

High discharge capacity of VB₂-Ni as anode for VB₂/air battery

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Abstract. The compound powders of VB₂ with 25 wt% and 50 wt% Ni were mixed uniformly using a planetary ball miller, respectively. The discharge capacity of VB₂/air battery with VB₂-Ni as anode in KOH electrolyte was investigated at room temperature and ambient pressure. Meanwhile, the microstructure of VB₂-Ni anode before and after discharge were analyzed by scanning electron microscope (SEM). The results indicate that the sintered anode material of VB₂ with 25 wt% Ni has the highest discharge capacity. Moreover, the discharge capacity of VB₂/air battery reached 7574 mAh with sintered VB₂-Ni25wt% anode, which was much higher than that with unsintered VB₂-Ni25wt% anode. However, the discharge capacity of VB₂/air battery with sintered VB₂-Ni50wt% anode was much lower than that with unsintered VB₂-Ni50wt% anode. The VB₂-Ni25wt% anode sintered at 1050 °C for 30 min is an effective way to improve the discharge capacity of VB₂/air battery.

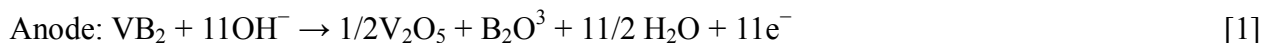
Introduction

Metal-air battery with a high theoretical energy output is a promising power source used for emergency lighting, portable electronic equipment, and energy storage of smart grids [1-4]. The most prominent feature of this battery is the combination of a metal anode with strong discharge activity and an air electrode with an open structure to draw cathode active materials (i.e., oxygen) from air [1]. During the battery discharge, the corrosive electrolyte storing in a separator favors the electrolytic dissolution of the metal anode to deliver electrons for power generation, and the oxygen drawn from air is catalytically reduced at the air electrode when it meets up with the circulating electrons [5].

Since the metal anode acts as the fuel in the battery system, selecting proper metal to serve as the anode plays an important role in enhancing the battery performance. Several metallic anodes have been investigated for metal-air batteries. Aluminium, lithium, calcium, magnesium and zinc all have attractive energy densities for this application [2] [6-11]. Of these potential candidates, zinc has received the most attention because of its relative stability in aqueous and alkaline electrolytes. Commercial primary zinc/air batteries are used in long term, low current discharge applications in a range of technologies including hearing aids, pagers, remote railroad signals and communications [9].

To provide high energy density cells, there has been an effort to develop high capacity multi-electron per molecule charge storage processes [12-22]. Vanadium diboride (VB₂) undergoes a multiple electron oxidation process, which to its completion involves an extraordinary 11 electron per molecule oxidation, including oxidation of the tetravalent transition metal ion, V(+4 → +5), and each of the two borons 2xB(−2 → +3). VB₂ has an intrinsic gravimetric capacity of 4060 Ah/kg, which is five-fold higher than that of the Zn anode electrode (820 Ah/kg). The intrinsic volumetric anodic capacity of the VB₂ anode (20.7 kAh/L) is tenfold higher than that of the lithium anode (2.06 kAh/L) [13] [14] [20-24].

A VB₂ anode within a battery can be coupled with oxygen from external air to provide extremely high energy density VB₂/air batteries [24]. The anode half cell, cathode half cell, and fuel cell reactions based on generalized discharge products are as follows [21]:



The VB₂/air battery has a theoretical discharge potential of 1.55 V, as calculated from the thermodynamic free energy of the cell reactants and products [21]. The VB₂/air battery's intrinsic volumetric energy density of 32 kWh/L is substantially greater than that of gasoline (<10 kWh/L) and has an intrinsic specific energy of 5,300 kWh/kg, which is four times higher than the theoretical specific energy of zinc/air batteries (1,353 kWh/kg). The VB₂/air couple uses an alkaline electrolyte, such as aqueous KOH or NaOH. Oxygen from the air reacts at the cathode in a manner similar to that of the zinc/air cell [25]. Concentrated aqueous hydroxide electrolytes ranging from 8 molar to saturated KOH or NaOH yield a similar electrochemical discharge in the VB₂/air cell [20] [21]. The VB₂/air cell shows an experimental open circuit potential of ~1.3 V, and under load, the cell can release its capacity over a flat, highly singular discharge potential plateau.

