Recycling process of spent battery modules in used hybrid electric vehicles using physical/chemical treatments

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Abstract The physical treatment/chemical treatments for recycling of spent lithium-ion battery modules in used hybrid electric vehicles as cathodic active materials were performed. The result by physical treatment showed that over 95 % valuable metals such as Co, Li, Ni, and Mn were concentrated in 65-mesh during a grinding time 2 min, while just 2.7 % Al was concentrated from spent lithium-ion batteries which were completely electric discharged after 70 min. Through reductive leaching with H_2O_2 and H_2SO_4, leaching efficiency of valuable metals with 65-mesh powder was almost 99 % Co, Mn, Ni, and Li under the conditions of 2 M H_2SO_4, 5 vol% H_2O_2, 60 °C, 300 rpm, 50 g/500 mL, and 2 h. After removing some impurities such as Cu, Al, and Fe, the leaching solutions containing Co, Mn, Ni, and Li could be utilized for manufacturing the precursor of cathodic active material of Li-ion battery. The precursor was manufactured by co-precipitation from the filtrate after calibration of Co, Mn, and Ni concentration adding NaOH and NH_4OH under the conditions over pH 11, 30 °C, 150 rpm, and 24 h. To maintain the pH, 11 is most important level for making homogeneous spherical Co–Mn–Ni hydroxide.

Introduction

The most promising near-term alternative to fuel cell-driven vehicles is probably hybrid electric vehicle (HEV or EV) technology. HEV technology combines the best characteristics of fuel-driven engines, electric motor drives, and energy storage

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components [1]. It is designed with a combustion engine that functions as the primary power source, and an electric power storage system that functions as the secondary power source. The presence of the secondary power source allows designers to size the combustion engine for cruising power requirements [2, 3].

A new energy source for HEV or EV market will become lithium-ion batteries (LIBs) in the near future [4]. LIBs for HEV or EV have large scales more than $10,000\times$ the small sized one for IT devices in order to achieve high electric density/capacity and high efficiency, etc. [5, 6]. For those reasons, physical treatment of the batteries is more difficult for stable dismantling in comparison with the smaller one [7]. Hybrid vehicle sales will grow by nearly 400 % during the next 7 years, according to a new report from analyst firm ABI Research. By 2013, hybrids will make up 6 % of annual U.S. auto sales. The traction battery pack will become air-cooled LIBs which consists of several modules of Li-ion battery and connected in series/parallel configuration to provide about >450 VDC, >150 kW peak power, and >80 Ah capacity. As the use of these batteries will tend to increase significantly over the next years, it is relevant that the development of new recycling methods as well as optimization of existing processes to treat spent LIBs for HEV are being addressed in order to obtain sustainability [8].

In order to supply many more LIBs for HEV, it is essential to secure the raw materials such as lithium, cobalt, manganese, and nickel. However, there are no resources of these metals in Korea. Korean manufacturing companies of cathode active materials are now importing their resources from overseas. In accordance with the necessity for security of the raw materials, the recycling of spent HEV batteries should be commercialized in Korea. The present research work is aimed at establishing the recycling process of spent battery modules in used hybrid electric vehicles using physical and chemical treatments.

Materials and methods

Physical treatment

A flow chart of the experimental system for physical treatment is shown in Fig. 1. A spent battery pack was disassembled into modules, which were separated into a circuit board, battery cell, and frame, and, finally, the battery cell was disassembled again from which cathode/anode materials and Al case were separated. The cathode/anode materials were discharged in distilled water, dried, and separated into separators, cathode materials, and anode materials. To recover the cathode active materials, the cathode materials went through crushing/particle-size separation to concentrate the cathode active materials within the cathode materials, and Al, an impurity, was separated in the process.

