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High capacity alkaline super-iron boride battery

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Abstract

A high capacity alkaline redox storage chemistry is explored based on a novel Fe^{6+}/B^{2-} chemistry. The alkaline anodes based on transition metal borides can deliver exceptionally high electrochemical capacity. Over 3800 mAh/g discharge capacity is obtained for the commercial available vanadium diboride (VB_2), much higher than the theoretical capacity of commonly used zinc metal (820 mAh/g) alkaline anode. Coupling with the super-iron cathodes, the novel Fe^{6+}/B^{2-} battery chemistry generates a matched electrochemical potential to the pervasive, conventional MnO_2–Zn battery, but sustains a much higher electrochemical capacity. Stability enhancement of super-iron boride battery is also studied. A zirconia coating effectively prevents both the decomposition of boride anodes and the passivation of Fe(VI) cathodes, and sustains facile both anodic and cathodic charge transfer. Reversibility of boride anodes is demonstrated with TiB_2 and VB_2. It is shown that these two boride anodes exhibit the reversibility in a certain extent.

Keywords: Boride anodes; Super-iron boride battery; Zirconia coating; Stabilization; Reversibility

1. Introduction

Electrochemical batteries have been widely used as convenient power sources for various portable electronic devices and electric vehicles. Searching for advanced electrode materials is a continuous need for the development of higher energy density batteries. A number of new materials, such as metal hydride and intercalation compounds have been successfully applied to the high performance Ni-MH and Li-ion batteries [1,2]. However, aqueous primary batteries, predominately used in consumer market, are still based on MnO_2 cathode and zinc metal anode. The battery chemistry remains almost the same as a century ago.

A new battery type, super-iron battery based on the high Fe(VI) cathodic charge storage was reported in 1999 [3]. Followed the primary alkaline super-iron battery, recently, rechargeable thin layer super-iron cathode has been reported [4,5], and a high performance composite Fe(VI)/AgO composite cathode stabilized by a 1% zirconia coating has also been successfully developed [6]. In 2004 it was reported that metal borides could be used as anodic alkaline charge storage materials [7,8]. Representative transition metal borides include TiB_2 and VB_2 which can store several folds more charge than a zinc anode through multi-electron charge transfer [7]:

$$TiB_2 + 12OH^- \rightarrow Ti(amorphous) + 2BO_3{}^{3-} + 6H_2O + 6e^- \quad (1)$$

$$VB_2 + 20OH^- \rightarrow VO_4{}^{3-} + 2BO_3{}^{3-} + 10H_2O + 11e^- \quad (2)$$

However, two obstacles were evident towards implementation of this alkaline boride (MB_2, M = Ti or V) anodic chemistry. There is a significant domain in which the boride anode materials corroded spontaneously generating hydrogen gas, and the electrochemical potential of the boride anodes was more positive than that of zinc. Therefore a boride MnO_2 cell was subject to decomposition, and secondly the voltage of this cell was low compared to the electrochemical potential of the pervasive Zn–MnO_2 redox chemistry. In our recent communication, we introduced a novel Fe^{6+}/B^{2-} battery chemistry in which the super-iron (Fe^{6+}) cathode provides the requisite additional electrochemical potential for the boride (B^{2-}) anode [9]. Therefore, the Fe(VI)–MB_2 couple generates a similar potential to the Zn–MnO_2 battery. In addition, the obstacles of the boride

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anode decomposition are overcome by the applying a zirconia hydroxide-shuttle overlayer on the anode particle surface [9]. This paper is a continuous study of the Fe^{6+}/B^{2-} redox chemistry. More boride anodes are studied in super-iron boride batteries. The reversibility of boride anodes is also investigated in alkaline electrolyte by coupling with NiOOH cathode.

2. Experimental

Batteries studied in this paper are prepared as 1 cm button cell configuration. The cells are prepared with a saturated KOH electrolyte. Preparation of the cathodes and anodes will be detailed in Section 3. Cathode materials used in this paper include MnO_2 (EMD, EraChem K60), NiOOH (taken from the commercial Ni-MH button cell (Powerstream®)) and lab synthesized K_2FeO_4 (97–98% purity, according to our previous publication [10,11]). Anode materials TiB_2 (10 μm powder), VB_2 (325 mesh powder) TaB (325 mesh), TaB_2 (325 mesh), MgB_2 (325 mesh), CrB_2 (325 mesh), CoB_2 (325 mesh), Ni_2B (powder, 30 mesh) and LaB_6 (powder, 10 μm) are from Aldrich®. Conductive medium used in cathode and anode preparation is 1 μm graphite (Leico Industries Inc.). Graphite foil served as the current collector is from Alfa Aesar®. The cells are discharged at a constant load (will be indicated in Section 3). In the secondary battery studies (with boride anode and NiOOH cathode), cells are additionally charged at a constant current of 4 mA. Primary discharge or charge/discharge cycling is measured as the cell potential variation over time, and is recorded with LabView Acquisition on a PC, and cumulative discharge, as milliampere hours, determined by subsequent integration.

