Video Article

Fabrication of VB₂/Air Cells for Electrochemical Testing

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Abstract

A technique to investigate the properties and performance of new multi-electron metal/air battery systems is proposed and presented. A method for synthesizing nanoscopic VB₂ is presented as well as step-by-step procedure for applying a zirconium oxide coating to the VB₂ particles for stabilization upon discharge. The process for disassembling existing zinc/air cells is shown, in addition construction of the new working electrode to replace the conventional zinc/air cell anode with a the nanoscopic VB₂ anode. Finally, discharge of the completed VB₂/air battery is reported. We show that using the zinc/air cell as a test bed is useful to provide a consistent configuration to study the performance of the high-energy high capacity nanoscopic VB₂ anode.

Video Link

The video component of this article can be found at <http://www.jove.com/video/50593/>

Introduction

Vanadium diboride as an anode has among the highest volumetric charge capacity of any anode material. This protocol introduces a method for studying this fascinating material. Metallic zinc has been the predominant anode material in aqueous primary systems due to zinc metal's high two-electron volumetric and gravimetric charge storage capacities of 5.8 kAh L⁻¹ and 820 Ah kg⁻¹, respectively.* The zinc-carbon battery, known as the Leclanché cell, was first introduced in the 19th century, combining a zinc anode with a manganese dioxide (carbon current collector) cathode in a chloride electrolyte¹. The common alkaline battery utilizes the same couple, but replaces the chloride electrolyte with an aqueous alkali hydroxide electrolyte. Together zinc-carbon and alkaline batteries comprise the majority of primary batteries sold¹. When the manganese dioxide cathode in the alkaline cell is replaced by an air cathode, substantially higher energy storage capacities are achieved. This zinc-air battery utilizes oxygen from the air, and is commonly found in hearing-aid batteries¹⁻³.

Our search for higher capacity battery storage has focused on materials that can transfer multiple electrons per molecule⁴⁻¹¹. Among the wide variety of redox couples we have explored, VB₂ stands out as an extraordinary alkaline anode capable of releasing 11 electrons per VB₂, with volumetric and gravimetric capacities of 20.7 kAh L⁻¹ and 4060 Ah kg⁻¹ respectively.* In 2004, Yang and co-workers reported the discharge of VB₂, but also documented the extended domain in which VB₂ is susceptible to corrosion in alkali media¹². In 2007, we reported that a coating on the VB₂ particles prevents this corrosion¹³, leading to demonstration of the VB₂/air battery in 2008¹⁴.

In this paper, we present a protocol used to investigate new metal/air systems employing the technology previously developed for the zinc/air cell as applied to the VB₂/air cell. A nanoscopic VB₂ anode is presented as a high-energy high-power density anode capable of exhibiting an eleven-electron oxidation reaction approaching the theoretical intrinsic capacity of 4060 Ah kg⁻¹ at increased battery voltage and battery load capability. The VB₂/air couple uses an alkaline electrolyte of KOH/NaOH, employing the same oxygen air cathode extracted from the zinc/air cell¹. The carbon electrocatalyst cathode is not consumed during discharge.

There exists a need for a greater understanding the VB₂/air system in order to further improve cell performance. The properties and performance of nanoscopic VB₂ materials can be explored using the cell configuration of the zinc/air cell^{15,16}. Electrochemical testing can be performed for nanoscopic VB₂ to compare performance through percent efficiency at various rates.

Protocol

1. Preparation Nano-VB₂

Nanoscopic VB₂ is directly synthesized from elemental vanadium and boron via ball-milling in a 1:2 mole ration.

