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Letter

Mechanochemical synthesis and electrochemical characterization of VB_x as high capacity anode materials for air batteries

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ABSTRACT

A series of VB_x ($x = 0.1$, 0.25, 0.5, and 1) are prepared by a mechanochemical reaction of elemental B and V powders and tested as alternative high capacity anodic materials for alkaline air batteries. The VB_x ($x = 0.25$, 0.5, and 1) anodes tested can deliver an extraordinary capacity of >2000 mAh g^{-1}, twice higher than the theoretical capacity of metallic Zn currently used as high capacity anodes in aqueous primary batteries. The strong discharge capabilities observed from electrochemically inert boron (B) and passive vanadium (V) in the VB_x samples are suggested to result from a combined chemical interaction, in which the B atoms are electrochemically activated by bonding with V atoms to partially decrease the covalent stability of elemental B component. At the same time, the electrochemically activated B can alleviate, in turn, the anodic polarization of metallic V element by clamping the electrode potential to a region where elemental V is in active state.

1. Introduction

In the past two decades, a variety of battery materials have been explored in order to meet the urgent demands for high energy density power sources originated from the various applications ranging from portable consumer electronics to electric vehicles. A most effective way to enhance the energy density of batteries is to utilize multi-electron redox compounds for electrode-active materials [1]. In this respect, superiron [2,3] and permanganate [4,5] demonstrated superiorly high capacities as cathodic materials and some transitional metal diborides [6–9] exhibited a capacity several times higher than conventional Zn anode. Particularly, among the metal borides reported, crystalline VB_2 showed the highest discharge capacity of >3300 mAh g^{-1} [8], which even exceeds the volumetric energy density of gasoline [8]. This exceptional high capacity is attributed to a complete 3-electron electro-oxidation of boron, due to the improved electronic conductivity and weakened B–B bonding of the elemental B atoms when existed in the transitional metal diborides [5]. However, except for the crystalline metal diborided, a number of amorphous borides were also found to realize their full oxidation capacity contributed from both of transition metals and boron atoms [6]. The question remained unsolved is whether the superior energy capability of VB_2 comes from a special structure of the diborides or represents a more general electrochemical behavior for other types of V–B alloys.

In this work, we synthesized a series of VB_x ($x = 0.1$, 0.25, 0.5, and 1) by a mechanochemical reaction of elemental B and V using high energy ball-milling and characterized the electrochemical discharge performances of these alloys as anodic materials for air batteries. The aim of this work was intended to develop a simple synthetic route for high capacity VB_x alloys and also to provide additional information for understanding the muti-electron oxidation behaviors of the VB_x alloys for further development of boride-based high capacity anode-active materials.

2. Experimental

2.1. Preparation of VB_x

VB_x used in this work were prepared by ball-milling of the mixture of elemental vanadium and boron powders with different atomic ratio of V:B, using a high energy shaker ball-miller (QM-3A, Nanjing University Instrument Plant, China). The vanadium power (Beijing Mountain Technical Development Center, China, 200 mesh, 99.9% purity) and boron power (Changsha Hengrui New material development Co. Ltd, China, 325mesh, 95% purity) were used as purchased without any further treatment. The weight ratio of the mixture to stainless steel milling balls was selected to be 1:12. The ball-milling process was performed for 10 h under the protection of argon atmosphere in order to prevent the surface oxidation. The shaker speed was set at 1200 rpm. The synthesized products with different atomic ratio of vanadium to boron, i.e. V:B = 1:1, 1:0.5, 1:0.25, 1:0.1, were denoted as VB, $VB_{0.5}$, $VB_{0.25}$ and $VB_{0.1}$, respectively.

2.2. Materials characterizations

The resulting VB_x products were measured by powder X-ray diffraction (XRD) using a SHIMADZU Lab XRD-6000 diffractometer with CuKα source. The scan speed was set as 4° min^{-1} and the data were collected over a scattering angle range of 10–80°.

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All the electrochemical characterizations of the VB_x samples were carried out using thin film powder electrode. The thin film electrodes were prepared firstly by mixing 85% VB_x powders, 7% polytetrafluoroethylene (in emulsion) and 8% acetylene black into paste, then roll-pressing the paste into a 0.15 mm thick film, and finally pressing film onto a stainless steel mesh.

