Effective utilization of waste: development of CH₄ dry reforming catalysts from spent nickel metal hydride battery for resource recovery

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Abstract

The resource recovery of nickel metal from the spent nickel metal hydride (Ni-MH) battery was investigated by using the CH_4 dry reforming, aiming at reusing it as a raw material of the Ni-MH battery. From the results, a compound identified as a single phase of NiO by XRD was successfully prepared from the spent Ni-MH battery by a series of chemical processes using HCl and NH_3 aq. solutions followed by calcinations. The resulting NiO exhibited excellent CH_4 conversion in the CH_4 dry reforming, i.e., the CH_4 conversion higher than 96% continued for 50 h when the flow rates of injection gases were controlled at $CH_4/CO_2/Ar$ = 10:10:80 ml·min^{-1}. Although the XRD pattern revealed the reduction of NiO to Ni^0 and the deposition of carbon after the CH_4 dry reforming, the deposition of carbon could be suppressed by changing the injection gas ratio. The resource recovery of nickel metal was, therefore, concluded to be possible through the CH_4 dry reforming over NiO prepared from the spent Ni-MH battery.
Keywords: resource recovery, nickel metal hydride secondary battery, nickel metal, CH_4 dry reforming, nickel-based catalyst.

1   Introduction

Resource recovery of waste is one of important subjects for sustainable development. Technological development of resource recovery has, however, fallen behind, compared with that of creation of high functional materials using pure raw materials. In the battery field, nickel metal hydride (Ni-MH) batteries

with high power and rechargeable features have been developed and widely used as power sources of cell phones, digital cameras, hybrid cars, etc. On the other hand, about four hundreds tons of spent Ni-MH batteries have been disposed in Japan even though they contain valuable transition and rare-earth elements. It is, therefore, desired to develop environmentally-friendly resource recovery technologies of spent Ni-MH batteries.

   CH_4 dry reforming, Eq. (1), which produces synthesis gas with lower H_2/CO ratio than steam reforming, Eq. (2), attracted a great deal of attention, because the syntheses of liquid fuels such as methanol and dimethyl ether require the synthesis gases with lower H_2/CO ratio.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad H_2/CO = 1 \qquad\qquad (1)$$
$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad H_2/CO = 3 \qquad\qquad (2)$$

Furthermore, CH_4 in natural gas and CO_2 in flue gas can be effectively used in the CH_4 dry reforming. The natural gas is cleaner energy source than oil and coal, since it contains CH_4 as a main component, little NO_x and no SO_x.

   It has been known that noble metal (Pt, Rh, Ru, Pd and Ir) supported catalysts had good catalytic performance for the CH_4 dry reforming [1–9]. However, the development of cheap metal catalyst has been desired, because the noble metal catalyst is not suitable for utilizing on a large scale. Supported Ni-based oxides [10, 11] and lanthanoid perovskite type oxides [12–15] are promising as the alternative catalysts for this reaction. We took note of the CH_4 dry reforming, referring to previous reports, because spent Ni-MH batteries contained Ni as a main element. In the present study, we report the resource recovery process of Ni from Ni-MH batteries by using the CH_4 dry reforming, aiming at reusing it as a raw material of Ni-MH batteries.

2   Experimental

Anode material of spent Ni-MH battery, which was provided by Mitsui Mining and Smelting Co. Ltd., Japan, was employed in the experiment.   Nickel component was separated from the anode material according to a procedure as shown in fig. 1.

   The anode material was characterized by powder X-ray diffraction (XRD; Rigaku RINT2100/PC) with monochromated CuKα radiation and an X-ray fluorescence technique (XRF; Rigaku RIX3000). The separated specimens were identified by XRD, and their chemical compositions were analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES; Seiko Instruments SPS7700). Thermal analysis (TG-DTA; Rigaku TG 8120) was carried out to estimate amounts of deposited carbon over the samples.

   The CH_4 dry reforming was performed at 780ºC under atmospheric pressure, using a vertical fixed-bed reactor of quartz tube with 12 mmφ in internal diameter. The resulting powder sample of 1 g was held in place by glass wool. The flow rates of injection gases were controlled in the range from $CH_4/CO_2/Ar$ = 10:10:80 to 6:14:80 ml·min^{-1}.   The vent gases were cooled with an ice-cooler to remove H_2O produced by side reactions. The gaseous products were analyzed

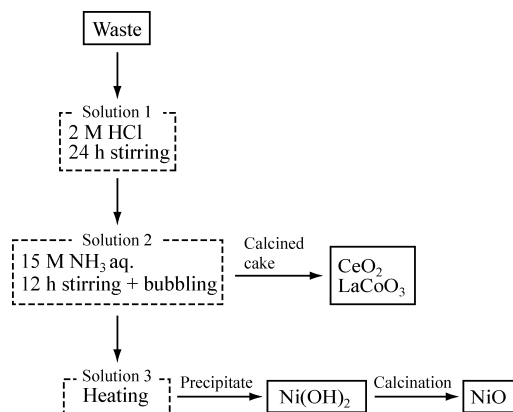by an on-line gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector.

