Ternary Co–Ni–B amorphous alloy with a superior electrochemical performance in a wide temperature range

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\textbf{Abstract}

Ternary Co–Ni–B amorphous alloy was synthesized by a chemical reduction method. Used as a negative electrode in the alkaline rechargeable batteries, the as-prepared alloy exhibits an excellent electrochemical performance in the temperature range of \(-30\) to \(50\) \(^\circ\)C. Specifically, the discharge capacity after 100 cycles still keeps up at 395.2, 403.7, and 379.1 mAh/g at \(\sim 15\), 0 and 25 \(^\circ\)C, respectively. Even at a much lower temperature of \(-30\) \(^\circ\)C, the maximum discharge capacity remains to be 408.3 mAh/g and slowly decays to 317.1 mAh/g after 100 cycles. Moreover, the high-rate dischargeability at 900 mA/g is 29.6\% at \(-30\) \(^\circ\)C. When the temperature increases to \(50\) \(^\circ\)C, the discharge capacity of the Co–Ni–B alloy electrode decreases from 675.6 to 283.1 mAh/g after 100 cycles. These properties are very superior to those of conventional hydrogen storage alloy electrodes at the corresponding temperatures. The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and anodic polarization (AP) tests show that the temperature has a crucial effect on the electrochemical kinetics of the Co–Ni–B alloy electrode.

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Introduction

To address the novel energy crisis and environmental pollution, a number of novel materials have been developed in the advanced high-energy batteries [1–5]. Traditional hydrogen storage alloys, such as AB5-type alloys, A2B7-type alloys, AB2-type alloys, AB-type alloys and Mg-based alloys, have been widely explored in nickel-metal hydride (Ni-MH) batteries due to their high charge–discharge capacity, long charge–discharge cyclic life, and environmental friendliness [6–11]. But they are hampered in the practical applications because of the poor properties at low or high temperatures and the dissatisfactory energy density.

In recent years, some transition metal borides, especially Co–B alloy, were reported to exhibit very exciting electrochemical properties in alkaline solution [12–14]. For example, the amorphous Co–B alloy prepared in the water/cetyl-trimethyl-ammonium bromide/n-hexanol microemulsion system has a maximum discharge capacity of 357 mAh/g and still keeps up at 347 mAh/g after 50 cycles [12]. And in 6 M KOH + 0.028 M 8-hydroxyquinoline (8-HQ) or 6 M KOH + 0.09 M ethylenediamine (EDA) as electrolyte, the Co–B alloy has a reversible discharge capacity of exceeding 400 or 600 mAh/g at 55 °C [13,14]. The multi-electron reaction of Co/Co(OH)2 (Co(OH)2 + 2 e− ↔ Co + 2 OH− ) is regarded as the principle of the electrochemical capacity of Co-based alloy. In addition, the adsorption of hydrogen atoms onto the Co surface is also involved during the charge cycle [15]. Generally, the performance of these rechargeable alkaline batteries is measured at room or a little bit higher temperature. However, to the best of our knowledge, the applied temperature has an obvious influence on the electrochemical properties. As an important performance for the practical application, the properties of the Co–B related alloys as negative electrodes at low temperatures were rarely reported.

In order to understand the effect of the temperature on the electrochemical properties, the ternary Co–Ni–B amorphous alloy was prepared via a chemical reduction method in aqueous solution, and the electrochemical properties of Co–Ni–B were investigated systematically in the temperature range of −30 to 50 °C.

Experimental

Sample preparation

The Co–Ni–B ternary alloy was prepared via the reduction of the mixture of CoCl2·6H2O and NiCl2·6H2O with NaBH4 aqueous solution according to the literature [14]. Typically, two solutions (A and B) were prepared before the chemical reduction. Solution A: 10 g CoCl2·6H2O and 0.56 g NiCl2·6H2O was dissolved in 150 mL distilled water. Solution B: 8 g NaBH4 was dissolved in 40 mL distilled water, and then the pH value of the solution was adjusted using aqueous ammonia. Subsequently, solution B was pumped into the solution A under a moderate stirring. The black precipitate was obtained and washed with distilled water and absolute ethanol, finally dried under vacuum at 60 °C for 8 h.