1. Clean a 50 ml tungsten carbide milling jar and ten 10-mm tungsten carbide balls. Dry under air in an oven at 100 °C for 1 hr to ensure all water has evaporated.
2. Wipe clean the inside of the milling jar to ensure no residue remains, repeat step 1.1 if residue is visible.
3. Purge the antechamber of a glove box with argon 3x for 10 min each time. Transfer the milling jar, balls, and clean spatula into the argon filled glovebox.
4. Weigh out vanadium and boron powders in a 1:2 molar ratio, 0.500 g of vanadium and 0.212 g boron into the milling jar, add the balls, and seal the milling jar.
5. Remove the sealed milling jar from the glovebox, place it into a planetary ball mill set to 600 rpm and to mill for 4 hr.
6. After completion, allow the milling jar to cool to room temperature before removing from the ball mill.
7. Purge the antechamber of a glove box with argon 3x for 10 min each time. Transfer the milling jar, round bottom flask, paraffin film, spatula, and magnetic stir bar into the glove box.
8. Apply the zirconium oxide coating to the prepared nanoscopic VB₂ as follows:
 1. Inside the glove box collect the nano-VB₂ previously prepared using a spatula to scrape the walls of the milling jar until the bulk of the starting mass has been recovered. Weigh and transfer the collected nano-VB₂ into a round bottom flask.
 2. Weigh out 3.5 weight percent of zirconium chloride compared to the collected VB₂ and then add the powder to the round bottom flask containing the collected nano-VB₂.
 3. Add a magnetic stir bar to the flask and using paraffin film seal the opening prior to removing from the glove box. Alternatively, a septum has been used with equivalent results Remove the round bottom flask from the glove box.
 4. Using a 10 ml syringe, transfer 10 ml of diethyl ether into the round bottom flask. Quickly cover the hole created by the syringe in the paraffin film with an additional piece of Parafilm.
 5. Mix the flask on a stir plate for one hour on a medium setting.
 6. After one hour, evaporate the remaining diethyl ether off of the nano-VB₂ using a rotary evaporator or other pump configuration until coated nano-VB₂ appears dry.
 7. After Zr coated nano-VB₂ is completely dry, collect.

2. Preparation of Electrolyte

1. Prepare a mixture of 4 M KOH and 4 M NaOH solution for use as the electrolyte. (NOTE: Make only enough to last a few weeks, repeat as needed to form new cells). Aqueous hydroxide electrolytes of NaOH and KOH have been explored in the past ranging in concentration ranging of 8 M to saturated. The combination of 4 M NaOH and 4 M KOH yields marginally improved high rate performance compared to earlier results using a pure NaOH electrolyte.

3. Disassembling Zinc/Air Batteries

See the table of reagents and materials for details about battery manufacturer and model number.

1. Opening the zinc/air cell for later fabrication of VB₂/air cells.
 1. Create a cut in the lip of the coin cell casing using diagonal cutting pliers.
 2. Crimp the outside edged of the lip outward. After going completely around the cell twice, it should be easy to open.
 3. Using a razor blade, push up on the edges of the cap slowly, gently force open the cell. NOTE: It may take awhile to get the cell open. Be patient and careful not to crack or damage any part when doing this step. The cell will need to remain intact.
2. Preparing the battery for use
 1. Once the cell is opened into two parts (the cap and the bottom) begin to gently remove the zinc anode material from the cap and in the bottom.
 2. Remove as much solid zinc as possible with the razor blade. Do not scrape the bottom; it is important not to damage any parts. The separator (bottom) and the gasket (sides) form a single opaque overlay that can easily be punctured by the applying too much pressure with the razor blade. Piercing the separator will result in damaging the air cathode. Additionally, if the gasket is disturbed the reliability of the cell to be electrically isolated is lost.
 3. Using a cotton swab carefully wipe the remaining zinc and residue from the cap, bottom, and separator.
 4. Clean off the cap and outside of cell with isopropyl alcohol.

4. Preparation of a 5 mAh Working Electrode with a 70/30 dry mixture

1. Using synthesized Zr coated nano-VB₂ as the active material, weigh out 0.0012 g per electrode to be fabricated (usually 5 - 10 cells are tested at a time) and transfer into a mortar and pestle.

