Hydrometallurgical processing of Li-Ion battery scrap from electric vehicles

H. Wang, M. Vest, B. Friedrich

RWTH Aachen University
IME Process Metallurgy and Metals Recycling
Intzestraße 3
52056 Aachen, Germany

Keywords: Li-ion batteries, recycling, hydrometallurgy, lithium, cobalt, nickel

Abstract

The Li-Ion battery scrap from electric vehicles was treated with a hydrometallurgical process. The process comprises leaching, solution purification, Co-Ni-Mn recovery and Li_2CO_3 precipitation. The batch-wise leaching step revealed extraction rates of Li, Co, Ni, Mn and Al are higher than 95 % at optimum leaching conditions. The extraction rate of Cu varied between 40 % and 50 % without presence of hydrogen peroxide. The solution purification step is realized by adjusting the pH of the leaching solution. Al, Cu and Fe can be precipitated from the solution in the form of metal hydroxide by increasing the pH of the solution to 5.5 (40 °C). More than 99 % of Co, Ni and Mn can be subsequently removed from the solution by either hydroxide or sulphide precipitation methods. The Co-Ni-Mn mixture is available for the new batteries electrode powder production or further hydrometallurgical separation processes. The lithium is to be precipitated from the solution by adding Na_2CO_3 at 95 °C.

Introduction

At the beginning of the 20th century 3 motoring solutions were nearly equally used for road transportation (i.e. engine, steam engine, electric motor). It appeared from the beginning of the second decade that alternative of internal combustion engines (ICE) had captured the market for all different types of road vehicle. With emerging of climate changing and global warming issues in the recently 30 years, CO_2 reduction, fuel saving and utilisation of clean energy are obligatory in modern society. In automobile industry, scientists began to focus on pure electric vehicle (EV), Hybrid electric vehicles (HEV) and Plug-in hybrid electric vehicles (PHEV) which are assumed as the best alternatives for the conventional vehicles. [1], [2]

In the near future, the need for automotive lithium ion batteries (LIBs) will increase dramatically. However, the problem people must face is the recycling of them. LIBs consist of many valuable metals, such as lithium, cobalt, nickel, manganese, copper and aluminium. Many attempts, including pyrometallurgical and hydrometallurgical methods, have been done to recycle spent LIBs. [3] However, they need further improvement to winning the valuable metals more efficiently, economically and environmental friendly. With the financial support of German Federal Ministry of Education and Research BMBF in the project “LiVe!”, the innovative research works has been performed and the goal has been achieved.

1. Lithium-ion batteries for vehicles

Lithium-ion batteries are considered to be the best choice for electric vehicles. Figure 1 shows the energy density per unit volume (Wh/l) and per unit weight (Wh/kg) of different rechargeable batteries. The performance of lithium-ion batteries is apparently superior to lead acid and nickel cadmium batteries. The voltage of lithium-ion battery is around 3.7 V, which is three times that of conventional nickel batteries, such as Ni-Cd, Ni-MH. Besides, Lithium-ion batteries have no memory effect and have high cycle times. [4]

The electrical energy requirements, i.e. the requirements of lithium-ion batteries, are different depending on the type of vehicles. For pure electric vehicles, a large amount of energy must be stored in order to transport the vehicle over an acceptable distance. Typical EV battery packs store on the order of 35 kWh. It is possible to store as much energy as desired in batteries by simply increasing their number, but this increases the weight to unacceptable high values. Therefore, an important objective in development of batteries for EV is to maximize energy density, the energy stored per unit volume, or specific energy, the energy stored per unit mass. [5]

For HEV, the main source of energy is fuel. What is needed from the battery is a power boost for rapid acceleration. Therefore, the attribute of the battery to be maximized is specific power of power density. High-power lithium-ion batteries currently achieve a specific power greater than 1300 W/kg and a power density greater than 2700 W/L. In addition, the high-power cells must be smaller than the high-energy cells in order to dissipate the higher generated heat. [5]

