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ORIGINAL PAPER

Electrooxidation and dischargeability of transition-metal borides as possible anodic materials in neutral aqueous electrolytes

Y. Wang · X. Y. Guang · Y. L. Cao ·
X. P. Ai · H. X. Yang

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Abstract A number of transition-metal borides were studied as anodic materials for neutral aqueous batteries. These borides are shown to have considerably high electrochemical activities in neutral electrolytes. The discharge capacities for TiB_2 reach 1,350 mAh g^{-1} at a constant current density of 50 mA g^{-1}, exceeding those for all the metal electrodes reported so far. Amorphous CoB_x can deliver a discharge capacity of >650 mAh g^{-1}, and even simply ball-milled FeB_x can also give a discharge capacity of >200 mAh g^{-1}. These results suggest the possible use of boride compounds as a large family of new anodic materials for constructing neutral aqueous batteries with high electrochemical capacity and rate capability.

Keywords Metal borides · Anodic materials · Aqueous batteries · Neutral electrolytes · Electrooxidation

1 Introduction

Aqueous batteries commercialized so far are mostly based on the use of strongly acidic or alkaline electrolytes; examples are Pb–PbO_2, Zn–MnO_2, Ni–Cd batteries. In comparison, neutral electrolyte batteries are now experiencing reduced market share because of their poorer discharge performance, although the use of neutral electrolytes for batteries has the advantages of lower cost and less pollution in battery manufacture and usage. The obstacles hindering the development of neutral electrolyte batteries arise mainly from two limitations: one is the lower ionic conductivity of neutral electrolyte solutions compared with acidic or alkaline solutions, which leads to severe deterioration of battery performance in high-drain applications. The other difficulty is the poor electrochemical utilization of common metal anodes in neutral electrolyte solutions due to surface passivation. For example, the discharge capacity of traditional ‘dry cells’ (Zinc chloride cell) is only 20% of that of alkaline Zn–MnO_2 cells [1].

Recently, we investigated the multi-electron oxidation behaviors of some metal borides in alkaline electrolytes [2, 3]. Their exceptional discharge capabilities can be realized in laboratory batteries [4, 5]. In order to reveal the working mechanism for the electrochemical activation of these metal borides, we also examined the electro-oxidation properties of metal borides in various neutral electrolytes and found that some transition metal borides have considerable electrochemical activity and can serve as high capacity anode materials for construction of aqueous batteries using neutral electrolytes. In this article, we report the electrochemical properties and discharge characteristics of some crystalline and amorphous metal borides as anodic materials in neutral aqueous solutions.

2 Experimental

2.1 Materials and electrode preparations

Crystalline transition-metal diborides (VB_2 and TiB_2, 325 mesh powder) were purchased from Aldrich and used as received. Amorphous Fe–B and Co–B alloy particles were

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Y. Wang (✉)
State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China
e-mail: ywang@whut.edu.cn

X. Y. Guang · Y. L. Cao · X. P. Ai · H. X. Yang
Department of Chemistry, Wuhan University, Wuhan 430072, China

synthesized by chemical reduction of bivalent iron and cobalt sulfate with aqueous sodium borohydride solution, respectively [3]. Transmission Electron Microscope (TEM) images and X-ray diffraction (XRD) patterns for Fe–B and Co–B alloys can also be found in [3]. The chemical composition of Fe–B and Co–B alloy particles have an atomic ratio (Fe:B or Co:B) of 1.75 ~ 1.9, as determined by inductively coupled plasma (ICP) analysis using a JY38S spectrometer. All chemical reagents were of analytical grade (Shanghai Chemical Reagent Company) and used as received without further purification.

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

The voltammetric measurements were performed in a three-electrode cell using a small piece (about 9 mm^2) of the boride electrode as working electrode, a large area air electrode as counter electrode and a saturated Ag/AgCl as reference (0.197 V. v. SHE). The preparation procedures of the air electrode were similar to those described elsewhere [6, 7]. The discharge performances of the boride electrodes were evaluated by galvanostatic discharge experiments using laboratory cells with 6 cm^2 boride electrode as anode, 25 cm^2 air electrode as inexhaustible cathode and 2 mol L^{-1} KF solution as electrolyte.

