Renewable highest capacity VB_2/air energy storage†

Stuart Licht,*[ab] Huiming Wu,[b] Xingwen Yu[b] and Yufei Wang[b]

Received (in Cambridge, UK) 9th May 2008, Accepted 2nd June 2008
First published as an Advance Article on the web 17th June 2008
DOI: 10.1039/b807929c

The first renewable electrochemical energy system which stores more energy than gasoline is presented, and with an order of magnitude higher capacity than lithium-ion batteries, VB_2 opens a pathway towards electric vehicles with a viable driving range.

A fundamental impediment to electric, *versus* gasoline, vehicles has been the lower volumetric capacity of electrochemical energy, which had limited the vehicle driving range, and which is directly related to the practical capacity of gasoline (2.7 kWh L^{-1}) compared to state of the art Li-ion (0.5 kWh L^{-1}). The volumetric energies are compared in Fig. 1, and include Zn/air cells which exhibit among the highest volumetric energy of commercialized electrochemical systems. Zn/air was demonstrated with an alkaline carbon air(O_2) anode in 1932.[1] Zinc, FW (Formula Weight) = 0.0654 kg mol^{-1}, d (density) = 7.1 kg L^{-1}, releases 2 F (Faraday) mol^{-1} stored charged, for a capacity Q(zinc) = 5.82 kAh L^{-1}. With a thermodynamic 1.6 V potential, the intrinsic capacity of the cell is 9.4 kWh L^{-1}. Commercial zinc air cells using external air and internal zinc have been referred to as both battery and fuel cell, and with a practical cell voltage of 1.3 V, currently have a practical 1.75 kWh L^{-1} cell capacity, inclusive of the carbon anode and all other cell components.[2]

Borides can exhibit even higher charge and energy capacities than zinc. VB_2 undergoes an oxidation of both the tetravalent transition metal ion, V (+4 → +5), and each of the two boron's 2 × B (−2 → +3), for an exceptional $11e^-$ per molecule oxidation. Hence, VB_2 has an intrinsic gravimetric capacity of 4060 Ah kg^{-1}, five-fold higher than that of the Zn anode electrode, and with d = 5.10 kg L^{-1}, has a volumetric capacity of $Q(VB_2)$ = 20.7 kAh L^{-1}.

In this study, we have considered a variety of borides including TaB, TaB_2, MgB_2, CrB_2, CoB_2, Ni_2B and LaB_6 as alternative active anode materials for alkaline electrochemical storage cells. The two tantalum boride salts exhibit alkaline anodic charge storage capacity, although less than that of the zinc anode. The other borides did not exhibit significant primary discharge behavior due to their high solubility in alkaline solution or their excessive reactivity with an alkaline electrolyte. In 2004, Yang and co-workers reported the discharge of VB_2, but also documented the extended domain in which VB_2 is susceptible to corrosion in alkali media.[3] In 2007, we reported that a zirconia overlayer on VB_2 prevents this corrosion[4] and provides an effective alkaline anode counterpart to a super-iron cathode.[5–7]

Stabilization studies of the boride anode, as used in the super-iron boride battery,[4] can be advanced towards a boride air fuel cell. In this study we present a renewable boride air fuel cell, which utilizes a conventional air cathode and a zirconia stabilized vanadium boride anode. The standard redox potential we observe for the $11e^-$ VB_2 alkaline anodic redox reaction is:

$$VB_2 + 11OH^- \rightarrow \tfrac{1}{2}V_2O_5 + B_2O_3 + \tfrac{11}{2}H_2O + 11e^- \qquad (1)$$
$$E = 0.9\ \text{V}\ vs.\ \text{SHE}$$

The eqn (1) oxidation products are generalized as B_2O_3 and V_2O_5, which are the respective anhydride salts of boric acid (H_3BO_3 with $pK_{1,2,3}$ = 9.1, 12.7 and 13.8) and vanadaic acid (H_3VO_4 with $pK_{1,2,3}$ = 3.8, 7.8 and 13.0). In solution, the products will vary with hydroxide concentration and depth of discharge, including hydrogen and metal cation containing species, such as in either a KOH or NaOH electrolyte: $K_xH_zBO_3^{3-x-z}$ or $Na_xH_zBO_3^{3-x-z}$ (where x ranges from 0 to 3, and z from 0 to 3 − x), as well as polymeric species, such as related to the boric condensation reaction forming borax species: $Na_yB_4O_7^{2-y}$, $K_yB_4O_7^{2-y}$, and analogous vanadium species, *etc.*

