

Effect of synthesizing temperature on the electrochemical properties of nitrogen-doped Co-B alloys

Y L Liao, W Zhao, S J Qiu¹, H L Chu, Y J Zou, C L Xiang, H Z Zhang, F Xu, L X Sun

Guangxi Key Laboratory of Information Materials, Guangxi Collaborative Innovation Centre of Structure and Property for New Energy and Materials, and School of Materials Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, PR China

¹ E-mail: qiushujun@guet.edu.cn

Abstract. Using urea as nitrogen source, nitrogen-doped Co-B alloys were prepared by chemical reduction method at different reaction temperatures (25, 50, and 75 °C). The structure and surface morphology were characterized by XRD and SEM. Then they were used as negative electrode materials for alkaline secondary batteries (ASBs). The electrochemical properties were measured by galvanostatic charge-discharge, electrochemical impedance spectroscopy (EIS), and anodic polarization (AP). The experimental results show that the lower the synthesizing temperature is, the better the electrochemical performance of nitrogen-doped Co-B alloy is. For example, nitrogen-doped CoB alloy prepared at 25 °C has an initial discharge capacity of 825.8 mAh/g. After 100 charge/discharge cycles, the discharge specific capacity has remained to be 369.5 mAh/g with capacity retention of 44.7%.

1. Introduction

With the development of social economy, the consumption of fossil energy is remarkably increased, which results in the coming of energy crisis and environment pollution. The development of green new energy can not only resolve energy problems, but also mitigate environment pollution. But new energies such as tidal energy, wind energy and sun energy, are needed to be converted into electrical energy to be stored in specific devices [1]. As a kind of energy storing device, alkaline secondary battery (ASB) employing alkaline aqueous solution as electrolyte is a general term. Among ASBs, nickel/metal hydride (Ni/MH) batteries are used as power supply for electronic products and portable electrical tools in recent years because of high specific energy, low cost, and stable functions in a wide temperature range [2-4]. Current ASB's negative electrode materials including Fe [5], Zn [6] and rare earth-based hydrogen storage alloys [7] cannot meet the ever-increasing requirements due to low capacity and fast capacity fading. Therefore, it is urgent to develop new materials used as negative electrodes.

Initially, Co-B alloy received an extensive research because it can accelerate hydrolysis of metal borohydride to produce hydrogen [8]. Later, some researchers found that it exhibited a reversible charge and discharge capacity in alkaline electrolyte, so they tried to improve its overall electrochemical properties [9]. As negative electrodes in ASBs, the theoretical electrochemical capacity and cycle stability of Co-B alloy have achieved a great progress compared to commercialized AB₅-type alloy and Mg₂Ni-type alloy [4]. Furthermore, Co-B alloy does not need any activation in



charge/discharge cycles, which means that it can achieve its maximum discharge capacity at the first cycle. Therefore, Co-B alloy has great potential to be used as negative electrode in ASBs.

Herein, urea was introduced into the chemical reduction process to prepared nitrogen-doped Co-B alloy in order to further improve the electrochemical properties. Also the synthesizing temperature was systematically studied, especially its effect on the morphology, structure and electrochemical properties of Co-B alloys. There was a literature recording that urea can be broken down when the temperature reaches 90 °C [10]. In this study, the synthesizing temperatures should be lower than its decomposition temperature. Therefore, 25, 50, and 75 °C were selected as the synthesizing temperatures.

2. Experimental

2.1. Materials

CoCl₂·6H₂O (≥99%, Xilong Scientific), NaBH₄ (>98.0%, Tianjin Guangfu Fine Chemical Research Institute), CO(NH₂)₂ (>99.3%, Alfa Aesar), Ni powder (99.999%, Tianjin Jinbolan Fine Chemical Co., Ltd.), KOH (≥85%, Xilong Scientific). All raw materials were used without any further purification.