Structural and morphological characterization

The crystal structure and surface morphology of the Co–Ni–B alloy were characterized by means of PANalytical X-ray Diffractometer (XRD, X’Pert MPD PRO, Co Kα) and scanning electron microscopy (SEM, QUANTA FEG450). The bulk elemental composition of Co, Ni, and B in the as-prepared sample was measured by an inductive coupled plasma atomic emission spectroscopy (ICP–AES). The BET test was conducted using a Quantachrome Autosorb-iQ2 sorptometer.

Electrochemical tests

Each tested electrode was fabricated through homogenously mixing the as-prepared alloy powder with Ni powder. The mixture was then pressed into a pellet with a diameter of 10 mm under a pressure of 30 MPa. Each side of the anode pellet was coated with a rounded foam nickel sheet of about 25 mm in a diameter, then pressed at 6 MPa and tightly spot-welded at the edge of foam nickel. A nickel lead wire was attached to this pressed foam nickel sheet by spot welding. High-rate dischargeability (HRD) and charge/discharge cycles were tested on an automatic instrument (LAND). The anodes were charged for 3 h at a current density of 300 mAh/g, rested for 5 min and then discharged to the cut-off potential of −0.6 V vs. Hg/HgO reference electrode at a current density of 100 mAh/g. To determine the HRD of the alloy anodes, the discharge capacities at different discharge current density were measured. The electrochemical impedance spectroscopy and anodic polarization were conducted on a Zahner Elektrik IM6e electrochemical workstation [16]. The charge–discharge cycle was conducted in a tri-electrode cell containing a counter electrode (Ni(OH)2/NiOOH), a reference electrode (Hg/HgO), and a working electrode (Co–Ni–B alloy) in an alkaline electrolyte (6 M KOH + 0.5 M LiOH). The testing temperatures were set at 50, 25, 0, −15 and −30 °C (±1 °C), respectively.

Fig. 1 – XRD pattern and SEM micrograph of as-prepared Co–Ni–B alloy.
Results and discussion

XRD pattern of the Co–Ni–B alloy (Fig. 1) shows a very broad diffraction peak appearing at $2\theta = 45–60^\circ$ with very minor peaks observed at 40 and 70°, indicating that the main phase is an amorphous structure in nature [17]. SEM micrograph of the Co–Ni–B alloy (Fig. 1) shows that, similar to the Co–Ni–B ternary alloy reported in Refs. [18], the particles are aggregated into a fine powder with good uniform distribution in a loose-packed structure. The composition of the as-prepared Co–Ni–B samples by ICP-AES is CoNi$_{0.05}$B$_{0.4}$. The corresponding specific surface area obtained by BET test is 15.1 m$^2$/g. Wang et al. [19] observed an ultra-fine amorphous alloy particles of the Co–Ni–B alloy electrode at different temperatures. Compared to hydrogen storage alloy electrodes [20], the Co–Ni–B alloy electrode exhibits such an excellent electrochemical activity that the maximum discharge capacity is achieved at the initial cycle even at a much lower temperature of $-30^\circ$C. It can be seen that the maximum discharge capacity ($C_{\text{max}}$ for short) of the Co–Ni–B alloy electrode is significantly affected by the applied temperatures. For example, $C_{\text{max}}$ could reach to a value as high as 731.9 mAh/g at 25 °C. However, $C_{\text{max}}$ decreases with the decrease of the testing temperature from 25 to $-30^\circ$C (Table 1). When the temperature is increased to 50 °C, $C_{\text{max}}$ is also decreased to 675.6 mAh/g. This variation is similar to that in the La–Mg–Ni-type alloy [23,24]. The higher discharge capacity of the Co–Ni–B alloy electrode may be due to the following factors: 1) reversible formation of Co hydroxide, 2) hydrogen adsorption on the electrode surface, and/or 3) possible hydrogen absorption in the bulk [12,19]. However, the drastic decrease of the capacity in the first discharge cycle is observed at different temperature except for $-30^\circ$C, indicating an irreversible hydrogen desorption reaction [25]. In the temperature range of $-15$ to 25 °C, the Co–Ni–B alloy electrode shows much better cycling life in 100 charge–discharge cycles. The discharge specific capacity after 100 cycles still keeps up at 395.2, 403.7, and 379.1 mAh/g at $-15$, 0 and 25 °C, respectively. At a much lower temperature of $-30^\circ$C, the Co–Ni–B alloy electrode has a relatively lower reversible discharge capacity of 317.1 mAh/g after 100 cycles, which is still far higher than that of hydrogen storage alloy electrodes at lower temperatures [26,27]. At a higher temperature of 50 °C, the Co–Ni–B alloy electrode shows a relatively rapid capacity decay from 675.6 to 283.1 mAh/g after 100 cycles, which is probably resulting from the accelerated dissolution of an active substance Co in the alkaline electrolyte at a high temperature [28–30].