The VB_2 cell reaction for an $11e^-$ boride air fuel cell couples eqn (1) with reduction at an oxygen/air cathode, eqn (2), to yield

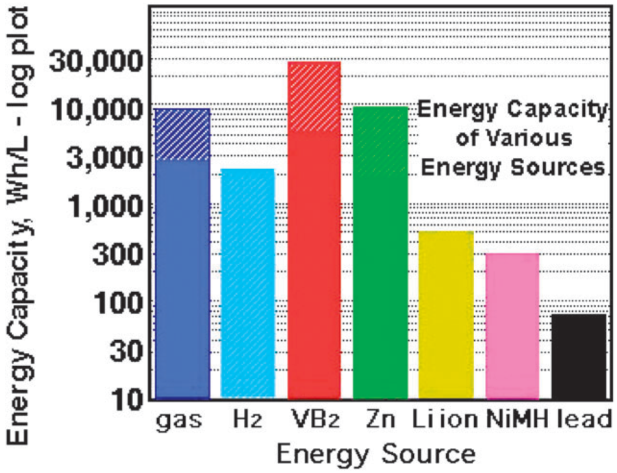


Fig. 1 Energy capacity comparison of gasoline (petrol), hydrogen and electrochemical energy sources. The intrinsic energy of gasoline yields a maximum practical efficiency of 30% due to Carnot and friction losses. Air fuel cells do not have this Carnot inefficiency, and have practical capacities instead constrained by overpotential losses, and the requisite volume of the air anode and all other cell components. Volumetric capacity of liquid H_2 is constrained by its density of 0.0708 kg L^{-1}. Shaded superimposed on solid, colors, compare intrinsic and practical capacities.

---

[a] *Division of Chemistry, National Science Foundation, 4201 Wilson Blvd, Arlington, VA 22230, USA. E-mail: slicht@NSF.gov; Fax: +1 703 292 9037; Tel: +1 703 292 9037*
[b] *Department of Chemistry, University of Massachusetts, 100 Morrissey Blvd, Boston, MA 02125, USA. Fax: +1 617 287 6030; Tel: +1 617 287 6130*

† Electronic supplementary information (ESI) available: Optimization studies. See DOI: 10.1039/b807929c

the vanadium boride air cell discharge:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \; E = +0.4 \text{ V } vs. \text{ SHE} \quad (2)$$

$$VB_2 + \tfrac{11}{4}O_2 \rightarrow B_2O_3 + \tfrac{1}{2}V_2O_5 \; E_{\text{cell}} = 1.3 \text{ V} \quad (3)$$

Consistent with eqn (3), the VB_2/air cell has an intrinsic volumetric energy capacity of (1.3 V) × (20.7 kAh L^{-1}) = 27 kWh L^{-1} (= 97 MJ L^{-1} = 5.3 kWh kg^{-1}). As shown in Fig. 1, the vanadium boride air cell intrinsic volumetric energy capacity is substantially greater than that of gasoline, hydrogen, or a zinc air fuel cell, and is an order of magnitude greater than that of all rechargeable batteries, including Li ion, metal hydride or lead acid. Practical, compared to intrinsic, energy electrochemical capacity is limited by the delivered energy and system mass, incorporates all voltage losses, air cathode size, and all other cell components. For example, the practical energy of a small, portable commercial zinc air cell exceeds 18% of the intrinsic energy capacity,[2] and can be higher in an optimized, large fuel cell configuration. The relative practical capacity of the VB_2/air cell can be estimated as similar to that of the well studied Zn/air system (electrolytes and cathodes are similar). Based on this analog, the practical vanadium boride fuel has a lower limit of 18% of its intrinsic 27 kWh L^{-1}, for an estimated vanadium boride air practical storage capacity of 5 kWh L^{-1}.