The voltammetric measurements were carried out on a three-electrode cell using a small piece (about 3 mm × 3 mm) of the VB_x film electrode as working electrode, a large area air electrode as counter electrode and an Hg/HgO in the same electrolyte as reference electrode. The preparation procedures of air electrode are similar to those described in Refs. [10,11]. The air electrodes consist of a catalyst layer and a gas diffusion layer. The gas diffusion layer was composed of acetylene black (60 wt.%) and polytetrafluoroethylene (PTFE) (40 wt.%). The catalyst layer contains the MnO_2 catalyst (20 wt.%), activated carbon (65 wt.%) and PTFE binder (15 wt.%). Both of the catalyst layer and diffusion layer was produced by mixing the composing materials to form paste and then roll the paste into a film. The catalyst and gas diffusion layers were pressed together with a nickel mesh in-between at 80 kg cm^{-2} and sintered at 270 °C in air for half-an-hour to remove organic residues.

The discharge performances of the boride electrodes were evaluated by galvanostatic discharge experiments using laboratory cells with 2 cm × 2 cm VB_x electrode as anode, 5 cm × 5 cm air electrode as inexhaustible cathode and 30% KOH solution as electrolyte.

3. Results and discussion

Fig. 1 compares the XRD patterns of the ball-milled VB_x samples with elemental vanadium. At low content of boron, the as-prepared VB_x samples ($x \leq 0.5$) show discernible diffraction peaks of metallic vanadium, reflecting the presence of elemental vanadium in the VB_x samples. This is because the insufficient amount of boron cannot ensure the complete transformation of vanadium into vanadium borides. With increasing boron content, the XRD intensity of elemental vanadium decreased greatly and became indistinct and vanished eventually at V/B = 1 in the VB_x samples. Instead, the XRD pattern of the VB_x ($x \geq 1$) showed a number of featureless bands at $2\theta = 35–45°$, suggesting the formation of amorphous alloys of boron and vanadium during high energy ball-milling.

To reveal the electrochemical behavior of the as-prepared VB_x samples, we measured cyclic voltammograms (CV) for VB, $VB_{0.5}$, $VB_{0.25}$, $VB_{0.1}$, and V, respectively and compared their voltametric responses in Fig. 2. As shown in Fig. 2, all the samples showed well-defined anodic current bands, indicating electrochemical feasibility for anodic oxidation of these samples. However, the anodic current for electrochemical oxidation of all the VB_x materials arose from much more positive potentials (−0.9 V to −0.5 V vs. Hg/HgO) than the equilibrium potential of boron ($H_2BO_3^- + H_2O + 3e^- \rightleftharpoons B + 4OH^-$, −1.79 V vs. standard hydrogen electrode (SHE) [9]) and vanadium ($HV_6O_{17}^{3-} + 16H_2O + 30e^- \rightleftharpoons 6V + 33OH^-$, 1.154 V vs. SHE [12]). These huge electrochemical polarizations could be accounted for by the fact that vanadium is fully in passive state at its equilibrium potential in the alkaline solution [13] and also elemental boron is electrochemically inert due to its very poor electronic conductivity (1×10^{-6}–7×10^{-8} S cm^{-1} [7]). Nevertheless, we can still find that the electrochemical activity increased dramatically with increase in the boron content of the VB_x. When a small amount of boron was introduced to form the VB_x alloys, the $VB_{0.1}$ sample showed a doubly enlarged current peak with the onset potential of anodic oxidation negatively shifted from −0.5 V to −0.58 V in comparison with the CV band of metallic vanadium. With the boron content further increased, the $VB_{0.25}$ and $VB_{0.5}$ samples displayed a broadened and overlapped anodic band with their onset oxidation potential negatively shifted to −0.8 V and −0.7 V, respectively. These overlapped anodic bands are exclusively contributed by both the oxidation of boron and vanadium. Once the atomic ratio of boron to vanadium reached to 1, the VB alloy exhibited a large anodic peak starting from −0.9 V with a distinct shoulder peak centered at −0.5 V. Obviously, the observed anodic current peaks at more negative potential region is given rise by electro-oxidation of boron since vanadium must be always passivated at the potential region more negative than −0.8 V [14]. Thus, the electrochemical oxidation of the ball-milled samples can be considered to proceed through two steps: the electro-oxidation of VB_x at more negative potentials and then the successive oxidation of unreacted vanadium.