The purpose of the continuous crushing/classifying equipment is to recover cathode active materials ($LiNi_xMn_yCo_zO_2$) coated on the anode plate. As can be seen in the sample obtained through physical treatment, the separator or cathode plate can be recycled immediately because materials with singular composition are obtained. However, in the case of the anode plate, $LiNi_xMn_yCo_zO_2$ powder, a
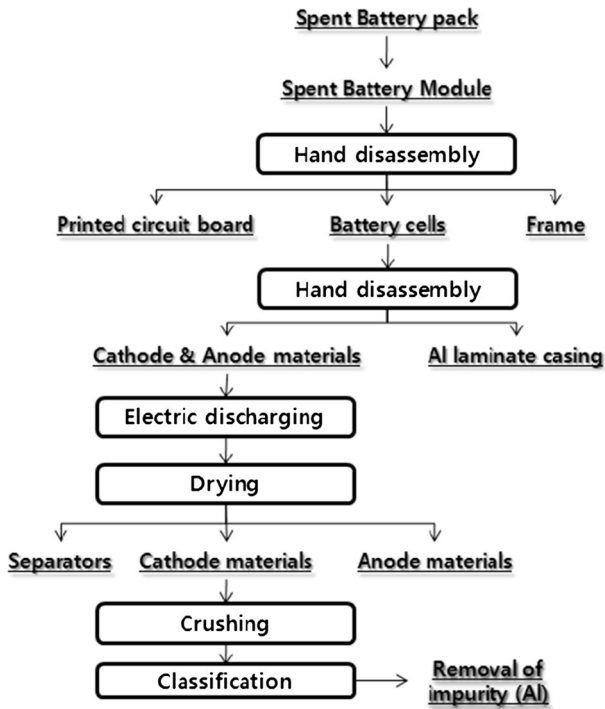
Fig. 1 The flow chart for physical treatment

cathode active material, is not separated from the Al foil on the top of the plate, which is a cathode collector, so a device to separate and recover this was designed.

Chemical treatment

Figure 2 shows the chemical treatment flow chart. The treatment was designed for crushed products obtained through particle-size separation. In order to manufacture a three-component system cathode active material precursor, leaching was conducted using sulfuric acid and reducing agent. At this point, observed leaching based on changes in sulfuric acid concentration, the amount of reducing agent, reaction temperature, agitation speed, solid–liquid ratio. Through pH control, impurities were removed from the leaching solution which was obtained through sulfuric acid leaching. By using co-precipitation, three-component system cathode active materials were manufactured from the leaching solution which had impurities removed. After co-precipitation, sodium carbonate solution was added to the filtrate which had remaining lithium in it, and Li was recovered in form of lithium carbonate after being precipitated, filtered, and washed. Co-precipitation was conducted in this research to establish a base technology for continuous recycling process by manufacturing Li filtrate and conducting Li recovery experiment.

Fig. 2 The flow chart for chemical treatment
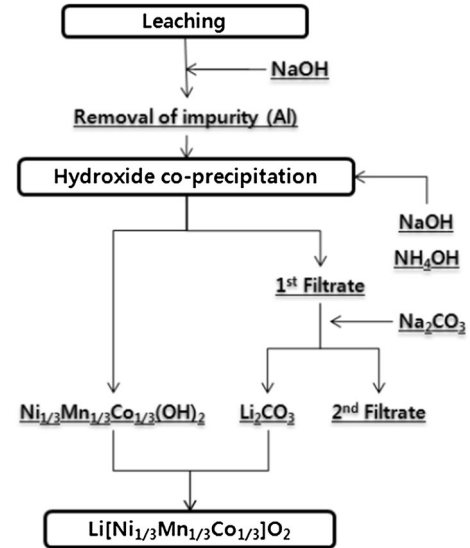
Co-precipitation

As shown in Fig. 3, co-precipitation was conducted in a 5-L beaker. The leaching solution was stirred using a Teflon impeller with 120 mm diameter, and the NH_4OH solution is prepared with the leaching solution as raw material, a NaOH solution with twice the concentration of the leaching solution, and a co-precipitator. After putting 500 mL of distilled water, which was adjusted to pH 9 using ammonium hydroxide, into the beaker, the 3 prepared solutions were put into the 5-L beaker using a quantitative pump (Master Flex) at a fixed feeding rate. The co-precipitation experiment was conducted for 48 h by controlling the pH within the reactor during reaction, and stirring the solution at 300 rpm.

Results and discussion

Physical treatment

Figure 4 show images of unit pack, modules, and cells that are separated from a spent battery pack when it is disassembled. There are series or parallel circuits, and cells are serially connected in modules. One pack has 6 modules and 1 module has 8 cells.