2.2. Sample preparation

First, 8.0 g NaBH₄ was dissolved in 30 mL distilled water to obtain solution A [11]. 10.0 g CoCl₂·6H₂O and 3.0 g CO(NH₂)₂ were dissolved in 60 mL distilled water to obtain solution B. Solution B was kept at 25 °C for 1 h using oil bath, and then solution A was dropwise added into solution B under moderate stirring. After the complete addition, this mixed solution was kept in oil bath at constant temperature of 25 °C until there was no gas bubbles produced. After naturally cooling to room temperature, the resulting sample was obtained through filtration and washing with distilled water and absolute ethanol for three times, and dried in vacuum at 60 °C for 12 h. Other samples were prepared under the same condition except for synthesizing temperatures. Here, these three samples were denoted by Y₂₅, Y₅₀, and Y₇₅ according to the synthesizing temperatures of 25, 50, and 75 °C, respectively.

2.3. Characterization

The crystal structure and surface morphology of nitrogen-doped Co-B alloys were characterized by X-ray Diffraction (XRD, Bruker-D8 Advance, Germany) and scanning electron microscopy (SEM, QUANTA FEG450, USA). The composition was measured by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima 8000, Perkin-Elmer, USA), and the content of N was measured by a CHNS elemental analyzer (EA, vario EL cube, Germany).

2.4. Electrochemical tests

About 100 mg of Co-B alloy powder and 300 mg of nickel powder was uniformly mixed, and then was pressed into a circular pellet of ø13 mm under 22 MPa pressure. Each side of the pellet was covered with a rounded foam nickel sheet of about ø25 mm, and then pressed at 4 MPa and spot-weld at the edge of foam nickel. The electrochemical tests were carried out in a standard three-electrode cell, including a Hg/HgO reference electrode, a Ni(OH)₂/NiOOH counter electrode, and a fabricated working electrode in 6 M KOH solution. Galvanostatic charge-discharge and high rate discharge performance tests were carried out on an automatic battery testing system (LAND-CT2001A, China). The electrochemical impedance spectroscopy (EIS) and anodic polarization (AP) were conducted on an electrochemical workstation (Zahner Elektrik IM6e, Germany). The testing temperature was held at 25 (±1) °C.

3. Results and discussion

3.1. Sample composition and structure

The composition of as-prepared Co-B alloys determined by ICP is $\text{CoB}_{0.40}$, $\text{CoB}_{0.33}$, and $\text{CoB}_{0.32}$ for Y_{25} , Y_{50} , and Y_{75} , respectively. Obviously, the content of B in these samples is decreased with the increase of synthesizing temperature. This result is consistent with the previous results reported by Lv et al., in which B content in Co-B alloy synthesized at 60 °C was higher than the sample prepared at 90 °C [4]. It has been reported that $\text{CO}(\text{NH}_2)_2$, as a precipitant, reacts with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and then produces an intermediate product that has a catalytic effect for accelerating the hydrolysis of NaBH_4 [12]. Meanwhile, the increase of the synthesizing temperature could also accelerate the hydrolysis of NaBH_4 to a certain extent. These factors result in the decrease of BH_4^- concentration, which leads to the reduction of B content in the samples. EA results show that the nitrogen content is 0.645, 0.560, and 0.470 wt% for Y_{25} , Y_{50} , and Y_{75} . This result confirms the successful doping of nitrogen in Co-B alloys. Clearly, the higher synthesizing temperature gives rise to a lower nitrogen content. The variation trend of N content is the same as B in these samples. This may be resulting from the formation of ultrafine powder particles from the nucleation between Co atoms and Co-B alloys and it can be regarded as a catalyst, which further promotes the reaction between B and N to form BN precipitation. Then BN precipitation is coated on the surface of Co/CoB particles [13]. Under the combined action of B and N, the loss of active material could be reduced effectively, even in the following charge/discharge cycles.

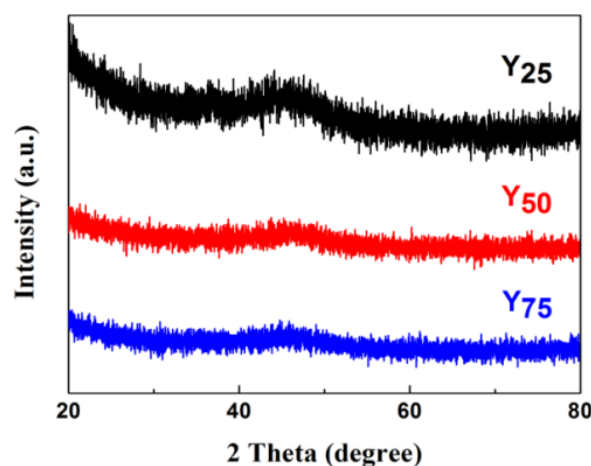


Figure 1. XRD patterns of as-prepared Co-B alloys.

