

The electrochemical hydrogenation properties of two boron-free crystalline Co powder samples were investigated. They exhibited almost the same maximum discharge capacities with 2-h charging, 415 and 428 mAh/g (corresponding to $CoH_{0.91}$ and $CoH_{0.93}$) for samples A and B, respectively. The high discharge capacity of Co powder was attributed to hydrogenation of Co and phase transition between the phases of hexagonal close-packed and face centered cubic. © 2006 The Electrochemical Society. [DOI: 10.1149/1.2189978] All rights reserved.

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Hydrogen can be stored in various forms such as high pressure gas, metal hydrides, adsorption on carbon materials, liquid hydrogen, etc. Many types of hydrogen storage alloy have been developed in the past few decades, including AB-type intermetallic compounds, 1 AB₂-type Laves phase alloys, 2 Mg-based alloys, 3 and AB5-type rare-earth alloys.⁴ For battery application, lower plateau pressure and good kinetics are required. For AB2-type alloys, although the theoretical discharge capacities are higher than those of AB5-type alloys, they are more difficult to activate to be used as a negative electrode material in batteries. For Mg-based alloys, their high discharge capacities are attractive, but the low cycling stability and poor kinetics are not suitable for practical application. The AB₅-type hydrogen storage alloys are more often used in commercial batteries because of their suitable plateau pressure and fast activation. However, the discharge capacities of AB5-type alloys are decreased by pulverization and oxidation of the alloys. Willems⁵ and Chartouni et al.⁶ pointed out that the cycle life of electrode could be improved by partial substitution of Ni by Co that lowers the hardness of the alloys. Mixing hydrogen storage alloy with Co powder might result in formation of a conductive layer of precipitate which ensures good electrical contact of the alloy powder, in addition to a slight increase in electrochemical capacity due to the reaction of cobalt in the charge and discharge cycling.⁷ Durairajan et al. pointed out that the discharge capacity of pure Co was only 50 mAh/g,⁸ that might be due to the faradaic reaction of $Co/Co(OH)_2$.

Recently, it has been reported that amorphous Co nanoparticles prepared by reduction with NaBH₄ can absorb a large amount of hydrogen. ⁹⁻¹² When ultrafine Co–B amorphous alloy particles were tested by electrochemical charging/discharging, the reversible maximum discharge capacity could be as high as 300 mAh/g.¹² In the cyclic voltammetry (CV) test, Mitov et al. proposed that the cathodic and anodic peaks are due to electrochemical adsorption and desorption of hydrogen, respectively. The residual B in the sample may play an important role by exchanging position with hydrogen atom in the metallic host lattice.⁹ Therefore, it would be possible to use ultrafine Co–B amorphous powder as a new hydrogen storage material.

During the charge process the negative electrode undergoes reduction reaction, pure cobalt cannot be reduced to other form because it is in the zero valence. Therefore, the decomposition of water might be progressed. The hydrogen fugacity in electrochemical systems could be as high as several GPas. This makes it possible to form hydrides for group VIII metals that can be identified by neutron scattering. The electroreduction of water allows a higher hydrogen fugacity to be reached than in conventional gas-phase hydrogenation technique. This paper is devoted to the study of electrochemical hydrogenation properties of B-free crystalline Co powder. The hydrogenation process is elaborated. The discharge performance and phase transformation of Co powder during repeated charging and discharging are discussed.

Experimental

Two Co powder samples were used for the electrochemical hydrogenation test. Sample A was a commercial powder purchased from OM Group. Sample B was prepared by a precipitation method. A precursor solution of 0.5 M of $Co(NO_3)_2$ dissolved in C_2H_5OH was prepared, and the pH value was controlled at 12–13 by addition of NaOH. N₂H₄ was then used as a reducing agent at 70°C. A black Co powder was formed, which was separated from the solution by a magnetic rod and dried at 50°C. Because N₂H₄ was used as the reducing agent, no boron was present in sample B. The structures of the samples were examined by X-ray diffraction (XRD) with a Cu K α radiation.

The charge and discharge curves were measured in an electrochemical test cell, which contained one piece of positive electrode, one piece of Co powder (0.02 g) as the negative electrode, and polypropylene as the separator. The electrolyte was 6 M KOH + 1 wt % LiOH. The positive electrode material consisted of nickel hydroxide, 5 wt % Co, and 5 wt % CoO. Each of the positive and negative electrode materials was mixed with 3 wt % poly(tetrafloroethylene) to form a paste and coated on a piece of Ni foam. The electrode plates were cold pressed at a pressure of 50 kgf/cm² for 30 s. Because the diffraction peaks of face-centered cubic (fcc) phase Co overlap with those of Ni foam, some pellets made of Co and Cr powder at a mass ratio 1 to 4 were also tested to identify the presence of fcc-phase Co during the charge-discharge process. The charge and discharge currents were both set at 10 mA (equivalent to 500 mA/g), and the cutoff voltage was 900 mV. The charging time was 1 or 2 h, and all experiments were conducted at 25 C.