Because fire or explosion can occur in the physical treatment process, a battery cell discharge experiment was conducted for a stable disassembly. Conducting the experiment with distilled water as the discharge solution six times and observing the voltage change, the voltage sharply decreased within 10 min and a complete discharge of the battery cell was possible under a 70-min discharge condition, as shown in Fig. 5.
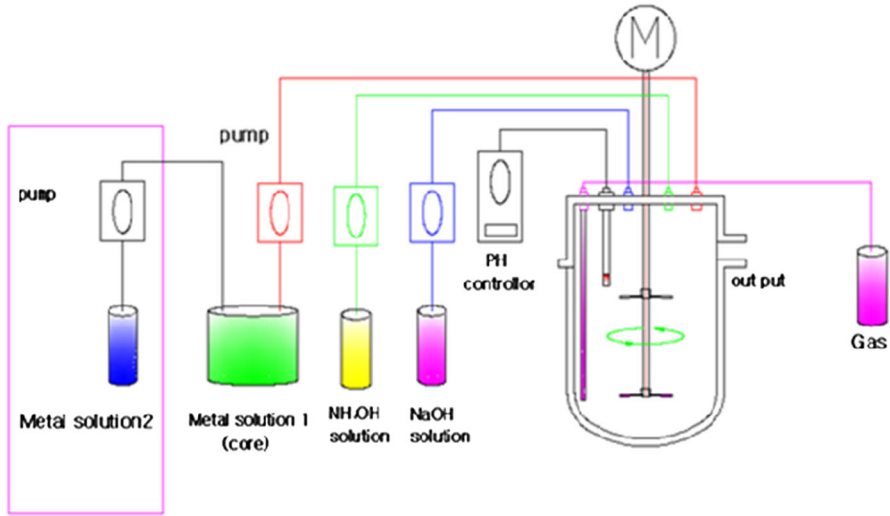
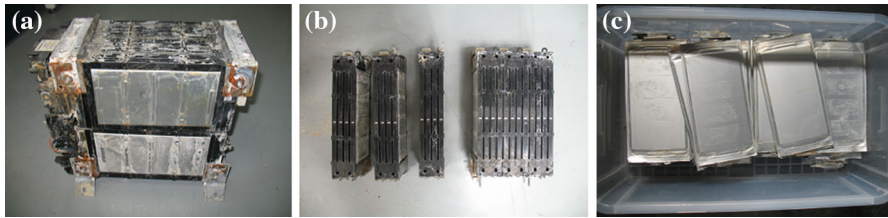**Fig. 3** Schematic diagram of the co-precipitation device

Fig. 4 a Pack, **b** modules, **c** cells in Avante HEV

In order to analyze the crushing efficiency, particle-size separation was conducted using 4 standard sieves, 8, 18, 40, and 65 mesh. The respective weight content rates of the 5 products, $+8$, $-8 + 18$, $-18 + 40$, $-40 + 65$, and 65 mesh, were measured and the levels of concentration for each particle-size were obtained. Using this information, the recovery rate of cathode active materials and the removal rate of impurities due to continuous crushing and classification were computed. By crushing/particle-size separation, recovered cathode materials at 65-mesh separation condition, over 95 % of valuable metals, such as Co, Li, Ni, and Mn, were concentrated and over 95 % of Al was removed as shown in Fig. 6.

Chemical treatment

By examining sulfur acid concentration, reducing agent concentration, and reaction temperature, the most optimum conditions are a pulverization product 100 g/L, 2 M H_2SO_4, 5 vol% H_2O_2, 300 rpm, 60 °C, and 2 h. At this condition, the leaching rate of valuable metals was over 98 %, and the concentrations of valuable metals after leaching at the optimum condition is shown in Fig. 7 and Table 1 below.
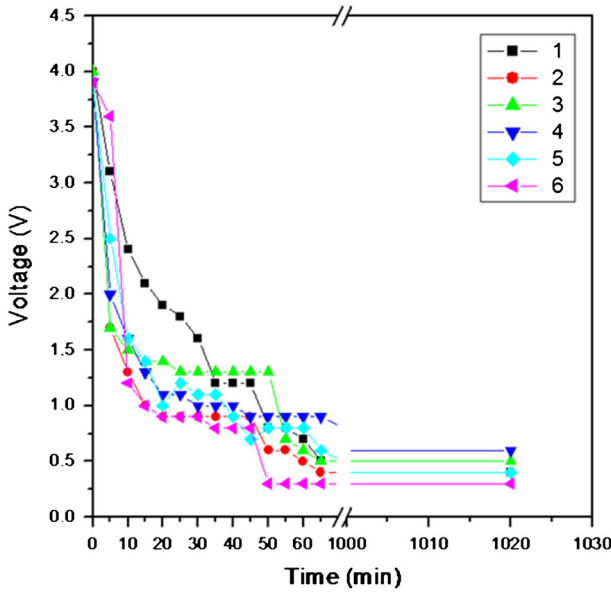
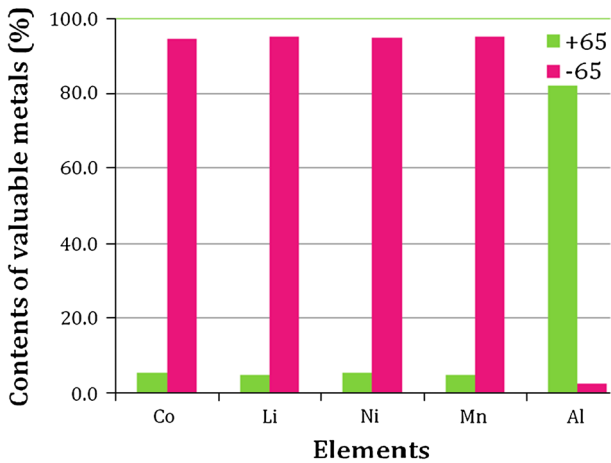**Fig. 5** Behavior of the decrease of the cell voltage by electric discharging