Figure 1 shows the XRD patterns of three Co-B samples. No obvious crystal diffraction peaks are observed except for a broad peak at $2\theta = 45^\circ$. This is consistent with the published results [14], indicating that nitrogen-doped Co-B alloys are in an amorphous state. SEM images and particle size distribution of Co-B alloys are shown in figure 2. It can be found that the three samples are free of agglomeration and the particles are evenly distributed with very fine particles. The average particle size is determined to be 59.7 nm for Y_{25} , 51.9 nm for Y_{50} , and 48.1 nm for Y_{75} . This phenomenon is in line with the reported result [4]: with the increase of reaction temperature, the particle size of the alloy is decreased accordingly. This can be attributed to the change of nucleation rate at different temperatures.

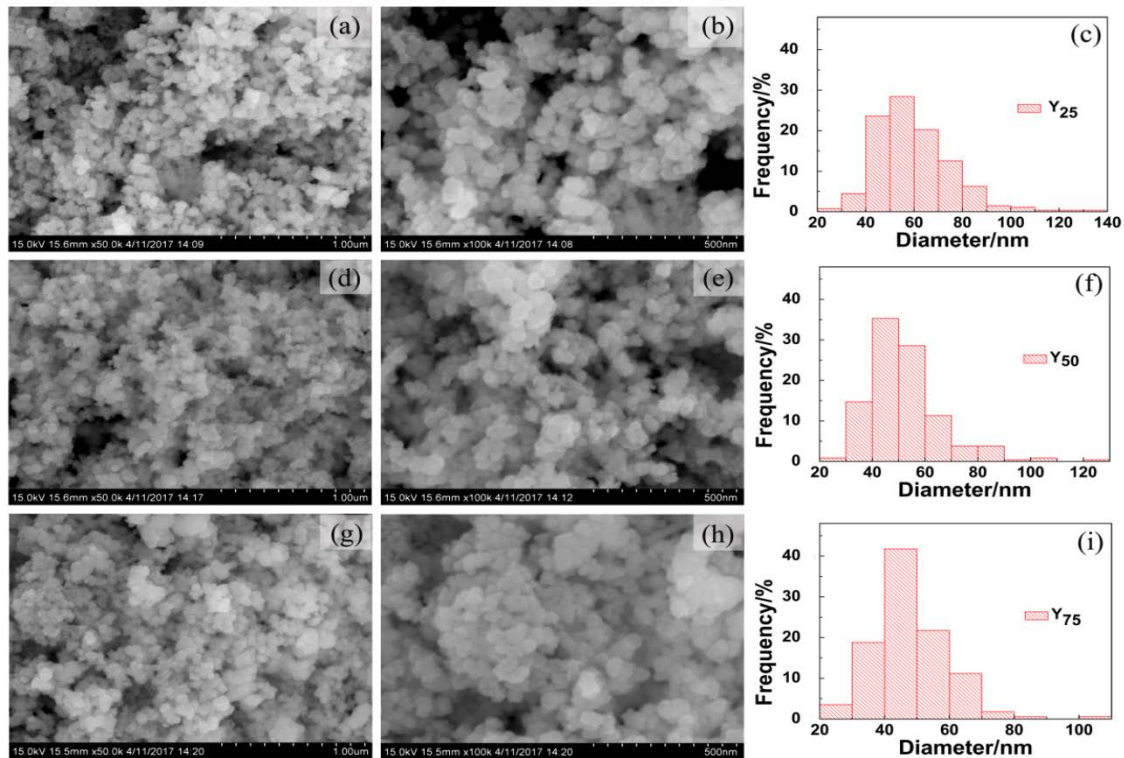
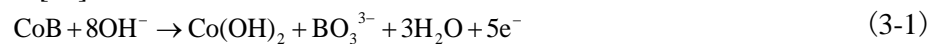


Figure 2. SEM and particle size distribution: (a, b, c) for Y₂₅, (d, e, f) for Y₅₀, and (g, h, i) for Y₇₅.

