VB_2 : TiB_2 (mAh:mAh)	Theoretical capacity (mAh)	Experimental capacity (mAh)	Theoretical specific capacity (mAh/g)	Experimental specific capacity (mAh/g)	Percentage of experimental/theoretical specific capacity (%)
TiB_2	T100-2.5 mAh	0	70	30	—	2.5	1.0	2,314	967	42
	T100-5 mAh	0	70	30	—	5	2.0	2,314	914	40
	T100-10 mAh	0	70	30	—	10	4.0	2,314	965	42
	T100-30 mAh	0	70	30	—	30	12	2,314	926	40
VB_2	VM100-10 mAh	70	0	30	—	10	5.0	4,060	2030	50
	VN100-15 mAh	70	0	30	—	15	7.2	4,060	2071	51
	VM100-30 mAh	70	0	30	—	30	12	4,060	1624	40
	VN100-30 mAh	70	0	30	—	30	15	4,060	1949	48
VB_2 : TiB_2 composites	VM50-T50-10 mAh	26	46	28	50–50	10	5.9	3,187	1753	55
	VM90-T10-30 mAh	63	7	30	90–10	30	14.8	3,885	1826	47
	VN50-T50-30 mAh	25	45	30	50–50	30	15.1	3,187	1657	52

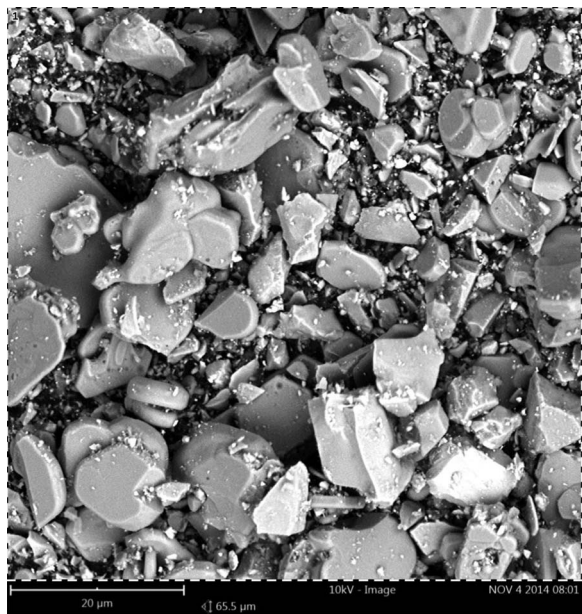


Figure 4. SEM image of macroscopic TiB_2 and VB_2 anodic composite without the presence of Timcal C65.

Further work is needed to determine the specific structural and electrochemical changes occurring during the discharge of the composite electrode.

Higher capacity boride/air battery discharge.— The synergistic effect, in which the composite TiB_2/VB_2 anode of the boride/air battery discharges to a higher energy than either of the TiB_2 or VB_2 cells alone, was additionally probed for larger capacity batteries. This is of particular importance due to the fact that the VB_2 anode exhibits a significant loss of coulombic efficiency with increasing capacity and anode thickness.¹⁶ Figure 6 presents characteristics of ~ 30 mAh intrinsic capacity cells, in which the discharge exhibits an average coulombic efficiency of $\sim 40\%$.

To further investigate the benefits of the composite cell, a small amount of the TiB_2 anode, approximately 4% of the total capacity (1:9 TiB_2 to VB_2 by weight), was added to the larger capacity macroscopic VB_2 anode. As presented in Figure 6, this relatively small addition of TiB_2 resulted in significant increase in the coulombic efficiency (to $\sim 50\%$), as well as a 0.2 V increase to the initial voltage of 0.8 V

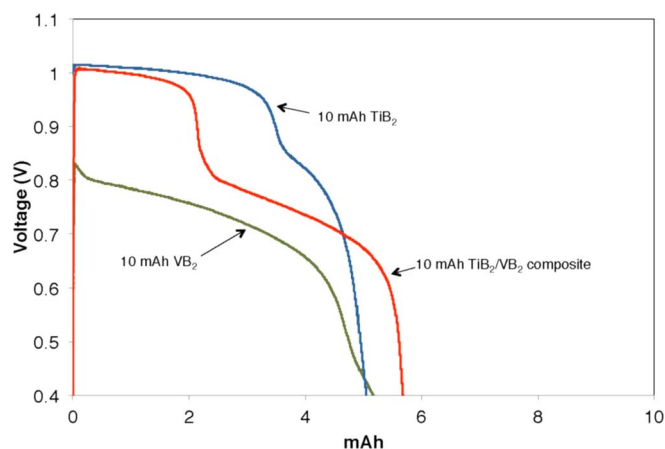


Figure 5. Discharge curves of 10 mAh TiB_2 (without VB_2) or VB_2 (without TiB_2) cells compared to that of the same 10 mAh composite (with TiB_2 and VB_2).

