Multi-electron reaction is a type of electrode reaction, which has very important significance for the development of new green battery system [1]. It is expected that the multi-electron reactions of light elements to help secondary batteries achieving much higher energy densities than conventional single-electron system [2]. In fact, the crucial factor for constructing high energy density battery systems is developing multi-electron materials, namely, one mole such material can achieve more than one mole electron transfer in a specific electrochemical reaction process [3]. In recent years, some typical multi-electron electrode materials, such as metal borides, metal fluorides, sulfur composite electrodes and ferrates have shown their promising potential.

In aqueous solution based secondary batteries, metal borides had shown excellent potential as multi-electron materials. For instance, VB$_2$ and TiB$_2$ in alkaline solution can achieve 11-electron and 6-electron reactions, and get electrochemical capacities of 3100 mAh/g and 1600 mAh/g, respectively [4]. They successfully show how multi-electron reactions help increasing the capacities of the electrode materials. Furthermore, several other metal borides have come into sight.

We synthesized amorphous Co-B powders via borohydride reduction of bivalent cobalt chloride, and heat-treated from 50°C to 700°C to get different Co-B alloys. With increasing heat-treating temperatures, the Co-B alloy powders change form an amorphous phase to a mixture of CoB and metal Co; and finally get a pure metal Co phase. It is found that the structural evolutions of Co-B alloys have remarkable effect on their discharge characteristics. For the Co-B alloy treated at 500°C, it contains crystal CoB, in which both Co and B are activated, and results in a superior cyclicly [5].

In order to improve the electrochemical performances of Co-B alloy, we use a vacuum freeze-drying method [6]. When compares with the Co-B synthesized via chemical reduction method, the one originated from vacuum freeze-drying method has better crystallinity, as well as a uniform particle size distribution. In addition, this material exhibits good reversibility as well as good cycle stability, and achieves a maximum discharge capacity of 437 mAh/g at a constant current density of 300mA/g, which is much superior to that of the Co-B alloy from traditional chemical reduction method. Furthermore, for the maximum discharge capacity of 437 mAh/g, the total electric charge n is 4, which indicates the Co-B alloy from vacuum freeze-drying method can carry on a 4-electron reaction [7].

Ternary Mg-Co-B alloys, have also been successfully synthesized through borohydride-reduction of divalent metal salts, and then applied in alkaline secondary batteries as reversible anode materials. The electrochemical performances of the Mg-Co-B alloys are affected by their microstructures, including their crystalline phase and surface structure. All of the as-prepared alloys show excellent electrochemical reversibility. Moreover, the Mg-Co-B-300 alloy has been found to consist of a combination of amorphous and crystalline phases, and achieves a discharge capacity of 336mAh/g at a rate of 60mA/g, which is promising for practical application in alkaline secondary batteries [3].

In consideration of high cost of cobalt-based borides, cheap and abundant elements may be good choices for practical application. FeB alloy was successfully prepared by an electric arc method, and used as the anode material for alkaline secondary batteries. It is found that the multi-electron reaction of the FeB alloy during charge-discharge process is not accomplished in one step, but two or more steps. And some steps of the multi-electron reaction of the FeB alloy are irreversible. The FeB alloy achieves an excellent reversible discharge capacity of 312 mAh/g at a charge input of 360 mAh/g, as well as a good cycleability. Owing to the abundance of Fe in the earth, FeB alloy can be a promising low-cost and high performance electrode material for alkaline secondary batteries [2].

In a word, metal borides have set good examples for multi-electron reactions in aqueous solutions, and they are potential high-capacity anode materials for new alkaline secondary batteries.

Acknowledgments
This work was supported by the National 973 Program of China (2002CB211800, 2009CB220100), and the Program for New Century Excellent Talents in University (Grant No. NCET-12-0047).

References