3. Results and discussion

3.1. Various boride anodes super-iron batteries

Many transition metal borides have thermodynamic parameters and electronic conductivities similar to those of the corresponding transition metals [12,13]. Therefore, from the electrochemical energy conversion viewpoint, transition metal borides may constitute a large class of promising electrochemically active materials for batteries [14,15]. In addition to TiB_2 and VB_2, the use of, FeB and CoB as anode materials for batteries has also been previously mentioned [8]. But either FeB or CoB exhibits an anodic capacity less than TiB_2 and VB_2 [8]. In the study herein, various transition metal borides TaB, TaB_2, MgB_2, CrB_2, CoB_2, Ni_2B, and LaB_6 are considered as the anodes for alkaline battery. Similarly as TiB_2 and VB_2 [7], electrochemical potentials of the borides are more positive than zinc metal, thus the cell voltage of MnO_2–boride batteries are much lower than the pervasive, conventional MnO_2–Zn battery. The alkaline thermodynamic potential of the three electron reduction of super-iron cathodes Fe(VI → III) via Eq. (3), is approximately 250 mV higher than the one electron reduction of MnO_2 via Eq. (4), with potentials reported versus SHE (the standard H_2 electrode):

$$FeO_4{}^{-}+\tfrac{5}{2}H_2O+3e^{-} \rightarrow \tfrac{1}{2}Fe_2O_3+5OH^{-}, \quad E=0.60\,V \qquad (3)$$

$$MnO_2+\tfrac{1}{2}H_2O+e^{-} \rightarrow \tfrac{1}{2}Mn_2O_3+OH^{-}, \quad E=0.35\,V \qquad (4)$$

Table 1
Open circuit potentials (OCP) of various boride anodes alkaline super-iron (K_2FeO_4) batteries

Anode	OCP (V)
TaB	1.65
TaB_2	0.83
CoB_2	1.22
MgB_2	1.50
CrB_2	1.53
Ni_2B	1.30
LaB_6	1.16
VB_2	1.42
TiB_2	1.55

Electrolyte used is saturated KOH.

Coupling with super-iron cathode (K_2FeO_4), open circuit potentials of these super-iron boride batteries are listed in Table 1.

In addition to the previously studied TiB_2 and VB_2 [7,9], in Table 1, only the first two (tantalum) boride salts exhibit a degree of anodic charge storage, each of the other borides did not exhibit significant primary discharge behavior due to their high solubilities in alkaline solution or their reaction with alkaline electrolyte. As previously reported [7,9], the alkaline reduction of the TiB_2 anode produced amorphous titanium, and similarly we expect the reduction of TaB_2 can yield tantalum. According to the half cell oxidation reaction of TaB_2 (FW 202.57 g/mol) or TaB (FW 191.76 g/mol) to a Ta product, the theoretical (intrinsic) anodic reaction in an alkaline medium will yield:

$$TaB_2 + 12OH^{-} \rightarrow Ta + 2BO_3{}^{3-} + 6H_2O + 6e^{-} \qquad (5)$$

$$TaB + 6OH^{-} \rightarrow Ta + BO_3{}^{3-} + 3H_2O + 3e^{-} \qquad (6)$$

Intrinsic capacity of TaB_2 and TaB would accordingly be 793.8 and 419.3 mAh/g, respectively.

Discharge profiles of TaB or TaB_2 anode, K_2FeO_4 cathode button cells are shown in Fig. 1a. Button cells are prepared with excess cathode capacity and discharged at a low current to probe the anode's limits and characteristics. As seen in the figure, the TaB_2 exhibits an anodic storage capacity comparable to the widely used conventional alkaline zinc anode (820 mAh/g). Compared to their intrinsic capacity (793.8 mAh/g and for TaB_2 and 419.3 mAh/g for TaB), 88% for TaB_2 and 93% for TaB of the coulombic efficiency were obtained for these two anodes.

The discharge of TiB_2, rather than TaB_2, to the amorphous metal product is comparable to a significantly higher gravimetric charge storage capacity due to the lighter weight of this metal (47.87 g titanium/mol compared to 180.95 g tantalum/mol), in accord with Eq. (1). As seen in Fig. 1b, a significant advantage of the titanium boride anode is the higher capacity compared to the conventional alkaline zinc anode (820 mAh/g). The TiB_2 anode discharge is in excess of 1300 mAh/g at moderate discharge rates (a 3 kΩ load over a 1 cm diameter electrodes) and is in excess of 2000 mAh/g at low discharge rates (a 100 kΩ load discharge). In accord with Eq. (1), and a formula weight, $W = 69.5$ g/mol, TiB_2, has a net intrinsic 6 electron anodic capacity of $6F/W = 2314$ mAh/g (F is the Faraday constant).