As recently as 1997 it was noted that basic physical chemical properties of VB_2 are scarce.[8] Boride corrosion is not only a chemical loss of the electrochemical capacity, but evolved hydrogen is flammable, and the evolved gas can swell or even crack a cell. Zirconia is highly stable in aqueous alkaline media, maintaining effective charge transfer during boride anodic discharge. A zirconia coating may be readily applied to a boride salt, for example in this study *via* $ZrCl_4$ (AR grade, ACROS®), which is dissolved in ether (Fisher®). The VB_2 (insoluble in ether) is stirred as a suspension in this solution for 30 min, followed by vertex suction, then vacuum removal of the remaining solvent, and air drying overnight. The Zr^{2+} equivalents, in the coating solution, control the weight percent and thickness of the coating. As is evident in the inset of Fig. 2, ZrO_2 is readily distinguished from VB_2 *via* its IR absorbance. With this, the extent of ZrO_2 coating on VB_2 is observed using ATR/FTIR (Attenuated Total Reflectance Fourier Transform Infrared) as we have detailed in references 4, 7 and 9. The effects of corrosion are accelerated at higher temperature, and this domain is used to accelerate long-term anode stability studies. Stored at 45 °C for one week, and then discharged at room temperature, the uncoated VB_2 alkaline anode loses 10% of its original charge capacity, but with a 1% ZrO_2 coating retains 100% of that capacity. Similarly, stored at 70 °C for 1 week, the uncoated VB_2 retains only 65% of its original capacity, but with a 1% ZrO_2 coating retains 85% of that charge capacity (thicker coatings further improve stability[9]).

A series of impediments to effective discharge of the vanadium boride fuel cell have been overcome. The supplementary information contains extended, systematic optimization studies.† As summarized by the optimization studies in Fig. 3, the vanadium boride air cell can be efficiently discharged. This figure compares the discharge of these cells under a variety of anode, capacity and load conditions. As is evident in the black curve, the substantial capacity of VB_2 is experimentally realized (89% of the theoretical capacity; this $11e^-$ efficiency is the measured integrated charge to a discharge cutoff of 0.6 V, compared to the 4260 mAh g^{-1} intrinsic capacity of VB_2). As seen in the blue and green curves, anode additives, of up to 10 wt% solid NaF or NaOH, can improve both coulombic efficiency and potential, although at higher weight fractions these salts are deleterious to the observed discharge. The observed VB_2 $11e^-$ anode efficiency consistently improves with either an increase in added anodic graphite or in the discharge load, or a decrease in the anode thickness (example: efficiency is 30, 76, or 89%, respectively for otherwise equivalent 50, 15 or 5 mAh capacity cells). Hence, the VB_2/air cell is limited by the rate of charge transfer or resistance to the anodic current collector. As seen in the violet and bronze curves, this limitation is overcome by decreasing the VB_2 particle size. Ground (ball milled) VB_2 exhibits higher anodic discharge efficiencies. When separated by particle size, the smallest particle (<28 μm) VB_2 anode discharges to the highest (82%) coulombic efficiency and exhibits a higher initial discharge potential.

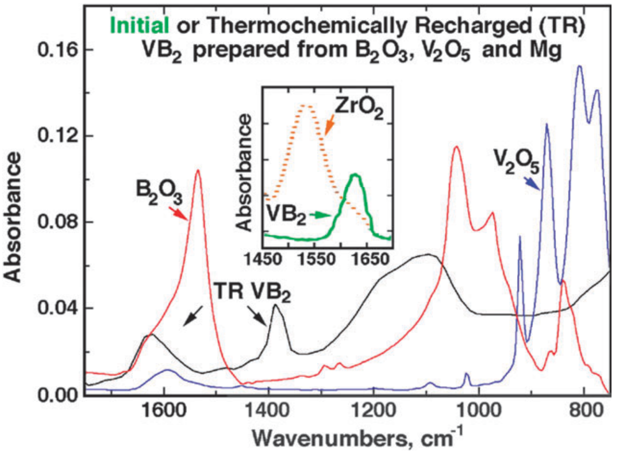


Fig. 2 Inset: IR spectra of pure VB_2 or ZrO_2. Main figure: The IR of thermochemically recharged (TR) VB_2, prepared as described in the text, is comparable to that of the initial VB_2, and is distinct from that of the vanadate and borate fuel cell discharge products.