In this work, the VB₂ and Ni powders were mixed uniformly using planetary ball miller. The VB₂-Ni anode sheets were formed by tablet press, and then sintered in tube furnace. The microstructure of VB₂-Ni anode and discharge capacity of VB₂/air battery were further investigated.

Experimental

Preparation of materials

The VB₂-Ni compound powders used in this work were prepared by ball-milled the mixture of VB₂ and Ni powders with different weight ratio (VB₂:Ni=1:1, VB₂:Ni=3:1) of VB₂:Ni using a high energy planetary ball miller (QM-3SP2). The VB₂ powder (2~5μm, 99.9% purity) and Ni powder (~2.2μm, 99.9% purity) were used as purchased without any further treatment. The weight ratio of the mixture to agate balls was selected to be 1:2. The ball-milling process was performed for 4 h with the velocity of 240 rpm under the protection of argon atmosphere in order to prevent the surface oxidation. After milling, the sheets of diameter 20 mm were formed by impressing mixture powders, and then the sheets were heat treated at 1050 °C for 30 min in tube furnace under the protection of argon atmosphere.

The air electrode consists of three layers: a catalyst layer, a current collecting layer, and a gas diffusion layer. The catalyst layer was made of synthesized manganese dioxide catalyst, active carbon and polytetrafluoroethylene. At first, the MnO₂ catalyst and active carbon were mixed uniformly, and then added appropriate anhydrous ethanol under stirring for 30 min. The PTFE (60 wt% emulsion) was added at last, and the mixture was stirred for 10 min. The catalyst layer was formed by a roller press (DYG-703R roller). The gas diffusion layer was made of acetylene black, PTFE and appropriate anhydrous ethanol. The fabrication process of gas diffusion layer refers to the preparation of the mentioned catalyst layer. Copper mesh was selected as a current collector. The catalyst layer and gas diffusion layer were pressed together with a copper mesh current collector in-between, under 20 MPa pressure for 1min. Then, the air electrode was finished by sintering at 200 °C for 30 min in vacuum. The details of preparation process can be found in earlier results from the literature [26-28]

Measurements

The microstructure of VB₂-Ni anode was characterized by scanning electron microscope (SEM, S-3400). Before SEM analysis, the electrodes removed from the test cells were rinsed with distilled water and then dried in air. The VB₂-Ni flake, air electrode and 7.3M KOH aqueous solution were used as anode, cathode and electrolyte, respectively. Once the fabrication process had been completed, the discharge capacity of VB₂/air battery was investigated by means of constant current discharge test (NEWARE 5V3A), and the change in voltage with time during discharge was measured. The active area of the cathode is 2.5 cm × 4 cm, the test current is 100 mA, and the cut-off voltage is 0.3V. At the same time, the discharge capacity of VB₂/air battery with unsintered

VB₂-Ni anode was also measured for comparison.

Results and discussion

Figure 1 shows the SEM images of sintered VB₂-Ni anode before and after discharge. As can be seen from figure 1(a), the net structure with high porosity was formed in VB₂-Ni25wt% anode after sintered at 1050 °C for 30 min. However, as shown in figure 1(b), the porosity of sintered VB₂-Ni50wt% anode was very low because of excessive Ni content in VB₂ anode. In the discharge process, the VB₂ acts as active material which takes place electrochemical reaction with KOH electrolyte. It is quite obvious that the increasing metal Ni content will decrease the VB₂ active material in anode. Thus, after discharge, as shown in figure 1(c), the VB₂-Ni25wt% anode presented much more porosity than that before discharge. Nevertheless, the porosity of VB₂-Ni50wt% anode nearly remain unchanged, which is most likely due to the excessive Ni encapsulates the VB₂ active material and then impedes the electrochemical reaction between VB₂ and KOH electrolyte.