Results and Discussion

Phase characterization.— The XRD patterns for the two samples are shown in Fig. 1. In general, Co has two structures, fcc (γ -phase) and hexagonal close-packed (hcp) (ε -phase). The former is metastable and the latter is stable at room temperature and ambient pressure.¹³ Sample A shows almost a pure hcp-Co phase. The particle size is calculated to be ~31 nm by Scherrer's equation. For sample B, the relative intensities of the three major peaks are different from those of sample A. Based on the standard pattern of the hcp phase, the (101) peak at 47.57° is the strongest, followed by the (002) peak at 44.76°. For sample B, it is noted that the (002) peak is stronger, presumably because of the presence of a small amount of fcc phase, whose strongest (111) peak is located at 44.22°, and the second strongest peak (200) is at 51.52°. The particle size of sample B is approximately 46 nm.

Electrochemical hydrogenation properties.— Initially, without charging, a blank discharge test with a fresh commercial Co powder sample used as the negative electrode and NiOOH as the positive electrode was made. The maximum discharge capacity was only 80 mAh/g. This means that the discharge capacity from the Co/Co(OH)₂ faradaic reaction is low. Figure 2 shows the cyclic discharge capacities of the two Co powder samples with two different charge times. The activation rates for both samples were very fast compared with those of typical hydrogen storage alloys. The

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Figure 1. XRD patterns of the Co powder samples.

maximum discharge capacity could be obtained in the first few cycles. When the charging time is 1 h, the maximum discharge capacities are 379 and 399 mAh/g for samples A and B, respectively. As the charge time is extended to 2 h, the maximum discharge capacities are increased to 415 and 428 mAh/g, respectively. Both samples have almost the same discharge capacity, near 350 mAh/g, after 30 cycles of test. The maximum discharge capacities and equivalent hydride formula (CoH_x) of the two samples are summarized in Table I.

In gas-phase hydrogenation, Co reacts with H_2 to form $CoH_{0.6}$ and $\text{CoH}_{1,0}$ for the hcp and fcc structures, respectively, as hydrogen pressure increases.¹³ By theoretical calculation, the maximum discharge capacities of Co are 459 mAh/g for fcc-Co and 275 mA/g for hcp-Co, based on the compositions of CoH_{1.0} and CoH_{0.6}, respectively. Since the discharge capacity due to the faradaic reaction Co/Co(OH)₂ is only 80 mAh/g, the cyclic discharge capacities observed for this electrochemical test are attributed to the CoH_x/Co reaction rather than from the faradaic reaction. With the above discharge capacities, the maximum hydrogen storage capacity of sample A is equivalent to 1.54 wt %, which corresponds to a composition of CoH_{0.91} in between CoH_{0.6} and CoH_{1.0}. Therefore, it is believed that both hcp-Co and fcc-Co coexist during the electrochemical test. If the samples behave like gas-phase hydrogenation during electrochemical charging, the hcp-Co in sample A starts to absorb hydrogen until saturation has been reached. Some of the hcp-Co phase then transforms to fcc-Co. From Fig. 1, although there is some fcc-Co present in sample B, the hcp phase is the main phase. Therefore, the discharge behavior of sample B is almost the same as that of sample A.

Figure 3 shows the electrochemical charge and discharge poten-



Figure 2. Discharge capacity curves of the two Co powder samples.



Figure 3. Electrochemical charge and discharge curves of the Co samples for the second cycle. Both samples are charged for 60 min, rest for 10 min, and then discharged to a cutoff potential of 0.9 V.

tial curves of the two samples at a constant current of 500 mA/g during the second cycle. The cell voltage is between 1.3 and 1.7 V in charging and between 1.3 and 1.1 V in discharging. It is noted that there are two stages in the curve during the charging process. The first stage has a higher slope which might be ascribed to easier hydrogenation of the hcp phase, while the second stage with a smaller slope is due to more difficult hydrogenation of the fcc phase. The discharge plateaus of both A and B are almost the same. The discharge plateaus of both samples can be compared with those of AB₂-type and AB₅-type alloys. In general, the discharge plateaus are between 1.3 and 1.2 V and between 1.3 and 1.1 V for AB₂- and AB₅-type alloys, respectively.¹⁴ Therefore, the discharge capacities of samples A and B can be attributed to the desorption of hydrogen from Co.

Phase transition .--- The XRD patterns of the samples after charge and discharge are shown in Fig. 4 and 5, respectively. After charge, the hcp-Co phase can be observed in both samples and no secondary phase appears, as shown in Fig. 4. Based on the peak positions, the unit cell volumes of samples A and B are calculated to be 22.16 and 22.11 Å³, respectively. Compared with the standard unit cell volume hcp-Co (22.03 Å³), the unit cell volumes of both samples have been expanded after charging, presumably because hydrogen atoms could occupy the interstitial sites in the hcp-Co lattice. After discharge, as shown in Fig. 5, the peak intensity of hcp-Co has decreased and more $Co(OH)_2$ appears in both samples. This means that the faradaic reaction Co/Co(OH)₂ might have also occurred. The unit cell volumes of samples A and B have been reduced to 22.09 and 22.07 Å³, respectively, because of release of the hydrogen atoms during discharge. However, they are still slightly larger than that of standard hcp-Co, implying that there is some residual hydrogen in the Co lattice. Based on this result, it proves that hydrogen is absorbed/desorbed by hcp-Co during the charge/discharge process.