2.2 Product analysis

The soluble discharge products in the laboratory cells were qualitatively and quantitatively analyzed by ICP spectrometry using a Perkin Elmer Optima 4300DV spectrometer. The solid discharge products in the electrodes were measured by powder X-ray diffraction (XRD) using a SHIMADZU Lab XRD-6000 diffractometer with CuKα source. Before XRD analysis, the electrodes removed from the test cells were rinsed with distilled water and then dried in air. The scan speed was set at 4° min^{-1} and data were collected over a scattering angle range of 10–80°.

3 Results and discussion

3.1 Crystalline metal diborides

To examine the anodic behavior of metal borides in neutral electrolytes, we firstly measured the cyclic voltametric (CV) responses of TiB_2 in a variety of electrolyte systems such as KCl, K_2SO_4, K_2CO_3 and $KClO_4$ solutions and found that there was no anodic current response for the boride electrode in these electrolytes. However, in the case of KF solution, the TiB_2 electrode showed a distinct large anodic band between −0.68 V and −0.28 V, as shown in Fig. 1, suggesting the feasible electrochemical oxidation of TiB_2, although neither elemental Ti nor B is electrochemically active in the electrolyte.

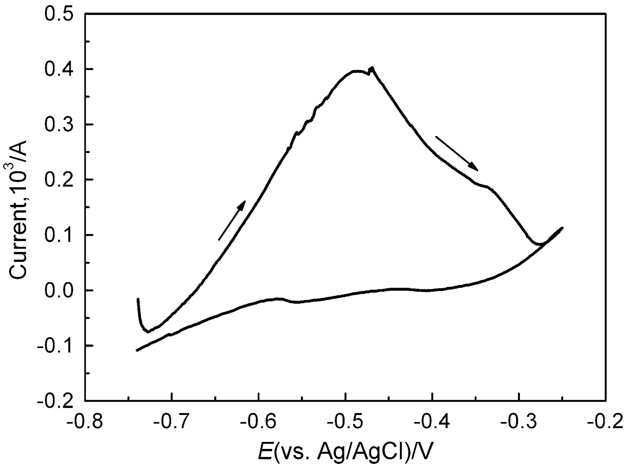

Fig. 1 Cyclic voltammogram of TiB_2 (1.8 mg) electrodes in a 2 mol L^{-1} KF solution. Potential sweep rate: 0.02 mV s^{-1}

To ensure the practical dischargeability of TiB_2 as an anodic material, we constructed simulated TiB_2-air cells and discharged the cells at constant current densities. Figure 2 shows a typical discharge curve of a TiB_2 powder electrode. The discharge profile of the TiB_2 electrode shows a very flat plateau at about 0.6 V with a capacity output of over 1,300 mAh g^{-1} at a current of 50 mA g^{-1}. This value is not only several times higher than the practical capacity of zinc in chloride solution(~ 200 mAh g^{-1}), but also exceeds the theoretical capacities of several common metals such as Zn, Cd, Cu and Fe which are used as anodes for aqueous batteries.

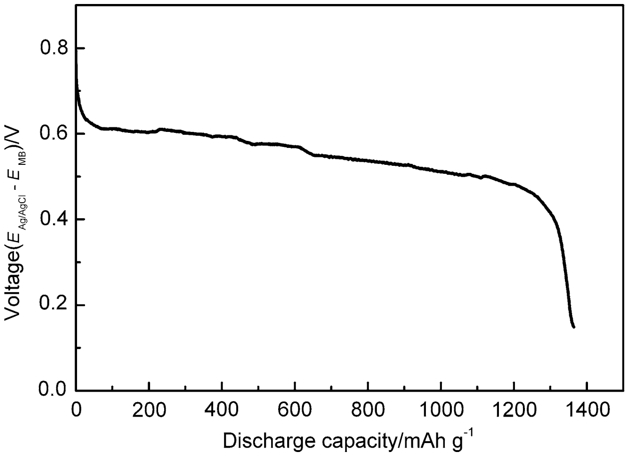

Fig. 2 Discharge curve of TiB_2 electrode in a 2 mol L^{-1} KF aqueous solution at 50 mA g^{-1}. The voltage profiles were recorded as E (Ag/AgCl) − E (metal boride)