2. Add 30% of the weighed VB₂, 0.0005 g of graphitic carbon black (per electrode), to the active material in the mortar and pestle and grind for 30 min.
3. Ensure that there are no large, visible clusters of material and collect powder.
4. Weigh out approximately 0.0017 g of the 70/30-powder mixture per clean electrode cap using a spatula. (If preparing multiple cells at a time, otherwise transfer the material to the electrode cap).
5. Add a single drop of isopropyl alcohol to each cap and swirl powder with a spatula or other small pointed tip until there are no clumps and suspension is evenly distributed across the top of the cap.
6. Allow electrodes to dry for 30 min.

5. VB₂-Air Cell Assembly - Dry Method

1. Assemble cells in reverse from the zinc/air cell with the working electrode, cap, upside down.
2. Organize each cell (the 5 - 10 being tested) in two rows, the caps in one and the corresponding bottoms in the other. Inspect each cap to ensure that the anode material is evenly spread and not cracked.
3. Add 27 μ l of 4 M KOH/4 M NaOH electrolyte mixture to each separator.
4. Gently remove excess electrolyte from the bottoms using cotton dabbing only once inside the bottom.
5. Carefully take each of the bottoms, turn them over, and place them on top of the caps so that the anodic material is in contact with the electrolyte.
6. Apply pressure and seal using a fast drying epoxy.

6. Nano-VB₂/Air Cell Testing

1. Once the fabrication process is completed, place cells on a discharge rack or battery holder.
2. Allow each cell an initial rest step of ten minutes to ensure that the cells equilibrate prior to discharging.
3. Discharge cells at a constant load of 3,000 Ω (or an alternative desired load) using a battery tester.
4. After the equilibration step, take a measurement of the open circuit potential.
5. Then discharge under a constant load until a stopping voltage of 0.4 V is reached.
6. Coulombic efficiency can then be calculated by the percentage of the measured capacity compared to the theoretical anode eleven-electron discharge capacity of 4,060 Ah kg⁻¹.

Representative Results

Electrochemical testing is performed to determine the performance of VB₂/air batteries. The results obtained for multiple cells provide evidence for reproducibility of the cell performance. **Figure 1** compares the VB₂/air batteries during a 3,000 ohm (left) and 1,000 ohm (right) discharge. Note that the discharge voltage, as well as the fraction of the 4,060 Ah kg⁻¹ intrinsic capacity is higher with the nanoscopic VB₂ anode compared to the macroscopic VB₂ anode cell, and that this cell also retains higher efficiency at higher rate (comparing the 1,000 to 3,000 ohm loads) with this anode. The labeling of cells is as follows, for example I-FC000, where I is an arbitrary constant, FC stands for a full cell, and 000 is the test number. **Figure 2** validates that blank, Zn or Zn/VB₂ cells discharge is as expected. **Figure 3** shows the zirconia overlayer present on the VB₂ nanoparticles. **Figure 4** photographs consecutive stages of the Zinc/air battery disassembly, and **Figure 5** stages of the replacement anode fabrication. Finally, **Figure 6** presents correct gluing of the cell to ensure good connections on both the anode and cathode to establish a good cell seal. The working electrode may also be fabricated using alternative processes to the dry method. For example, the VB₂ may be mixed as an aqueous dispersion (slurry), and then evenly distributed over the stainless current collector, or as seen in **Figure 7**, cast as a solid VB₂ disc with a Kynar binder on a stainless steel shim.

Figure 1. Data obtained for relatively slow discharge times (3,000 Ω and 1,000 Ω). Cells are typically discharged at 3,000 Ω to provide comparisons between experiments and cell performance.