![Fig. 2](image.png)

Fig. 2 – Cycling life (a) and charge–discharge curves (b) of the Co–Ni–B alloy electrode at different temperatures.

From the charge–discharge curves of the Co–Ni–B alloy electrode (Fig. 2b), it can be seen that the charging voltage plateau increases with the decrease of the applied temperature while the discharging voltage plateau shows an opposite trend. The increase of hysteresis between charge and discharge voltage plateau indicates that the polarization of the alloy electrode increases with the decrease of the testing temperature. As is well-known, the polarization has a negative effect on the electrochemical properties of alloy electrode. The Co–Ni–B alloy electrode shows larger polarization at lower temperature probably due to the poor electrocatalytic activity at the surface and/or slow proton transfer in the bulk of the electrode. That is to say, the low temperature is not beneficial for the reversible formation of Co hydroxide and the hydrogen adsorption on the electrode surface.

Fig. 3 shows the high-rate dischargeability (HRD) of the Co–Ni–B alloy electrode at different temperatures. Similar to hydrogen storage alloy electrodes [23,26,31], the HRD of the Co–Ni–B alloy electrode is closely dependent on the applied temperature. The HRD value decreases with the decreasing temperature (Table 1). It is worth noting that, even at lower temperatures, the HRD of the Co–Ni–B alloy electrode is much higher than that of hydrogen storage alloy electrodes [23,26,31]. This can be related to the fine particle of the Co–Ni–B alloy, which leads to a larger interface, an enhancing electrode reaction kinetics, and therefore a superior HRD [32].

In the CV curves of the Co–Ni–B alloy electrode (Fig. 4), the oxidation peak appears at about $-0.65$ V (vs. Hg/HgO), and the peak current is sharply decreased as the temperature decreases. This oxidation peak can be ascribed to the electrochemical oxidation of adsorbed hydrogen rather than the

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Table 1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Maximum Discharge Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30</td>
<td>675.6</td>
</tr>
<tr>
<td>-15</td>
<td>395.2</td>
</tr>
<tr>
<td>0</td>
<td>403.7</td>
</tr>
<tr>
<td>25</td>
<td>379.1</td>
</tr>
<tr>
<td>50</td>
<td>317.1</td>
</tr>
</tbody>
</table>

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**Note:** The table provides the maximum discharge capacity ($C_{\text{max}}$) of the Co–Ni–B alloy electrode at different temperatures. The capacity decreases from 675.6 mAh/g at -30 °C to 317.1 mAh/g at 50 °C.
oxidation of elemental Co or B (−0.83 and −1.81 V (vs. Hg/HgO)) [12]. For the case of cathodic scanning process, a reduction peak at about −1.08 V (vs. Hg/HgO) is observed at the temperature of 50 °C, which may arise from the hydrogen adsorption on the Co–B electrode [12]. When the temperature is decreased, the reduction peak is not detectable, suggesting that the reversible oxidation–reduction reaction in the Co–B alloy electrode is more difficult to take place at low temperature. This may be partially responsible for the decreased discharge capacity at lower temperatures.