To identify the reaction mechanisms of the diboride electrodes, we attempted to characterize the discharge products, either as solid phases on the electrodes or as soluble species in the electrolyte. Figure 3 shows the XRD patterns of a TiB_2 electrode before and after discharge. It is clear from Fig. 3 that the XRD lines of TiB_2 all decrease and accordingly a number of new XRD signals characteristic of crystalline phases of KBF_4 [8] are observed from the discharged electrode, implying that the anodic reaction of the TiB_2 electrode probably proceeds though the electrochemical oxidation of boron. In addition, it is found from ICP analysis of the electrolyte composition that the discharge product of TiB_2 appears predominately in the form of boron compound, and there is only an indiscernible amount of titanium detectable in the discharged electrolyte. Thus, the possible electrochemical oxidation and discharge reaction of TiB_2 can be expressed as

$$TiB_2 + 8F^- \rightarrow Ti + 2BF_4^- + 6e^- \qquad (1)$$

According to Eq. 1, the theoretical capacity of TiB_2 is 2,314 mAh g^{-1} if all the boron atoms are oxidized to B (III). Actually, the realized discharge capacity of the TiB_2 electrode is 1,350 mAh g^{-1}, about 58% of its theoretical capacity. This capacity utilization is not too low in comparison with the electrochemical inactivity of common metal anodes in neutral aqueous electrolytes. The incomplete discharge of the boride electrode is most likely due to surface blockage of sparingly soluble KBF_4 deposit as shown from XRD evidence in Fig. 3.

Very similar anodic behavior to the TiB_2 electrode can also be observed from other transition metal diborides. Figure 4 shows the cyclic voltammogram of a VB_2 electrode in 2 mol L^{-1} KF solution. Analogously, the VB_2 electrode also shows a strong irreversible oxidation band in the anodic scan from −0.60 to −0.20 V, which resembles very much the CV feature of TiB_2 except for the band position shifted ca. 80 mV to the more negative region. Also, the electrochemical oxidation of VB_2 can only be observed in aqueous KF solution but not in other neutral solutions using chlorides, sulfates and perchlorates. The discharge behavior of the VB_2 electrode is given in Fig. 5. The discharge capacity can reach 500 mAh g^{-1}, showing a quite strong dischargeability. Although the discharge voltage and capacity of the VB_2 electrode are considerably lower than that of the TiB_2 electrode and may not be practical for battery applications, the results from the VB_2 material do provide additional experimental evidence for the electrochemical activity of metal borides. Compared to the TiB_2 electrode, the VB_2 electrode shows a potential delay at discharge (Fig. 5). At present, we cannot give a clear explanation for this phenomenon. Possibly, this potential delay is due to the formation of some types of dense fluorides on the VB_2 surface in the KF solution, which dissolve slowly with development of the discharge process.

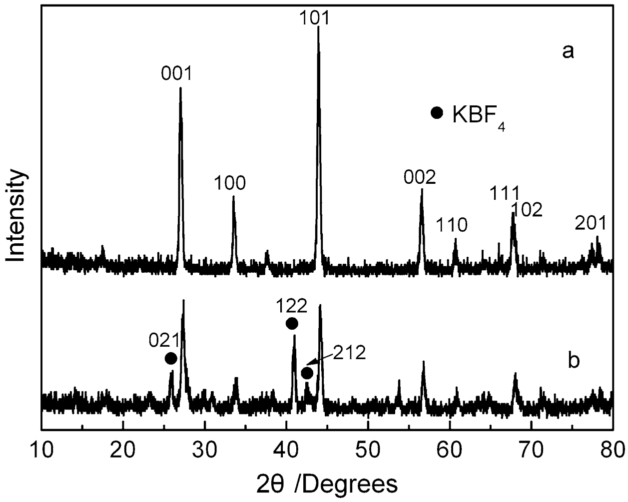

Fig. 3 XRD patterns of TiB_2 anodes: a. before discharge, and b. after completely discharged to 0.2 V (vs. Ag/AgCl)

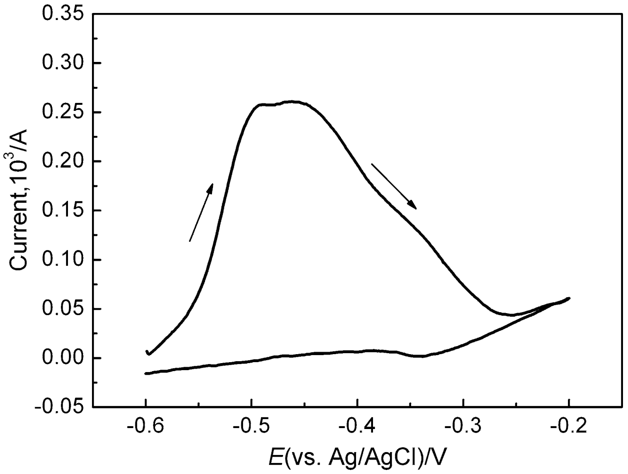

Fig. 4 Cyclic voltammogram of VB_2 (1.8 mg) electrode in a 2 mol L^{-1} KF solution

3.2 Amorphous metal borides

In order to ascertain if the observed electrochemical activity of the metal borides is a general phenomenon for different metal borides, we synthesized amorphous metal boride particles and characterized their electrochemical behavior in neutral electrolyte solution.