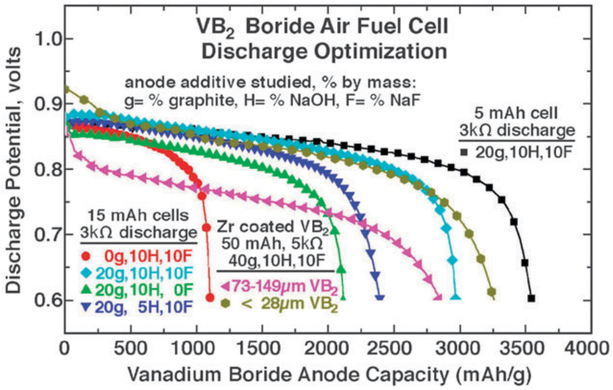
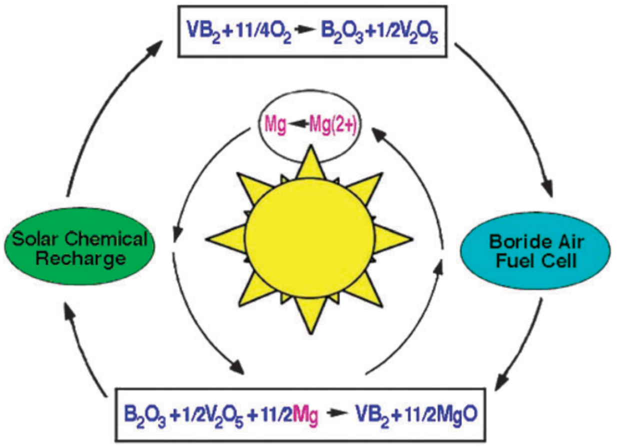


Fig. 3 Optimization of the vanadium boride air cell anode capacity as a function of the indicated anode composition, capacity, and discharge load conditions. The measured integrated discharge current is normalized by VB_2 mass in a 1 cm^2 cell, consisting of a zinc air coin (McMaster 1015K13 IEC PR44), with saturated NaOH electrolyte, in which the zinc anode is replaced with boride. The higher capacity (50 mAh) cells are prepared with ball milled VB_2 (of either <25 μm, or 73–149 μm particle size as indicated on the figure) which has been coated with an overlayer of (1%) zirconia. The lower capacity (5 and 15 mAh) cells are prepared with VB_2 which has been neither milled nor coated.



Scheme 1 Discharge and solar chemical charge of the VB_2 air cell.

Over a 1 kΩ discharge load, a thick (150 mAh) anode comprised of <28 μm VB_2 with 30% graphite sustains a higher coulombic efficiency and a higher discharge potential than a thinner (50 mAh) anode comprised of unsorted, ground, VB_2 containing 40% graphite. The uncoated smaller particle VB_2 tends to be less stable in the alkaline electrolyte, which is prevented by the zirconia coating. It is evident that smaller particles will be useful for efficient, high rate discharge, if thicker VB_2 anodes are needed. It is expected that a further decrease in particle size, by two orders of magnitude or more (to the submicron domain), can be available through conventional high energy ball milling techniques, and also as alternative VB_2 synthesis strategies are developed.

The boride air fuel cell exhibits electrochemical irreversibility. We present a viable alternative pathway to regenerate the vanadium boride fuel cell, as represented in Scheme 1. In the first (irreversible) electrochemical discharge cycle, the alkaline vanadium boride electrode approaches the intrinsic VB_2 anode capacity. However upon subsequent electrochemical charge/discharge cycles, and independent of charging conditions, we observe the anode yields less than 10% of this intrinsic capacity after the first discharge/charge cycle.

Chemical regeneration of VB_2 is explored here through Mg reduction of the fuel cell discharge products. Solar thermal and photothermal processes can regenerate metals from their salts.[10] An efficient solar powered laser has been reported to generate Mg from its oxide and/or chloride salts, including:[11,12]

$$MgCl_2 + h\nu(\text{solar}) \rightarrow Mg(l) + Cl_2(g) \qquad (4)$$

Traditionally, vanadium boride was prepared by high-temperature reaction of boron with metals,[8,13] or *via* carbothermal reduction of V_2O_5 and B_2O_3 above 1600 °C,[14] or as a self-propagating high-temperature reaction between VCl_3 and MgB_2.[15] To probe the feasibility of the chemical regeneration of the fuel cell discharge products in eqn (3), we explore here a Mg-assisted formation of vanadium boride, as expressed by eqn (5). Magnesium is sufficiently energetic to regenerate vanadium boride from its discharge products. Following chemical regeneration of VB_2, MgO is removed by dissolution in HCl (to $MgCl_2$ in H_2O):

$$B_2O_3 + \tfrac{1}{2}V_2O_5 + \tfrac{11}{2}Mg \rightarrow VB_2 + \tfrac{11}{2}MgO \qquad (5)$$