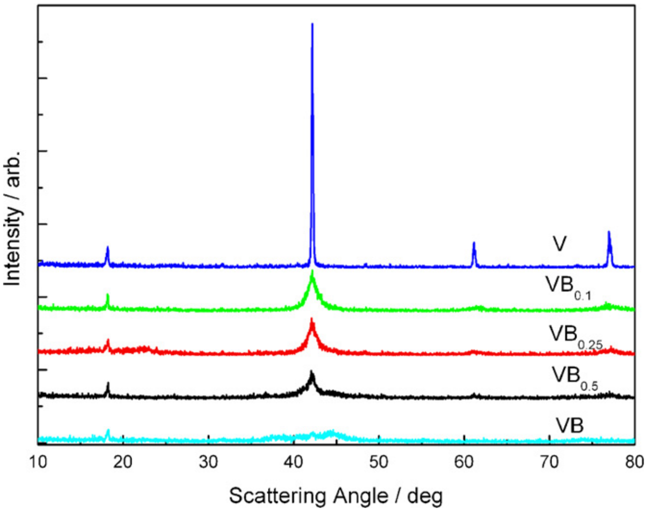

Fig. 1. A comparison of the XRD patterns of ball-milled VB_x (x = 0.1, 0.25, 0.5, and 1) and vanadium.

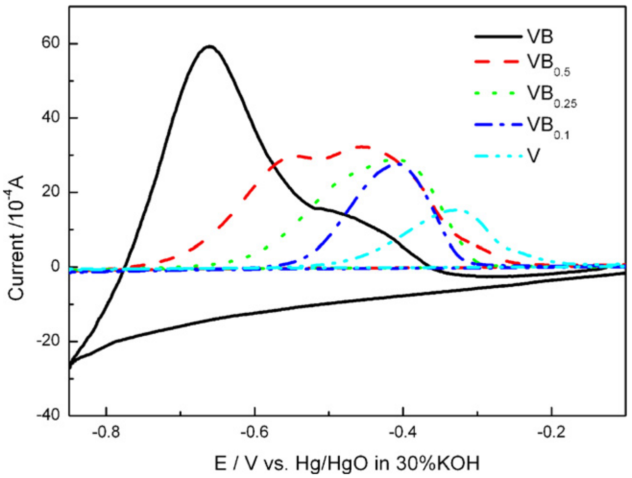

Fig. 2. Cyclic voltammograms of the VB_x (x = 0.1, 0.25, 0.5, and 1) and vanadium in a 30% KOH solution. Potential sweep rate: 0.05 mV s^{-1}.

Though elemental boron is potentially capable of donating 3 electrons for electrochemical oxidation in view of the thermodynamic equilibrium potential of boron as mentioned above, it is usually considered to be electrochemically inert and its 3-electron oxidation has never been realized in alkaline solutions. In previous paper, we reported complete oxidation of boron in crystalline VB_2 and attributed the electrochemical activation of boron to a special electronic bonding in the transition metal diborides. The CV data given above seem to indicate that as long as boron atoms are chemically combined with vanadium, the electrochemical activation of boron would take place despite what types of the crystalline structures they exist in. On the other hand, the large negative shift in the anodic current peaks of vanadium oxidation in the presence of boron as shown in Fig. 2 suggests that the electrochemically activated boron can effectively alleviates the passivation of the vanadium atoms, or in other words, diminish the electrochemical polarization of vanadium by clamping the electrode potential to more negative region, where vanadium is in active state.