3.2. Electrochemical properties

Figure 3 shows the cycling performance of three alloy electrodes. The discharge capacity is significantly increased with the decrease of the synthesizing temperature. It must be mentioned that Y₂₅ has a maximum discharge capacity of 825.8 mAh/g. After 100 charge/discharge cycles, the discharge capacity of Y₂₅, Y₅₀, and Y₇₅ is 369.5, 339.8, and 315.2 mAh/g, respectively. Lv et al. [4] prepared CoB alloy with CoSO₄·7H₂O and NaBH₄ at different synthetic temperatures without the introduction of urea. Their sample prepared at 60 °C has a discharge capacity of 388.8 mAh/g after 60 cycles. In our case, the discharge capacity of nitrogen-doped Co-B alloys is 429.4, 387.9 and 364.4 mAh/g after 60 cycles for Y₂₅, Y₅₀ and Y₇₅, respectively. Zhao et al. prepared CoB alloy through the reaction of CoCl₂·6H₂O and NaBH₄ under ultrasonication, which effectively improved the electrochemical performance of Co-B alloy with a maximum discharge capacity of 858.1 mAh/g. After 100 cycles, the discharge capacity is 322.6 mAh/g with capacity retention of 37.6% [11]. In our study, each sample achieves its maximum discharge capacity at the first cycle, but the capacity is decreased rapidly in the first few cycles. This can be attributed to the participation of B element during the first few cycles, which contributes to a high specific capacity of primary discharge. But its oxidation process is irreversible. In this case, the alloy electrode has the following reactions in the initial discharge process[14]:



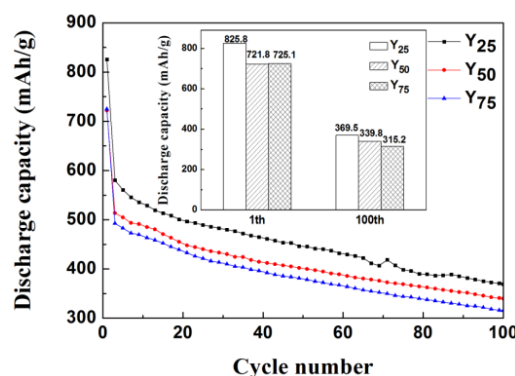


Figure 3. Cycling performance with discharge capacity at the 1st and 100th cycle shown in the inset.

At the same time, BO_3^{3-} is gradually dissolved into alkaline electrolyte, which thus increases the fresh surface of the alloy in this way. This indicates an increment of the electrochemical reaction area, which makes the reaction easier to take place and thereby improves the electrochemical performance [15-17]. As a result, the initial discharge capacity is greatly higher than that of the second one. After the second cycle, the discharge capacity has a slight decrease. Y₂₅ has the best electrochemical performance among these samples probably due to more BN precipitation coated on Co/CoB particles, effectively preventing the dissolution of the active material.

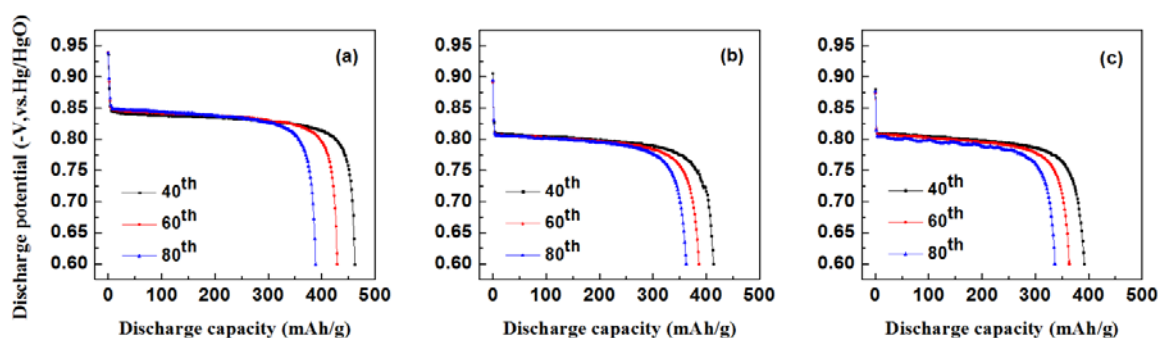


Figure 4. Discharge curves of (a) Y₂₅, (b) Y₅₀, and (c) Y₇₅.