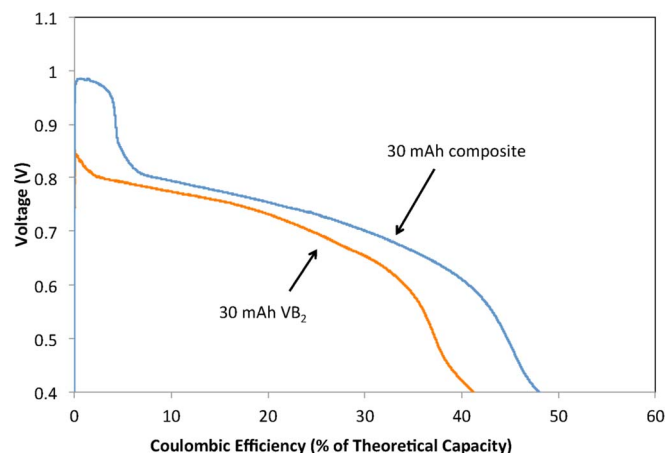


Figure 6. 30 mAh VB_2 /air discharge compared to a 30 mAh composite anode of 90% VB_2 and 10% TiB_2 by weight.

due to the first plateau of TiB_2 . The increase in the net capacity is further supported by analysis of the experimental and theoretical specific capacities for the composite and the individual electrode materials. As presented in Table I for the high capacity 30 mAh cells, the composite of macroscopic $\text{VB}_2:\text{TiB}_2$ (90:10) had a higher experimental specific capacity (1826 mAh/g, 47% of theoretical) compared with the individual 30 mAh VB_2 (1624 mAh/g, 40% of theoretical) or TiB_2 electrodes (926 mAh/g, 40% of theoretical).

In addition to using macroscopic VB_2 , we also investigated the effect of composites prepared using nanoscopic VB_2 based on our previous work that demonstrated that nanoscopic VB_2 resulted in higher voltages and specific capacities.^{13,16} Our recent work supports that the higher specific capacity and voltage of nanoscopic VB_2 compared to macroscopic VB_2 is related to the higher degree of vanadium and boron at the surface region for nanoscopic VB_2 compared to predominately oxide species at the surface region of macroscopic VB_2 based on X-ray photoelectron spectroscopic analysis.¹⁸ Shown in Figure 7 are high capacity (30 mAh) VB_2 anodes prepared with either nanoscopic or macroscopic vanadium diboride, which were used as a baseline for comparison with the composites. It is evident from the data in the figure that for the 30 mAh cells, the nanoscopic VB_2 discharges at a higher voltage and to a higher discharge capacity than the comparable cell prepared with the macroscopic VB_2 . The nanoscopic

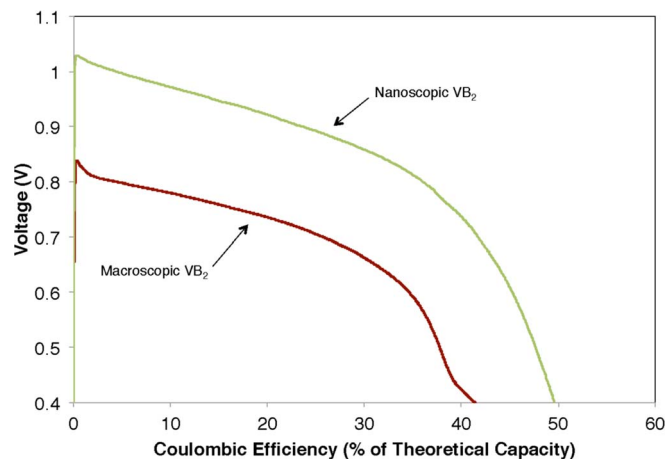


Figure 7. Characteristic discharge curves of higher capacity anodes containing either macroscopic VB_2 or mechanochemical synthesized VB_2 (from elemental vanadium and boron in a planetary ball mill). An increased VB_2 air battery capacity to ~ 30 mAh is presented.