To test the practical dischargeability of the VB_x as an anodic material, we constructed simulated VB_x-air cells for capacity mea-

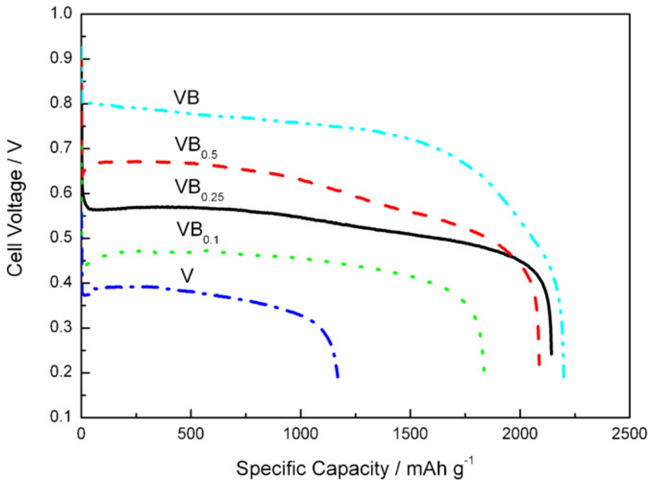

Fig. 3. Discharge curves of elemental vanadium and the ball-milled VB_x samples in a 30% KOH aqueous solution at 200 mA g^{-1}.

surements. The discharge of the cells was carried out at the constant current density. Fig. 3 shows the typical discharge curves of the VB_x powder electrodes at a current density of 200 mA g^{-1}. As shown in Fig. 3, metallic vanadium gives only a capacity of 1170 mAh g^{-1}, but the discharge voltage of the cells is only 0.38 V, implying a surface passivation or severe electrochemical polarization occurring on the vanadium anode. Once a very small amount of boron was added to form $VB_{0.1}$, the discharge capacity increased greatly to 1840 mAh g^{-1} and the output voltage of the cells rose up to 0.45 V. Since the theoretical discharge capacity calculated from the amount of B in the $VB_{0.1}$ sample is only 155 mAh g^{-1} of $VB_{0.1}$ according to 3-electron oxidation of boron, the large enhancement in the discharge capacity of the $VB_{0.1}$ anode by introducing a small amount of boron should be attributed to a depolarizating effect of boron for metallic vanadium. With further increase in boron content, the $VB_{0.25}$ and $VB_{0.5}$ electrodes delivered a remarkable capacity of >2000 mAh g^{-1}, meanwhile the voltage plateaus of these two cells increased to 0.55 V and 0.65 V, respectively. In addition, these cells show two closely overlapped discharge plateaus, characteristic of the stepwise oxidations of VB_x and metallic V.

The theoretical capacity of VB is calculated to be 3474 mAh g^{-1}, as expected from the complete 3-electron oxidation of boron and 5-electron oxidation of vanadium. However, the experimental capacity observed from the VB electrode as shown in Fig. 3 is 2198 mAh g^{-1}, about 63% of its theoretical capacity. This comparison indicates that there existed some unreacted boron or vanadium in the ball-milled VB_x samples, which resulted in incomplete utilization of both B and V. Nevertheless, these results demonstrate that a simple ball-milling of B and V elements can produce anode-active VB_x alloys with an extraordinary capacity of >2000 mAh g^{-1}, which exceeds twice the theoretical capacity (820 mAh g^{-1}) of zinc presently regarded as high capacity anode material.

The strong discharge capability of the VB_x alloys may be resulted from a cooperative interaction, in which the B atoms is electrochemically activated by alloying with the V atoms to decrease the sp^2 covalent character of B–B atoms in elemental B crystals and also to realize the electronic wiring of the B atoms, and in turn, the electrochemically activated B atoms can depolarize metallic V element by clamping the electrode potential to a more negative region where the elemental V is in electrochemically active state.

4. Conclusions

A series of VB_x (x = 0.1, 0.25, 0.5, and 1) were prepared by a mechanochemical reaction of elemental B and V using high energy ball-milling. The experimental results indicate that once a small amount of B was introduced into crystalline V samples, anodic activity of elemental V could be dramatically improved, showing strong discharge capability. All the VB_x (x = 0.25, 0.5, and 1) anodes tested can deliver an extraordinary capacity of >2000 mAh g^{-1}, twice higher than the theoretical capacity of Zn currently used as a high capacity anode in aqueous primary batteries.

Acknowledgments

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