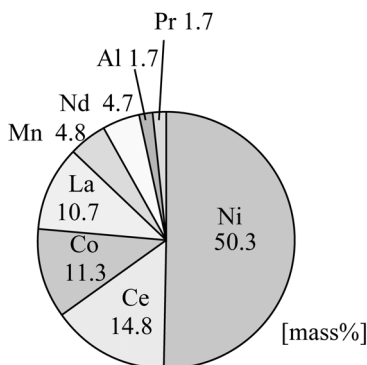Figure 1:   Flow chart of separation process from anode material of spent Ni-MH battery.

Figure 2:   Chemical compositions of anode material of spent Ni-MN battery.

3   Results and discussion

3.1 Sample preparation process

The chemical compositions, as shown in fig. 2, reveal that the anode material of spent Ni-MH battery contains Ni as a main element, Ce as a second element and much Co, La, Mn and Nd next to them. Main crystalline phases were identified as $LaNi_5$ by XRD. In the beginning of the recovery process, pre-experiments were carried out for the anode material of spent Ni-MH battery to search

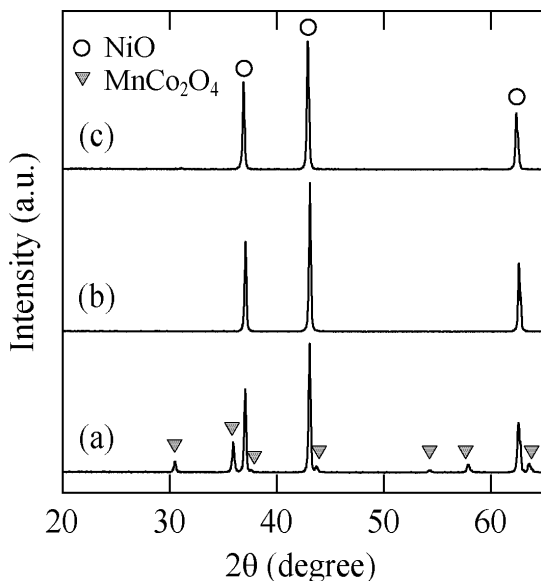optimum conditions. As a result, the proper recovery process was determined as shown in fig. 1.

Figure 3:   XRD patterns of products obtained with (a) stirring for 12 h, (b) stirring for 24 h and (c) stirring and bubbling air for 12 h.

The anode material of 10 g was treated with 2 M (mol· dm^{-3}) HCl solution of 200 ml for 24 h with stirring (solution 1). The anode material was completely dissolved into HCl solution, when HCl solutions with higher concentration than 2 M were used. Next, 15 M NH$_3$ aq. of 300 ml was added to "solution 1" to form Ni-ammonium complexes as well as precipitate dissolved metal ions as their hydroxides except nickel ions, and the solution (solution 2) was stirred for fixed time.   After filtration, the obtained reddish purple filtrate was slowly heated around 90ºC to decompose the Ni-ammonium complexes and to precipitate Ni component as Ni(OH)$_2$. NH$_3$ gas, which came out from the filtrate by heating, was recovered by passing in water. The obtained precipitates were calcined at 1000ºC for 1 h to dehydrate into oxides. The XRD patterns of the calcined precipitates are presented in figs. 3a and b. The resulting oxides were identified as NiO, accompanied with a small amount of MnCo$_2$O$_4$ when the stirring time was 12 h, whereas they were identified as a single phase of NiO when the stirring time was 24 h. This suggests that a long time stirring helps manganese and cobalt ions   precipitate as hydroxides and/or oxides through contacting with air. Thus, solution 2 was stirred with bubbling air to precipitate manganese and cobalt ions for 12 h, and the filtrate was heated around 90ºC. Consequently, the resulting oxides were identified as a single phase of NiO, as shown in fig. 3c. Namely, the treatment with bubbling air successfully prevented MnCo$_2$O$_4$ from mixing with NiO. The chemical compositions of the products by

ICP-AES are listed in table 1. Although manganese component was detected in the products obtained from solution 2 with stirring for 12 and 24 h, it was hardly detected in that with stirring and bubbling air for 12 h. Therefore, the stirring time with bubbling air was decided on 12 h. A slight amount of lanthanum was contained in every final product. It was considered that the resulting NiO formed a solid solution with CoO such as (Ni, Co)O containing a small amount of lanthanum.

Table 1:   Chemical compositions of products obtained from solution 2.

Stirring time	Metal content (mol%)			
	Ni	Co	Mn	La
12 h	82.6	13.9	3.5	0.02
24 h	84.8	15.1	0.07	0.03
12 h with bubbling air	85.7	14.3	0	0.03

The filter cake of "solution 2" was calcined at 1000ºC and identified by XRD. As a result, it was found the calcined filter cake was a mixture of CeO_2 and La-based perovskite. Considering the chemical compositions of anode material as shown in fig. 2, both of them were supposed to form solid solutions.