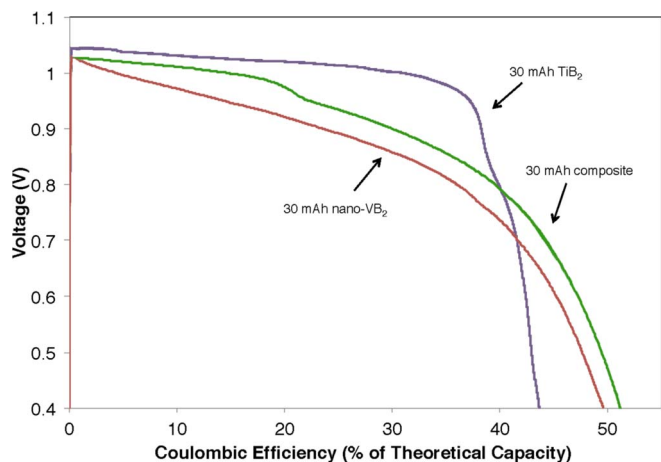


Figure 8. Comparison of the 30 mAh (15 mAh nanoscopic VB_2 and 15 mAh TiB_2) composite discharge to 30 mAh nanoscopic VB_2 and TiB_2 air battery discharges.

VB_2 anodic discharge voltage is not only high, but is also comparable to the discharge voltage of the TiB_2 cells in Figures 1 and 2.

Unlike the VB_2 analogy, attempts at synthesizing a nano- TiB_2 from the titanium and boride elements have been unsuccessful to date. However, an interesting composite anode has been formulated from a mix of the nano- VB_2 and commercial (macroscopic) TiB_2 . Figure 8 presents the discharge of a composite cell prepared with this TiB_2 and the nanoscopic, rather than macroscopic VB_2 . This alternative composite anode cell exhibits an advantageous, higher voltage that is higher than that observed for the pure nanoscopic VB_2 anode. The composite anode discharge occurs at predominately smooth discharge voltage plateau, although a minor discharge voltage slope is evident at ~ 1 V, and the 2nd discharge plateau evident at ~ 0.8 V for pure TiB_2 is not evident.

Similar to the 10 mAh and 30 mAh composites with macroscopic VB_2 , as presented in Table I the 30 mAh composite of nanoscopic VB_2 : TiB_2 (50:50) had a higher experimental specific capacity relative to the theoretical specific capacity (52% of theoretical) compared with the individual 30 mAh nanoscopic VB_2 (48% of theoretical) or TiB_2 electrodes (40% of theoretical).

Conclusions

This study establishes that the addition of TiB_2 to the anode of VB_2 /air batteries improves performance by increasing the battery discharge voltage as well as the coulombic efficiency of the cell. We have found that TiB_2 anodes comprised of various capacities (2.5, 5, and 10 mAh TiB_2) attained similar coulombic efficiencies. The titanium diboride anode discharges exhibit an initial plateau at ~ 1 V followed by a minor, secondary plateau at ~ 0.85 V, achieving an average discharge efficiency of 40–50%. From the comparisons of a composite cell containing 50% VB_2 /50% TiB_2 to both 5 and 10 mAh TiB_2 capacity anodes and to 5 and 10 mAh VB_2 capacity anodes, a synergistic effect of the composite $\text{VB}_2 + \text{TiB}_2$ anode cell is evident in enhanced

coulombic efficiency compared to either pure (VB_2 or TiB_2 anode) cell alone.

The VB_2 : TiB_2 composite anode exhibits improvement in both smaller (10 mAh) and larger (30 mAh) cells, as well as for composites containing either large or small (70 or 10) wt% of TiB_2 relative to VB_2 . There is an observed coulombic increase of the characteristic first (higher voltage) plateau of TiB_2 . Furthermore, there is an increase in the overall efficiency of the cell. Additionally, we report a substantial increase in the initial plateau region for the composite cell when compared to the macroscopic VB_2 discharge curve, characteristic of the TiB_2 discharge effects. The higher voltage may be attributed to the higher conductivity of the titanium based anodic material. This observed trend continues into the larger capacity cells where a typically ~ 30 mAh VB_2 cell discharges to an average percent coulombic efficiency of $\sim 40\%$. With the addition of only 10% TiB_2 by weight to the VB_2 anode composition, an increase in coulombic efficiency from 40 to 50% was observed, as well as a 0.2 V increase to the initial voltage of 0.8 V. These results provide evidence for an improved VB_2 anode by the addition of TiB_2 . Further work is needed to understand the specific changes that occur during discharge of the composite that result in increased capacities. We are also currently investigating (i) solution phase additives, and (ii) an enhanced current collector conductive matrix to further advance the coulombic efficiency and maintain high stability for the boride/air battery. We are also exploring molten electrolytes to transition boride/air from a primary to a rechargeable battery.^{19,20}

Acknowledgments

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