Figures 6, 7 show the CV curves of the Co–B and Fe–B electrodes in 2 mol L^{-1}KF solution, respectively. In parallel experiments, pure elemental Co and Fe or B alone did not give an appreciable current response in the sweeping potential region, because of surface passivation. However, in the case of Co–B (Fig. 6), a large anodic current peak appeared with the onset of oxidation at about −0.58 V,

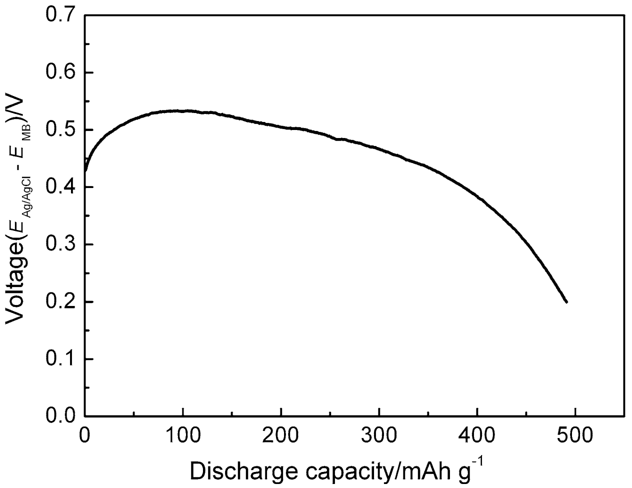

Fig. 5 Discharge curve of VB_2 electrode in a 2 mol L^{-1} KF aqueous solution at constant current of 50 mA g^{-1}. The voltage profiles were recorded as E (Ag/AgCl) – E (metal boride)

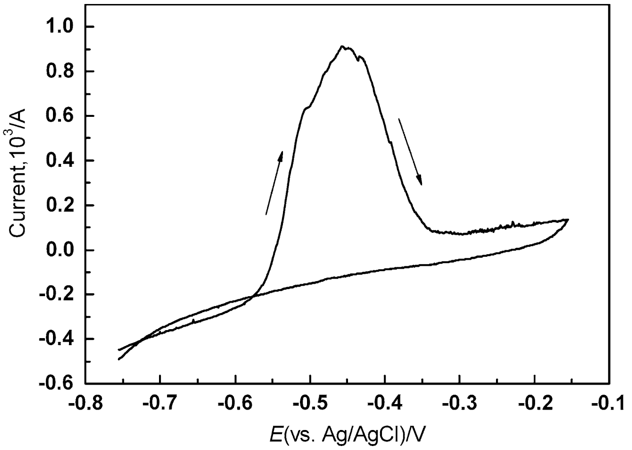

Fig. 6 Cyclic voltammogram of Co-B electrodes in a 2 mol L^{-1} KF solution. Potential sweep rate was set at 0.1 mV s^{-1}

suggesting the electrochemical activation of the Co–B alloy. Similarly, the Fe–B electrode (Fig. 7) also showed a distinct oxidation peak centered at about −0.70 V. Since both the oxidation potentials of elemental cobalt ($Co^{2+} + 2e^- =$ Co, $E^0 = -0.277$ V vs. NHE [9]) and iron ($Fe^{2+} +$ $2e^- =$ Fe, $E^0 = -0.44$ V vs. NHE [9]) are much more positive than the observed CV peaks in Figs. 6, 7, respectively, it may be exclusive to attribute these CV peaks to the anodic oxidation of boron in the boride electrodes.

Figure 8 show the discharge curves of the Co–B electrode. The discharge capacity of the Co–B electrode can reach 670 mAh g^{-1} at constant current of 50 mA g^{-1} and 620 mAh g^{-1} even at a quite high rate of 100 mA g^{-1},suggesting the considerable anodic capability of these materials in neutral electrolyte. Similar anodic behavior can also be seen from the Fe–B electrode. As shown in Fig. 9, the Fe–B electrode can deliver a discharge capacity of 360 mAh g^{-1} at 50 mA g^{-1} and the discharge capacity decreases only slightly at increased current density of 100 mA g^{-1}. In order to distinguish whether the discharge capacity of the boride electrodes come from the oxidation of boron or metal elements, we carried out comparative discharge experiments using very fine Co and Fe powders (~10 μm) as anodes and found that there was no capacity observable for the Fe powder electrode and only a small capacity of less than 100 mAh g^{-1} for the Co powder electrode. These results indicate that the discharge capacities of the metal borides are contributed to by the electrochemical oxidation of elemental boron in the boride compounds.