In a general way, the more stable the discharge voltage plateau is, the more uniform the phase structure is and the better the consistency is [18]. As shown from figure 4, three electrodes show good stability for discharge voltage plateau. For example, the discharge voltage plateau of Y₂₅ at 40th, 60th and 80th cycle is almost the same (about 0.83 V). However, the discharge voltage plateau of Y₅₀ and Y₇₅ has been attenuated in different degree. The discharge voltage plateau of Y₇₅ is decreased to 0.8 V at the 80th cycle, indicating that the discharge stability is gradually deteriorated as the synthesizing temperature increases. Combined with figure 2, it is found that Y₂₅ has larger particle size and more stable discharge voltage plateau. The result is in line with Zhao's report [11], in which larger particle size of the sample prepared under ultrasonication results in the improved electrochemical properties.

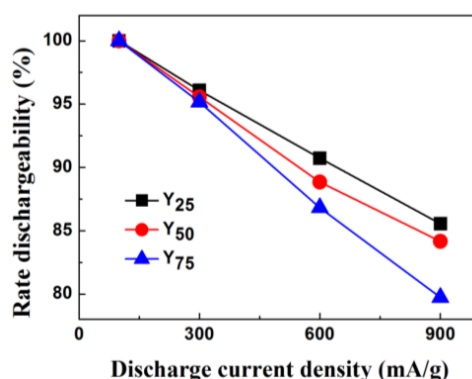


Figure 5. High-rate dischargeability (*HRD*) of as-prepared Co-B electrodes.

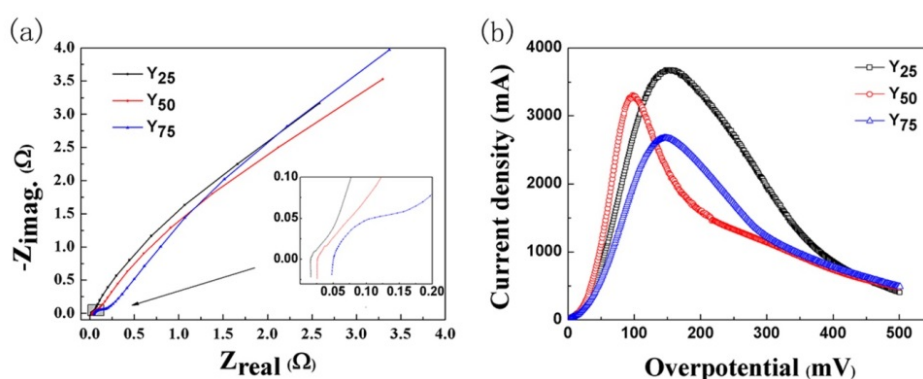


Figure 6. (a) EIS and (b) AP curves of as-prepared Co-B electrodes.

Figure 5 shows the high rate dischargeability (*HRD*) of the alloy electrodes, which is related to the electrochemical kinetics. It can be clearly seen that Y₂₅ has superior *HRD* among these samples. Especially, when the discharge current density is 900 mA/g, *HRD*₉₀₀ of Y₂₅ can still keep above 85%, which is higher than that of CoB-30wt%La_{0.7}Mg_{0.3}Ni_{3.5} (*HRD*₉₀₀ = 82.5%) [14]. In order to further demonstrate the superiority of Y₂₅, we studied the influence of the synthesizing temperature on the kinetic properties. The electrochemical impedance spectroscopy (EIS) and anodic polarization (AP) tests were performed when the discharge depth of the electrodes was 50% after full activation. As can be seen from EIS in figure 6 (a), each curve consists of a semicircle and a straight line [14]. The resistance of the charge transfer reaction is reflected by the semicircle radius. It can be seen from the inset that the radius is increased with the increase of the synthesizing temperature, indicating that the charge transfer resistance of Y₂₅ has a minimum value. This is consistent with *HRD* result. Figure 6 (b) showed AP curves of the alloy electrodes. Each curve has a peak that is defined as limit current density I_L . The larger I_L is, the better the diffusion properties in alloy electrode is [19]. It is found that I_L is decreased with the increase of the synthesizing temperature, indicating that the variation of the synthesizing temperature can significantly affect the diffusion behavior in the alloy electrodes. Y₂₅ has the highest I_L from AP curves. Also as shown in the aforementioned data, it has the highest charge/discharge capacity, the most stable discharge voltage platform and the superior *HRD* performance. This indicates that the optimal synthesizing temperature is 25 °C in this study.