Fig. 6 65-mesh-based valuable metal concentration rates

Co-precipitation

Using the leaching solution which impurity concentration was controlled by pH, 3-component system hydroxide $(Ni_{1/3}Mn_{1/3}Co_{1/3})OH_2$, a cathode active material manufacturing intermediary, was produced by co-precipitation. Because the
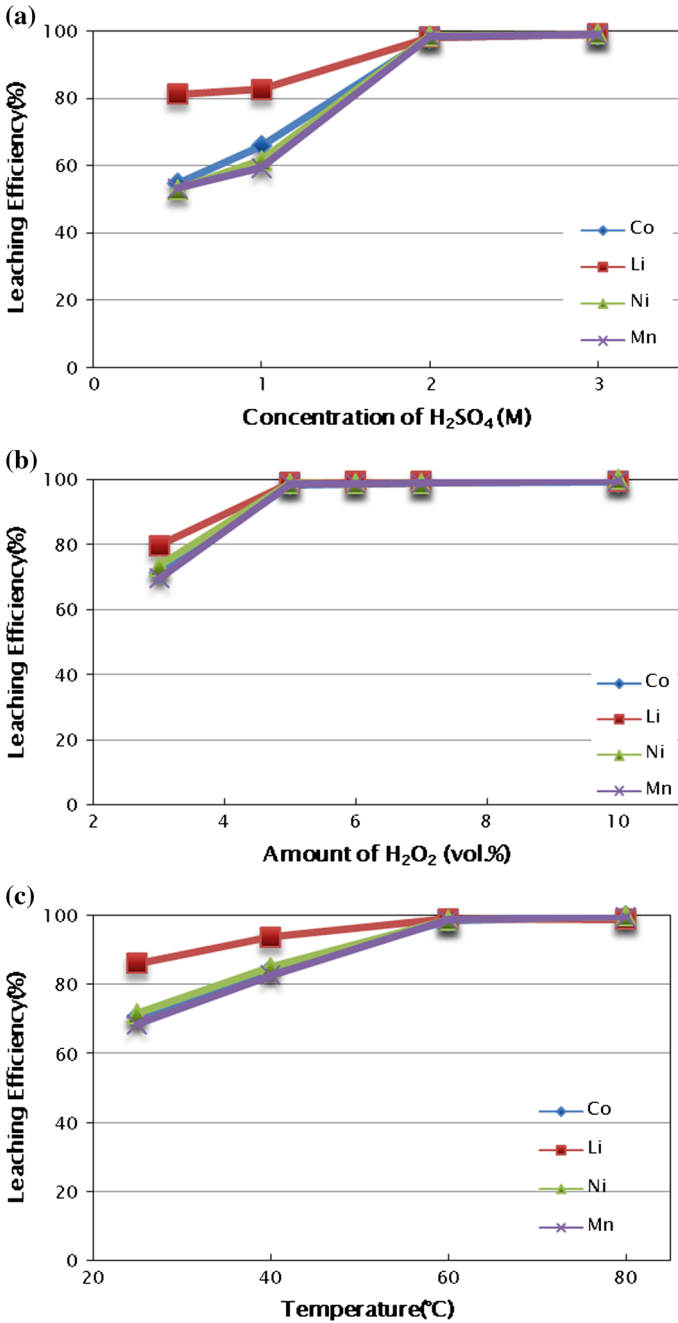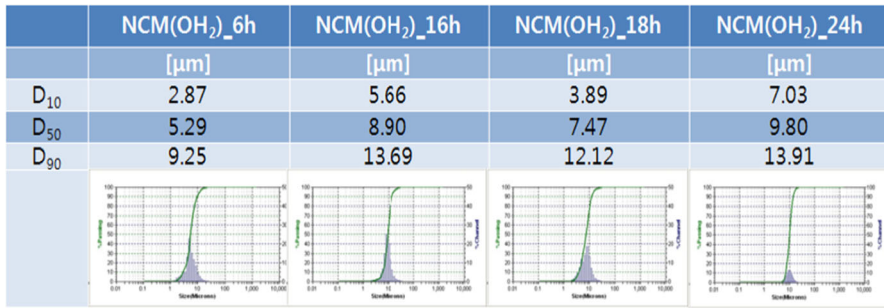
Fig. 7 Reductive leaching behavior: **a** effect of concentration of H_2SO_4, **b** effect of concentration of H_2O_2 as a reductant, **c** effect of temperature