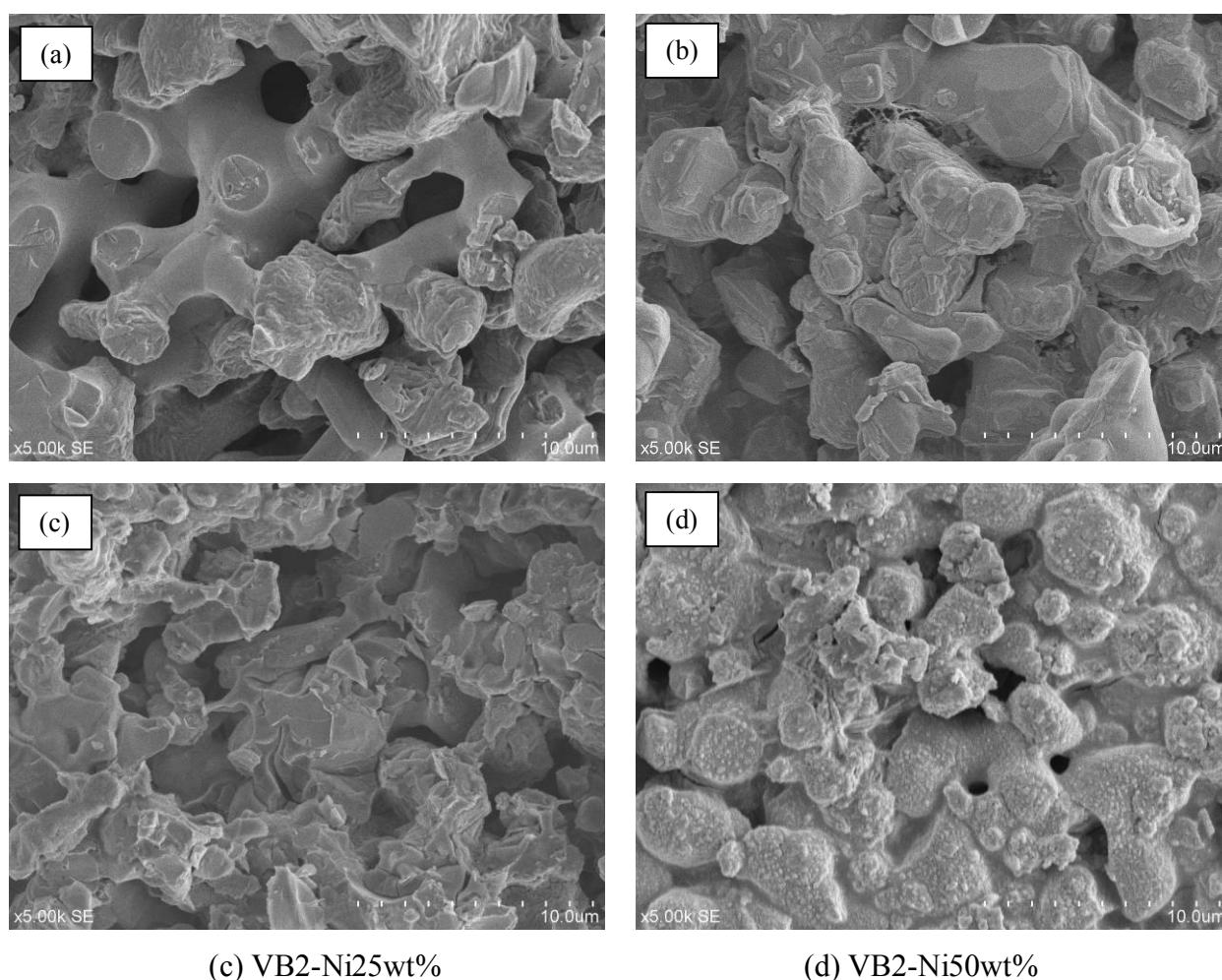


Fig.1. SEM images of sintered VB₂-Ni anode: (a) VB₂-Ni25wt% and (b) VB₂-Ni50wt% before discharge; (c) VB₂-Ni25wt% and (d) VB₂-Ni50wt% after discharge