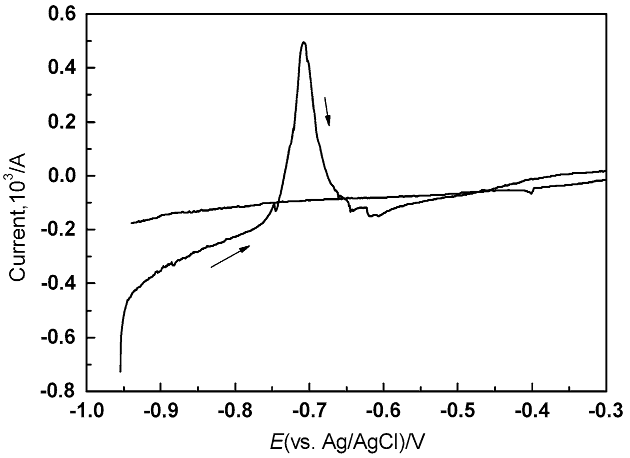

Fig. 7 Cyclic voltammogram of Fe-B electrodes in a 2 mol L^{-1} KF solution. Potential sweep rate was set at 0.02 mV s^{-1}

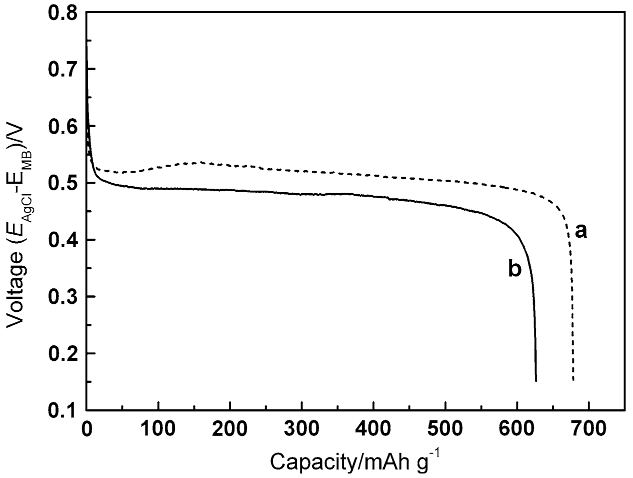

Fig. 8 Discharge curve of Co-B electrode in a 2 mol L^{-1} KF aqueous solution at constant current of: a. 50 mA g^{-1} and b. 100 mA g^{-1}

3.3 Discharge mechanisms

The experimental results given above clearly indicate that the electrochemical activation of elemental B takes place in

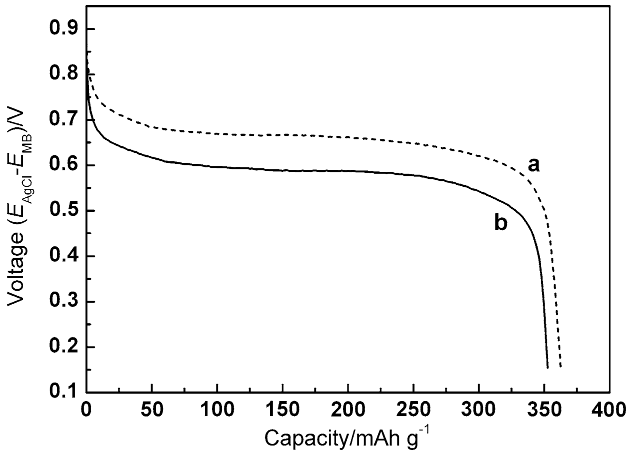

Fig. 9 Discharge curve of Fe-B electrode in a 2 mol/L KF aqueous solution at constant current of: a. 50 mA g^{-1} and b. 100 mA g^{-1}

both the crystalline and amorphous borides in neutral electrolyte. An important question is why the boron atoms can be electrochemically active in borides, while elemental boron alone and the transition metal elements are electrochemical inert. To understand these phenomena, several factors must be taken into account.