4. Conclusions

In this paper, urea was introduced into the chemical reduction process to prepare nitrogen-doped Co-B alloy. The synthesizing temperature was paid much attention. By comparison, we found that with the increase of synthesizing temperature, the electrochemical properties of Co-B alloy become gradually worse. When the synthesizing temperature is set at 25 °C, the initial discharge capacity of Co-B alloy

is 825.8 mAh/g and after 100 cycles, the discharge specific capacity is still 369.5 mAh/g with capacity retention rate of 44.7%.

Acknowledgements

This research was financially supported by NSFC (51361006, 51401059, 51461010, 51361005, 51371060, U1501242, and 51461011) and the Innovative training program for College Students of Guangxi (No. 201710595140).

References

- [1] Jamil M, Ahmad F and Jeon Y J 2016 *Renew. Sust. Energy Rev.* **55** 1181
- [2] Liu Y F, Pan H G, Gao M X and Wang Q D 2011 *J. Mater. Chem.* **21**(13) 4743
- [3] Taniguchi A, Fujioka N, Ikoma M and Ohta A 2001 *J. Power Sources* **100**(1) 117
- [4] Lv D 2009 *Electrochemical study on ultrafine Co-B alloy* (Doctoral thesis from South China University of Technology) p13-23
- [5] Li Y 2016 *The influence of battery additives on the performance of anode in Iron-Nickel battery* (Master thesis from Harbin Institute of Technology) p84
- [6] Feng Z B, Yang Z H, Huang J H, Xie X E and Zhang Z 2015 *J. Power Sources* **276** 162
- [7] Qiu S J, Huang J L, Chu H L, Zou Y J, Xiang C L, Zhang H Z, Xu F, Sun L X and Zhou H Y 2015 *J. Alloys Compd.* **648** 320
- [8] Patel N and Miotello A 2015 *Int. J. Hydrogen Energy* **40**(3) 1429
- [9] Wang Y D, Ai X P and Yang H X 2004 *Chem. Mater.* **16**(24) 5194
- [10] Yang P P, Su M P, Yang X W, Liu G Z, Yu J F, Wu T H, Zhao D X, Zhang T S and Li D Q 2003 *Chinese J. Inorg. Chem.* **19**(5) 485
- [11] Zhao W, Liao Y L, Huang J L, Chu H L, Qiu S J, Zou Y J, Xiang C L, Xu F and Sun L X 2017 *Key Eng. Mater.* **727** 751
- [12] Durano M M, Tamboli A H and Kim H 2017 *Coll. Surf. A* **520** 355
- [13] Shi G M, Dong Y, Huang Y and Zhang J H 2008 *Chinese J. Mater. Res.* **22**(4) 379
- [14] Huang J L 2016 *Investigation on electrochemical performance of CoB-type alloys in a wide temperature range* (Master thesis from Guilin University of Electronic Technology) p7-17
- [15] Wang Y D, Ai P, Cao Y L and Yang H X 2004 *Electrochem. Commun.* **6**(8) 780
- [16] Yu X W and Licht S 2007 *Electrochim. Acta* **52**(28) 8138
- [17] Yu X W and Licht S 2008 *J. Power Sources* **179**(1) 407
- [18] Lai W H and Yu C Z 1996 *Battery Bimonthly* **26**(4) 189
- [19] Kuriyama N, Sakai T, Miyamura H, Uehara I, Ishikawa H and Iwasaki T 1993 *J. Alloys Compd.* **202**(1-2) 183