Figure 2. Validation that cleaned Panasonic 675 Zinc/Air batteries provide a useful test bed for the nano-VB₂ anode; compared to the macro-VB₂ anode are an empty anode cell (top left), anode containing only packing carbon- no VB₂ (bottom left), anode with Zn- no VB₂ (top right), and anode with a composite of Zn and VB₂ (bottom right). Top Left shows the discharge of a fully gutted and closed Zinc/Air cell without any anode material (empty blank cell, no carbon and without VB₂) present with a typical nano-VB₂ discharge for comparison. Top Right shows the discharge of cell containing 20mAh of the zinc anode material. The zinc cell is used to validate the VB₂ cell configuration and uses the original zinc as reintroduced back into the cell. Bottom Left provides an example of a discharge containing only the appropriate amount of graphitic carbon black for a typical VB₂ discharge with a typical nano-VB₂ discharge for comparison. Bottom Right shows a nano-VB₂ cell with the presence of purposely added zinc in the anode, and the observed distinct voltage discharge plateaus are evidence that the VB₂-alone anode does not contain a significant zinc contaminant. The left figure validates that the blank cell exhibits an upper limit of less than 4% of the measured VB₂ containing anode capacity.

Figure 3. High resolution SEM image of the zirconia coated VB_2 .

Figure 4. Correct way to disassemble a Zinc/Air battery for VB_2 -Air Cell Assembly. Figures 4a and 4b show a factory cells prior to opening. Figure 4c and 4d demonstrate the initial cut and opening of the battery. Figure 4e (also labeled Top) and Figure 4f (Bottom) provides a view of the opened cell prior to removing the Zinc anode material. Upon removal the membrane is cleaned and wiped out as shown in Figure 4g. Figure 4h displays the area where the VB_2 anode is fabricated.

Figure 5. Fabrication of the working electrode. Figure 4a provides an example of how this is prepared. When constructing the electrodes it is important that no cracks or clumps are visible; the electrode surface should appear smooth as shown in Figure 4b.

Figure 6. Correct gluing of cells to ensure good connections on both the anode and cathode and a good seal on the cell.

Figure 7. The working electrode may also be fabricated using alternative processes to the dry method. Above is an example of cast nano-VB₂ anode preparation on a stainless steel shim.

*Intrinsic volumetric specific capacity is calculated as ndF/MW , from the molecular weight, MW (such as for Zn or VB_2 respectively $MW = 0.0654$ kg or $.0726$ kg mol^{-1}), the number of electrons transferred, (such as for Zn or VB_2 $n = 2$ or 11), the density, d (such as for Zn or VB_2 $d = 7.1$ kg $liter^{-1}$ or 5.1 kg $liter^{-1}$), and Faraday's constant of 28.8 Ah mol^{-1} .

Discussion

Construction of the VB_2 /air battery in this way provides the ability to study and probe the eleven electrons per molecule charge transfer that occurs, allowing the possibility for a new high capacity battery. If obtained results do not demonstrate reproducible results, ensure that all of the zinc anode material was removed from the battery, that there is an even dispersion of active material on the cap, and that the cells are properly glued without any leaks. If a problem continues to occur, ensure that the batteries are Panasonic 675 Zinc/Air cells made in Japan not Germany. The gasket of a Japanese cell should appear opaque and attached to the separator as one entity. If the gasket is separate and blue the cells are German. Limitations to this technique include not having the ability to control the humidity of cell, although previously there have been no issues observed. When constructing a VB_2 /air battery, there are several critical steps outlined in the Protocol section: opening of the cell, removing the zinc material, preparation of the anode material and insertion in the cell, closing the cell carefully, and proper gluing to ensure that there are no leaks and a good electrical connection.

X-ray powder diffraction is a convenient technique to confirm^{15,16} that the starting reactants (elemental vanadium and boron) are not present in the synthesized nano- VB_2 . Transmission electron microscope (TEM) images establish that the zirconium oxide coating is evenly covering the VB_2 particles. While disassembling and assembling the Zinc/Air batteries it is important to make sure that the casing remains intact and that the membrane and separator are not cut or damaged in anyway. During discharge, relatively small differences in the voltages and capacities observed for repeated cells may result from small mass differences, as well as from using a cell configuration that did not result in uniform pressure applied for each cell.

Disclosures

The authors, Chris Rhodes, Ruben Lopez, Xuguang Li, Mahesh Waje, and Matthew Mullings are employees of Lynntech Inc.

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