Supplementary Information for: Renewable Highest Capacity VB_2/Air Energy Storage

Optimization of the Vanadium Boride Air Fuel Cell

As presented by the systematic optimization studies presented in Table 1 the vanadium boride air fuel cell can be efficiently discharged. The anodic coulombic efficiency rapidly increases with decreasing anode thickness ($11e^-$ Efficiencies increase from 30, 76 or 89%, respectively for 50, 15 or 5 mAh cells under equivalent conditions), although the initial discharge potential marginally decreses (from 0.90 to 0.88 V). As summarized in Table 1, anode additives, of up to 10 wt % solid NaF or NaOH, can improve both coulombic efficiency and potential, although these salts are deleterious at higher weight fractions.

The observed 11e- efficiency of vanadium boride in Table 1 is consistently improved (increases) as either the fraction of graphite in the anode, or the discharge load resistance is increased. Hence, the vanadium boride/air fuel cell is limited by the resistance or rate of charge transfer to the anodic current collector. We predict, and observe in Table 1, that this limitation is overcome by decreasing the vanadium boride particle size. Ground (ball milled) VB_2 exhibits higher anodic discharge efficiencies, and when further 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. 3).

As summarized in Table 1, over a 1 kΩ discharge load, a thick (150 mAh) anode comprised of <28μm 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. It is evident that smaller particles will be useful if thicker VB_2 anodes are needed. The uncoated smaller particle VB_2 tends to be less stable in the alkaline electrolyte, which is prevented by the zirconia coating. It is expected that a further decrease in particle size, by two orders of magnitude or more (to the submicron domain), can be assessed through conventional high energy ball milling techniques, and also as alternative VB_2 synthesis strategies are developed.

A further route was investigated providing evidence that a thicker, high capacity, alkaline VB_2 anode can be efficiently discharged upon cell configuration optimization. These results includes an alternative cylindrical cell configuration, and will presented in a future publication.

Table 1. Stepwise, VB_2/air Fuel Cell Optimization. Measured coulombic efficiency for boride/air cells discharged at 25°C under various, discharge and anode conditions. Cell fabrication is described in the the Methods section. 11e-Efficiency is the measured integrated charge to a discharge cutoff of 0.6V, compared to the 4260 mAh/g intrinsic capacity of VB_2.

VB_2-treatment	Q(mAh)	graphite	NaOH	NaF	load	$V_{load-initial}$	$11e^-$ Efficiency
none	5	20%	10%	10%	3kΩ	0.88V	89%
none	15	0%	10%	10%	3kΩ	0.87V	28%
none	15	20%	10%	10%	3kΩ	0.89V	76%
none	15	20%	10%	0%	3kΩ	0.86V	53%
none	15	20%	10%	5%	3kΩ	0.87V	59%
none	15	20%	10%	10%	3kΩ	0.89V	76%
none	15	20%	10%	15%	3kΩ	0.88V	67%
none	15	20%	10%	20%	3kΩ	0.86V	51%
none	15	20%	0%	10%	3kΩ	0.83V	48%
none	15	20%	5%	10%	3kΩ	0.87V	60%
none	15	20%	10%	10%	3kΩ	0.89V	76%
none	15	20%	15%	10%	3kΩ	0.88V	62%
none	15	20%	20%	10%	3kΩ	0.88V	47%
none	50	0%	10%	10%	3kΩ	0.87V	16%
none	50	10%	10%	10%	3kΩ	0.90V	24%
none	50	20%	10%	10%	3kΩ	0.90V	30%
none	50	30%	10%	10%	3kΩ	0.90V	36%
none	50	40%	10%	10%	3kΩ	0.91V	42%
ball milled, 1%Zr	50	40%	10%	10%	0.5kΩ	0.85V	30%
ball milled, 1%Zr	50	40%	10%	10%	1kΩ	0.86V	40%
ball milled, 1%Zr	50	40%	10%	10%	2kΩ	0.87V	65%
ball milled, 1%Zr	50	40%	10%	10%	3kΩ	0.89V	72%
73-149μm, 1%Zr	50	40%	10%	10%	5kΩ	0.86V	71%
35-73μm, 1%Zr	50	40%	10%	10%	5kΩ	0.89V	76%
28-35μm, 1%Zr	50	40%	10%	10%	5kΩ	0.91V	78%
<28μm, 1%Zr	50	40%	10%	10%	5kΩ	0.92V	82%
<28μm, 1%Zr	150	30%	10%	10%	1kΩ	0.92V	46%
<28μm, 1%Zr	150	40%	10%	10%	1kΩ	0.92V	53%
<28μm, 1%Zr	150	40%	10%	10%	3kΩ	0.90V	71%