In the EIS of the Co–B alloy electrode shown in Fig. 5, there are a semicircle and a straight line in each spectrum.

The semicircle is corresponding to the charge-transfer reaction resistance ($R_{ct}$), which can be quantitatively determined using an equivalent circuit as that proposed by Kuriyama et al. [33]. The $R_{ct}$ of the Co–B alloy electrode increases from 159.0 to 1324.0 mΩ (Table 2). This means that similar to the La–Mg–Ni-based alloy electrodes, the Co–B alloy electrode shows poor electrochemical kinetics at lower temperatures, which can be ascribed to the unfavorable hydrogen adsorption on the electrode surface and/or the decrease of the conductivity of the electrolyte [23,34].

For hydrogen storage alloy electrodes, the limiting current density $I_L$, which related to the diffusion of hydrogen in the alloy electrode, is an important parameter for identify the kinetic property. To determine the effect of temperatures on the kinetics of proton transfer (diffusion of hydrogen) of the Co–B alloy electrode, the anodic polarization (AP) curves were plotted (Fig. 6). $I_L$ decreases from 3076.3 (50 °C) to 1072.9 (−30 °C) (Table 2), suggesting that the proton transfer...
(hydrogen diffusion) is decelerated with the decrease of the temperature.

Based on the HRD, CV, EIS and AP tests, it can be concluded that the electrochemical reaction kinetic properties of the Co–Ni–B alloy electrode is strongly dependent on the testing temperatures. At low temperature less than or equal to 0 °C, the Co–Ni–B alloy electrode shows a higher HRD than that of hydrogen storage alloy electrode while a lower HRD at the temperatures more than 0 °C [23,26,31]. For the case of La–Mg–Ni-based alloy electrodes [23], the diffusion of hydrogen is the rate-determining step at high temperatures, and the charge-transfer reaction is rate-determining step at low temperatures. Fig. 7 shows the relationship between HRD and Rct or Ilim at different temperatures. As the temperature increases, HRD and limiting current density increase while charge-transfer resistance decreases. Though the multi-electron reaction of Co/Co(OH)2 is regarded as the principle of the electrochemical capacity of Co-based alloy [15], the transformation of Co/Co(OH)2 is not observed in CV curve. Therefore, if the mechanism of the electrochemical hydrogen storage is considered in this study, it can be concluded that the rate-determining step for the electrochemical reaction of the Co–Ni–B alloy electrode may be ascribed to the combined effect of the charge-transfer reaction and the diffusion of hydrogen.

**Conclusions**

The overall electrochemical properties of the Co–Ni–B amorphous alloy synthesized by a chemical reduction method were studied systematically in the temperature range of −30 to 50 °C. The alloy electrode exhibits a high discharge capacity and a long cycle life. At 25 °C, Cmax could reach an extremely high value of 731.9 mAh/g. When the temperature is set at 50 or −30 °C, Cmax could stand at 675.6 and 408.3 mAh/g. After 100 cycles, the discharged capacity still keeps up at 283.1, 379.1, and 317.1 mAh/g at 50, 25 and −30 °C, respectively. The discharge capacity and the cycling life of the Co–Ni–B alloy electrode in a wide temperature range are superior to those of hydrogen storage alloy electrodes. The electrochemical reaction kinetics of the Co–Ni–B alloy electrode is systematically investigated through HRD, CV, EIS, and AP tests in a wide temperature range of −30 to 50 °C. This class of Co–Ni–B alloy could be applied as negative electrode in the high-energy secondary batteries operated in a wide temperature range, especially at lower temperatures.

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