particle-size of the 3-component system hydroxide was within 10 μm even after 24 h, it was confirmed that it can be used as a cathode active material in lithium-ion batteries (Fig. 8).
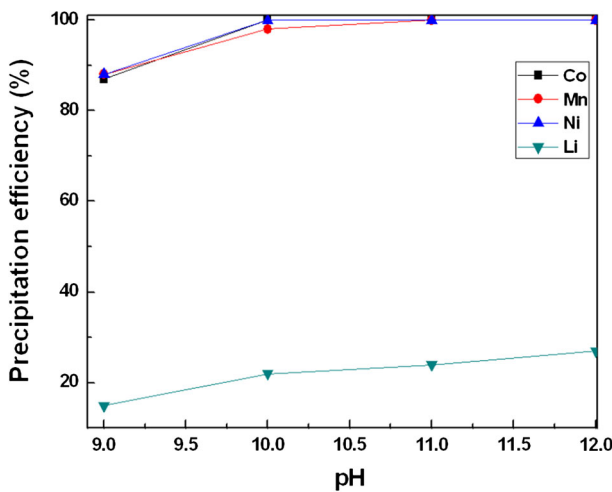
By controlling pH with NH_4OH and $NaOH$ precipitation solution (pH 9–12), the optimum co-precipitation condition was established at above pH 11 (Fig. 9; Table 2)

Table 1 Concentrations of valuable metals at the optimum condition for sulfuric acid reduction and leaching

Element	Co	Mn	Ni	Li	Al
Concentration (mg/L)	10,390	14,470	16,070	12,250	234
Leaching rate (%)	98.4	98.6	98.8	98.9	89.0

	NCM(OH₂)_6h	NCM(OH₂)_16h	NCM(OH₂)_18h	NCM(OH₂)_24h
	[μm]	[μm]	[μm]	[μm]
D_{10}	2.87	5.66	3.89	7.03
D_{50}	5.29	8.90	7.47	9.80
D_{90}	9.25	13.69	12.12	13.91

Fig. 8 Particle-size analysis with reaction time

Fig. 9 Co-precipitation behavior with pH

Table 2 Concentrations of valuable metal ions in solution before and after co-precipitation

Element	Co	Mn	Ni	Li
Leaching liquor	17,930	19,270	17,950	5,570
pH 9	2,386.4	2,302.9	1,779.1	4,893.6
pH 10	15.3	553.8	2.5	4,375.4
pH 11	0.3	0.0	0.5	4,225.8
pH 12	0.3	0.0	0.5	4,100.0

Conclusions

Spent HEV battery pack was physically treated for hand disassembly, electric discharged, dried, crushed, and classified as well as chemically leached with sulfuric acid and H_2O_2 as a reductant. The following conclusions can be drawn based on the experimental results:

1. The HEV battery pack which is series with 6 unit modules (48 unit cells) was dismantled to unit modules and unit cell by manual. The results of characteristics of electric discharging, drying, grinding, and classifying about unit cell were confirmed for chemical treatment.
2. Over 95 % of valuable metals from cathodic active material were concentrated by grinding and classifying, while Al is only 2.7 % concentrated. Weight percent of valuable metals with 65-mesh powder was 6.7 % Co, 34.4 % Mn, 6.7 % Li, 29.9 % Ni, and 0.11 % Al.
3. Under optimum conditions (2 M H_2SO_4, 5 vol % H_2O_2, 60 °C, 300 rpm, 50 g/ 500 mL), leaching efficiency of valuable metals (Co, Li, Ni, Mn) was over 98 % with concentrations of Co 10.4 g/L, Li 12.3 g/L, Ni 16.1 g/L, Mn 14.5 g/L, and Al 0.3 g/L, respectively.
4. For further study, separation/purification/recovery tests were performed using a mixed hydroxide method for $Ni_xCo_yMn_z(OH)_2$ for a cathodic active material precursor of a HEV battery, and electrical and chemical properties of that precursor were examined for the possibility of reuse of the cathode active material of LIBs using recovered salts.

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