Since Ni foam was used as electron collector in the present electrochemical measurement, the peaks of fcc-Co, if any, would have overlapped with those of Ni foam. Therefore, it cannot distinguish the phase transformation between hcp-Co and fcc-Co during the electrochemical charge/discharge cycling by using Ni foam. To

Table I. Electrochemic	al hydrogenation	capacities	of two (Со
powder samples.				

	Discharg (mA	e capacity h/g)	Storage (wt	capacity %)	Equivaler (x in (nt formula CoH _x)
Sample	1 h	2 h	1 h	2 h	1 h	2 h
А	379	415	1.40	1.54	0.83	0.91
В	399	428	1.48	1.58	0.87	0.93



Figure 4. XRD patterns of the samples after charge.

check the possibility of the presence of fcc-Co, non-fcc metallic binders have to be used. Furthermore, the powder has to be easy to deform, stable in KOH solution, and not absorbing hydrogen. Among common metallic powders that meet these requirements, Cr was selected for this purpose. Sample A was mixed with Cr powder to form a pellet and then tested in the same electrochemical system. The XRD pattern after charging at the seventh cycle is shown in Fig. 6. In addition to Co and a small amount of Co(OH)², both hcp-Co and fcc-Co phases can be observed. This demonstrates that hcp-Co has indeed, been partially transformed to fcc-Co, and this phase transformation results in increased discharge capacity for sample A. The standard unit cell volume of fcc-Co is 44.512 Å³. This was increased to 44.663 Å³ after charging, based on the peak positions shown in Fig. 6. It is also believed that similar phase transition between hcp and fcc takes place in sample B.

Hydrogenation mechanism.— For a nickel–metal hydride (Ni–MH) battery, the reactions of positive and negative electrodes during the charge process can be written as

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-$$
 [1]

$$M + H_2O + e^- \rightarrow MH + OH^-$$
[2]

If the hydrogen storage alloy electrode is replaced by pure cobalt powder, its charge reaction may be written as either of the following two reactions

$$Co(OH)_2 + 2e^- \rightarrow Co + 2OH^-$$
 [3]

$$\text{Co} + x\text{H}_2\text{O} + x\text{e}^- \rightarrow \text{CoH}_x + x\text{OH}^-$$
 [4]

It is well known that Co is difficult to form hydride by gas-phase hydrogenation at ambient pressures. Therefore, Co is commonly



Figure 5. XRD patterns of the samples after discharge.



Figure 6. XRD pattern of the pellet consisting of sample A and Cr after charge at the seventh cycle.

used as an alloying element to improve the cycle life of MH electrodes. It is also used in positive electrode to improve conductivity and to reduce degradation of the electrode. Is it possible to obtain CoH_x by electrochemical charging shown in Reaction 4? When Co was immersed in the KOH solution, it was observed that a thin cobalt hydroxide layer was formed on the surface. It also covered the cobalt electrode surface during cyclic charge/discharge. If the surface of cobalt electrode is covered by cobalt hydroxide, the Reaction 3 might occur. As mentioned above, with fresh commercial Co powder used as the negative electrode and NiOOH as the positive electrode, the maximum discharge capacity is only 80 mAh/g without prior charging. Therefore, the discharge capacity due to the Co(OH)₂/Co faradaic reaction is low. The discharge capacities obtained from the present study should be attributed primarily to the dehydrogenation of CoH_x. Although the electrochemical hydrogenation and dehydrogenation of Co are similar to those of conventional hydrogen storage alloys (i.e., AB₂, AB₅, etc.), Co must undergo phase transition during the charging process in order to reach the maximum discharge capacity. It is also believed that the electrochemical hydrogenation of Co is an intrinsic property, regardless of the synthesis process and crystallinity. Furthermore, alloying with boron is not a prerequisite for hydrogenation of Co.

Conclusion

In this paper, we report the electrochemical hydrogenation of two crystalline Co powders. The electrochemical hydrogenation properties were measured in KOH solution. Although Co is difficult to form hydride by gas-phase hydrogenation, high discharge capacities by electrochemical hydrogenation were observed. For samples A and B, the maximum discharge capacities with 2 h charging are 415 mAh/g (1.54 wt %) and 428 mAh/g (1.58 wt %), corresponding to compositions of $CoH_{0.91}$ and $CoH_{0.93}$, respectively. The phase transition between hcp-Co and fcc-Co takes place during the charge/ discharge process, resulting in high hydrogenation capacities.

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