Figure 2 shows the discharge capacity of VB₂/air battery with unsintered and sintered VB₂-25 wt%Ni and VB₂-50 wt% anode, respectively. As shown in the figure, the discharge capacities of VB₂/air batteries with sintered or unsintered VB₂-Ni25wt% anodes were both higher than that with VB₂-Ni50wt% anodes. The discharge capacity of VB₂/air battery with sintered VB₂-Ni25wt% anode reached 7574 mAh, which was much higher than that with unsintered VB₂-Ni25wt% anode. The enhancing discharge capacity of VB₂/air battery was due to the net structure of metal Ni

formed in VB₂-Ni anode when the anode sintered at 1050 °C for 30 min, and this net structure could deliver electrons efficiently. However, the discharge capacity of VB₂/air battery decreased when the Ni content in VB₂ anode increased to 50 wt%. The reason is that the VB₂ acts as the active material of electrochemistry for the VB₂ anode, and the more Ni content will lead to the fewer active material for VB₂/air battery. On the contrary, as it can be seen from the figure, the discharge capacity of VB₂/air battery with sintered VB₂-Ni50wt% anode decreased to 2843 mAh, which was much lower than that with unsintered VB₂-Ni50wt% anode. The main reason may be due to the fact that a part of VB₂ active material is encapsulated by metal Ni when the VB₂-Ni50wt% anode sintered, and then sharply decreases the discharge capacity of VB₂/air battery. This result is consistent with the above SEM images analysis.

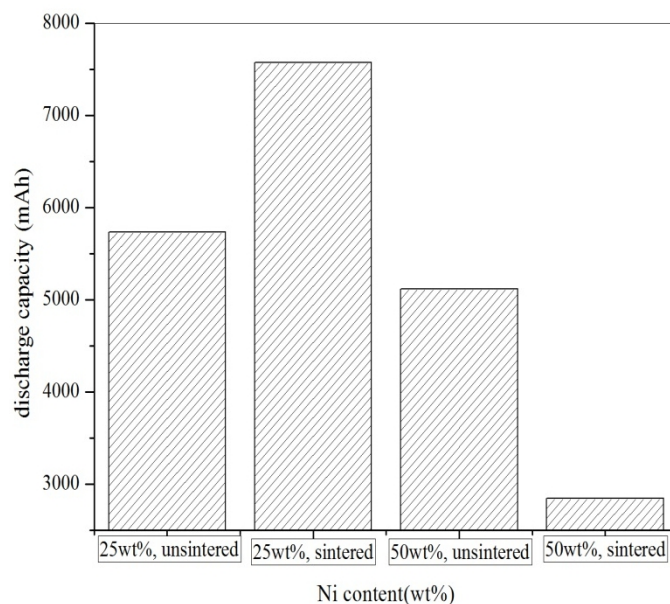


Fig. 2. The discharge capacity of VB₂/air battery with VB₂-Ni anode

Conclusion

In summary, the compound powders of VB₂ and Ni were mixed uniformly using planetary ball miller, and the discharge capacity of VB₂/air battery with VB₂-Ni as anode in 7.3M KOH aqueous electrolyte at room temperature and ambient pressure was investigated. The results show that the discharge capacity of VB₂/air battery reached 7574 mAh when Ni content was 25 wt% in VB₂-Ni anode and the discharge capacity would decrease with more Ni content. Meanwhile, the discharge capacity of VB₂/air battery with sintered VB₂-Ni25wt% anode was much higher than that with unsintered VB₂-Ni25wt% anode. However, the discharge capacity of VB₂/air battery with sintered VB₂-Ni50wt% anode was much lower than that with unsintered VB₂-Ni50wt% anode. Thus, the reasonable Ni content of VB₂ anode is 25 wt% for VB₂/air battery and the VB₂-Ni25wt% anode sintered at 1050 °C for 30 min is an effective way to improve the discharge capacity of VB₂/air battery.

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