Firstly, boron is a very electronegative element with an equilibrium potential of -1.06 V ($BF_4^- + 3e^- = B + 4F$, vs. NHE) in aqueous KF [9]. From the thermodynamic point of view, the electrochemical oxidation of boron in fluoride solution is thermodynamically allowable to produce chemically stable tetrafluoroborate ions. This may explain why the anodic oxidation of boron can only be observed in fluoride solution but not in other neutral electrolytes.

Secondly, though boron should have a large thermodynamic tendency to act as a high energy density anodic material, the electrochemical accessibility for boron oxidation has been thought to be impractical probably due to the very poor conductivity (1×10^{-6} to 7×10^{-8} S cm^{-1} [10]) of boron. However, in the case of boride compounds, boron is uniformly dispersed in the metal matrix, and the metal borides have electronic conductivities similar to common metals [11]. Thus, the conductive restraint of elemental B is eliminated. Besides, in the electronic structure of metal borides, there exists a finite ionic bond formed by electron donation from the metal atoms to the B atoms [12]. As a result, the chemical stability of the B atoms is weakened, which facilitate the electrochemical liberation of electrons from the B atoms. Since the strength of the ionic bonds between boron and different mental in borides is different, the effect of different metals on boron activation will be different. The higher discharge plateau for TiB_2 than that for VB_2 may indicate a strong ability of titanium for electrochemical activation of boron compared with vanadium.

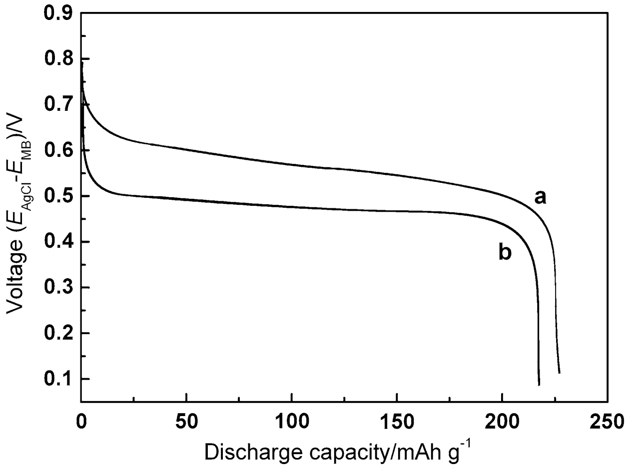

Fig. 10 Discharge curves of a $FeB_{0.5}$ electrode (a) and a $CoB_{0.5}$ electrode (b) in a 2 mol L^{-1} KF solution at constant current of 50 mA g^{-1}

To confirm this suggestion, we prepared a well-dispersed mixture of boron and transition metal powders by mechanical ball milling and used the materials for comparative study. Figure 9 shows the discharge curves of ball-milled $FeB_{0.5}$ and $CoB_{0.5}$ in KF solution. As shown in the Fig. 10, both the ball-milled $FeB_{0.5}$ and $CoB_{0.5}$ powders can deliver a discharge capacity of ~220 mAh g^{-1} with quite flat discharge plateaus at about 0.5 and 0.6 V, respectively. Since pure Fe or Co powders cannot give any practical capacity in KF solution, the discharge capacity as observed must be due to the anodic oxidation of boron. Because the simple ball milling process cannot provide a uniform dispersion of elemental boron and metals at atomic level, the electrochemical utilization of boron is relatively low. Nevertheless, these results suggest that as long as the boron atoms are very well electronically wired, the electrochemical oxidation of boron is expected.

4 Conclusions

We prepared a number of transition-metal borides and studied their electrochemical properties for possible use as aqueous negative electrode materials. The materials show superior high electrochemical activities in neutral electrolytes. The discharge capacities observed for TiB_2 reach 1,350 mAh g^{-1} at a constant current density of 50 mA g^{-1}, exceeding the performance of all the metal electrodes considered. Amorphous CoB_x can deliver a discharge capacity of 600 mAh g^{-1}, and even simply ball-milled FeB_x can also give a discharge capacity of 200 mAh g^{-1}. It is suggested that the electrochemical activity of the metal borides originates from the electrochemical activation of boron atoms in the compounds, which is brought about by weakening of the covalent B–B bond due to the electron back donation of metal atoms and the improved electron conduction in boron atoms.

The results suggest that metal borides may serve as a large family of new anodic materials for constructing neutral aqueous batteries with high electrochemical capacity and rate capability. Boron also has potential to serve as a high energy density anode material simply by effective electronic wiring.

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