Specifically, V_2O_5, B_2O_3 and Mg were added in accord with eqn (5) and ball milled for 24 h in an argon atmosphere at room temperature. Impurities (including the MgO product and residual reactants) were removed by leaching the as-milled powder with a 10% HCl solution for 1 h. The solution was decanted after leaching, the solid product was washed with deionized water, and finally vacuum dried. The secondary product, $MgCl_2$, is available for solar recharge to magnesium, as in eqn (4). The primary product, chemically recharged VB_2, sustains an electrochemical discharge at the expected potential, and exhibits characteristic IR absorptions matching commercial VB_2 (including at 1097, 1391, 1630, and 3401 cm^{-1}), and as seen in Fig. 2 is distinct from the discharge products and synthesis reactants.

The zirconium stabilized boride air cell is based on the unusual 11 electron per molecule storage capacity of VB_2, and is the first electrochemical system with a practical energy storage capacity comparable to that of gasoline. This high storage capacity is liberated at a uniform, single discharge potential plateau when the VB_2 is protected by a zirconia overlayer which prevents corrosion of the boride anode, stabilizes alkaline charge transfer chemistry, and is applied to form a functional, highest energy capacity VB_2/air cell. A stepwise optimization of the vanadium boride/air fuel cell is presented, and then a viable solar photochemical pathway is shown, which regenerates the vanadium boride to recharge the fuel cell. The large volumetric capacity of the fuel cell, and the pathway for a renewable (solar) energy recharge, are positive attributes of this novel vanadium boride air cell. Systems aspects will continue to be analyzed and optimized. Liquid (higher temperature, solar driven), rather than solid, Mg, should facilitate the recharge formation of VB_2 in eqn (5). The discharge studies indicate that sub micron particle size VB_2, as available following high energy ball milling, can further improve anodic kinetics and coulombic efficiency.

This material was based on work supported in part by the United States National Science Foundation, with research support to Stuart Licht while working at the Foundation.

Notes and references

1. K. Kinoshita, *Electrochemical Oxygen Technology*, Wiley-Interscience, Hoboken, NJ, USA, 1992, pp. 259–260.
2. *Zinc Air Technical Bulletin*, Duracell, 2005, http://www.duracell.com/oem/primary/Zinc/zinc_air_tech.asp.
3. H. X. Yang, Y. D. Wang, X. P. Ai and C. S. Cha, *Electrochem. Solid-State Lett.*, 2004, **7**, A212.
4. S. Licht, X. Yu and D. Qu, *Chem. Commun.*, 2007, 4341.
5. S. Licht, B. Wang and S. Ghosh, *Science*, 1999, **285**, 1039.
6. S. Licht and R. Tel-Vered, *Chem. Commun.*, 2004, 628.
7. S. Licht, X. Yu and D. Zheng, *Chem. Commun.*, 2006, 4341.
8. C. Bulfon, A. Leithe-Jasper, H. Sassik and P. Rogl, *J. Solid State Chem.*, 1997, **133**, 113.
9. S. Licht, X. Yu and Y. Wang, *J. Electrochem. Soc.*, 2008, **155**, A1.
10. S. Licht, *Chem. Commun.*, 2005, 4341.
11. T. Yabe, S. Uchida, K. Ikuta, K. Yoshida, C. Baasandash, M. Mohamed, Y. Sakurai, Y. Ogata, M. Tuji, Y. Mori, Y. Satoh, T. Ohkubo, M. Murahara and A. Ikesue, *Appl. Phys. Lett.*, 2006, **89**, 261107.
12. T. Yabe, T. Ohkubo, S. Uchida, K. Yoshida, M. Nakatsuka, T. Funatsu, A. Mabuti, A. Oyama, K. Nakagawa, T. Oishi, K. Daito, B. Behgol, Y. Nakayama, M. Yoshida, S. Motokoshi, Y. Sato and C. Baasandash, *Appl. Phys. Lett.*, 2007, **90**, 261120.
13. L. Y. Markovskii, *Poroshk. Metall.*, 1969, **77**, 13.
14. H. Blumenihal, *J. Am. Chem. Soc.*, 1952, **74**, 2942.
15. L. Rao, E. G. Gillan and R. B. Kaner, *J. Mater. Res.*, 1995, **10**, 353.