3.2 CH_4 dry reforming

The CH_4 dry reforming reaction temperature was examined, considering the temperature ranges based on the free energy changes of the main and side reactions. As the estimation indicates that the temperature range from 700 to 835 °C is appropriate for the CH_4 dry reforming, the reaction temperature was decided on 780°C in the present study. This temperature is consistent with those reported by a lot of researches [4, 5, 7, 8, 14].

Figure 4 shows the CH_4 conversion over NiO prepared from the anode material as a function of reaction time. Although NiO showed excellent performance, the CH_4 conversion slightly decreased from ca. 98 to ca. 96% for 50 h reaction, when the flow rates of injection gases were controlled at $CH_4/CO_2/Ar = 10:10:80$ ml·min^{-1}. The XRD pattern of NiO after the CH_4 dry reforming is displayed in fig. 5a. The XRD pattern exhibited that the NiO was reduced to Ni^0, and furthermore carbon coexisted with Ni^0 after the CH_4 dry reforming. No XRD peaks due to other than Ni^0 and carbon are observable, although Co component was contained in the prepared NiO. The appearance of carbon suggests that the CH_4 dry reforming reaction (1) shifts to reaction (3), which is a production reaction of carbon and water.

$$CH_4 + CO_2 \rightarrow 2C + 2H_2O \qquad (3)$$
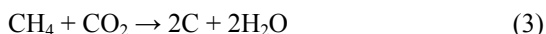
Next, the flow rates of injection gases were changed to $CH_4/CO_2/Ar = 8:12:80$ and 6:14:80 ml·min^{-1} in order to suppress reaction (3). Decreasing CH_4 flow rate and increasing CO_2 flow rate were expected to restrain the carbon deposition and accelerate reaction (4), which is a consumption reaction of carbon.
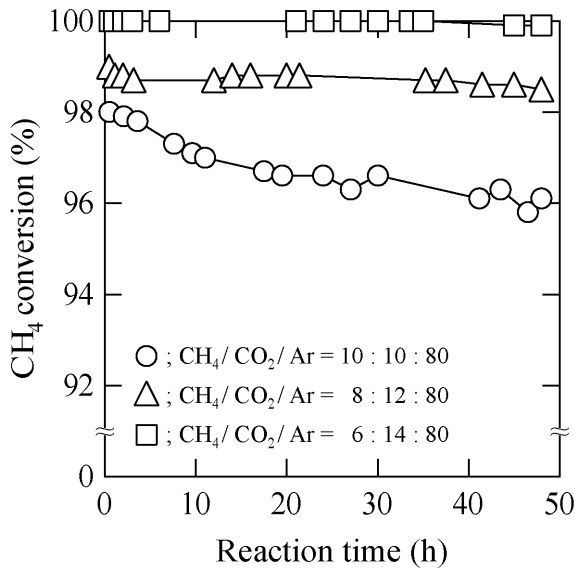
Figure 4: CH_4 conversion over prepared NiO at various gas flow rates as a function of reaction time.
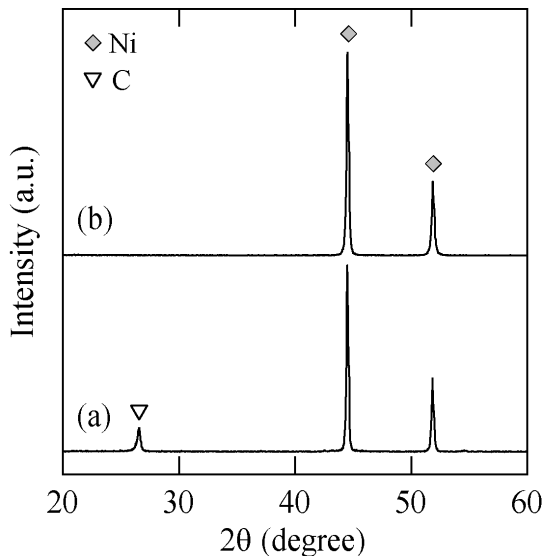

Figure 5:   XRD patterns of NiO after the CH_4 dry reforming at $CH_4/CO_2/Ar$ = (a) 10:10:80 and (b) 6:14:80 ml·min^{-1}.

$$C + CO_2 \rightarrow 2CO \qquad (4)$$

As a result, the CH_4 conversions were improved to higher than 98%, as seen in fig. 4. The XRD peaks due to Ni^0 were only detectable on the XRD pattern of

the product after the CH_4 dry reforming, as seen in fig. 5b. Thermal analyses exhibited that amounts of deposited carbon in the products decreased from ca. 60 to 1.5 mass%. Namely, these results revealed that changing the flow rates of the injection gases from $CH_4/CO_2/Ar$ = 10:10:80 to 8:12:80 and 6:14:80 ml·min^{-1} was effective in the stimulation of the CH_4 dry reforming reaction (1) as well as the inhibition of carbon and water production reaction (3).

   In conclusion, the resource recovery of nickel metal was possible through the CH_4 dry reforming over NiO prepared from spent Ni-MH battery.

Acknowledgements

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