PHEV are vehicles that can draw and store energy from an electric grid to supply propulsive energy for the vehicle. Different from EV and HEV, PHEV require intermediate designs, they have much larger batteries than HEV and can also be charged from the electric-grid when not in use, in order to maximise the range available to the electric motor. Therefore, they act as a halfway ground between hybrid electric vehicles (HEV) and electric vehicles (EV). [5]

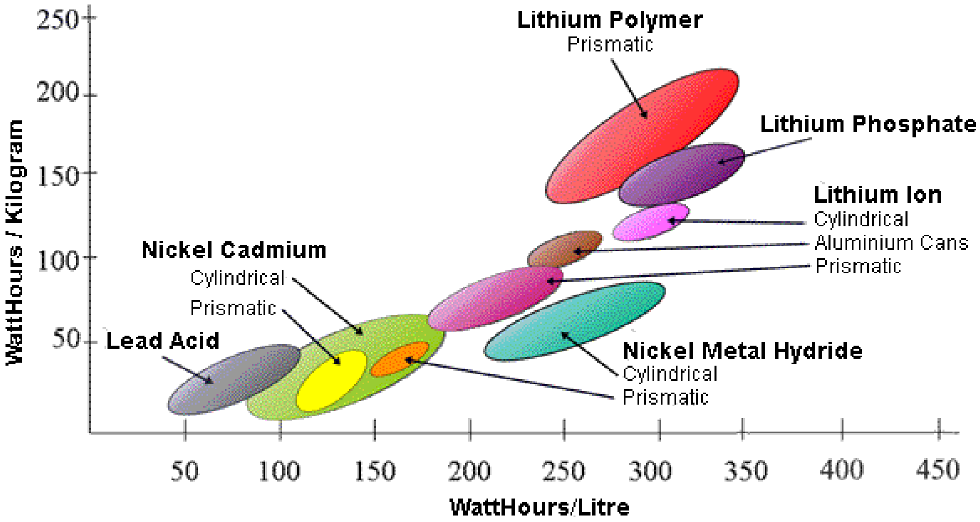

Figure 1: Energy density of different rechargeable batteries pro kilogram and litre. [6]

1.1 The redox reaction of lithium-ion batteries

The function of lithium-ion batteries is realized by transportation of lithium ions between the cathode and anode. The inorganic compounds, e.g. $LiCoO_2$, $LiNiO_2$, $LiFeO_4$, are used as cathode. Carbonaceous material is used as an anode material. During charging, lithium is deintercalated from the cathode layers, then transported and intercalated into the carbonaceous anode. In the discharge process, the lithium ions are deintercalated from the anode and intercalated again to the empty octahedral site between layers in the cathode. [4]

The total reaction in the lithium ion battery cell system with a $LiCoO_2$-cathode is

$$LiCoO_2 + C_6 \xrightarrow{charging} Li_{1-x}CoO_2 + Li_xC_6 \qquad (1)$$

$$Li_{1-x}CoO_2 + Li_xC_6 \xrightarrow{discharging} LiCoO_2 + C_6 \qquad (2)$$

1.2 Construction of lithium-ion batteries

The main components of a lithium-ion-battery are anode, cathode, electrolyte, separator and cell packaging. The anode is made by coating a carbon material (mixed with binder and conductive additive) on a copper foil as negative plate and cathode is made by coating lithium-containing metal compounds (also mixed with binder and conductive additive) on an aluminium foil as a positive electrode plate. A barrier membrane is placed between the anode and cathode plates. The electrolyte solution is injected into the battery and fully contacted with the electrode. The battery is sealed with steel or aluminium can body and encased with a plastic enclosure. [4]

2. Description of developed recycling process

Figure 2 shows the designed hydrometallurgical recycling process for the spent lithium-ion batteries of vehicles. The relevant proceedings are marked with numbers. The reason to recycle Lithium-ion batteries in hydrometallurgical way is the consideration of high selective, low energy requirement in comparation with the pyrometallurgical way.

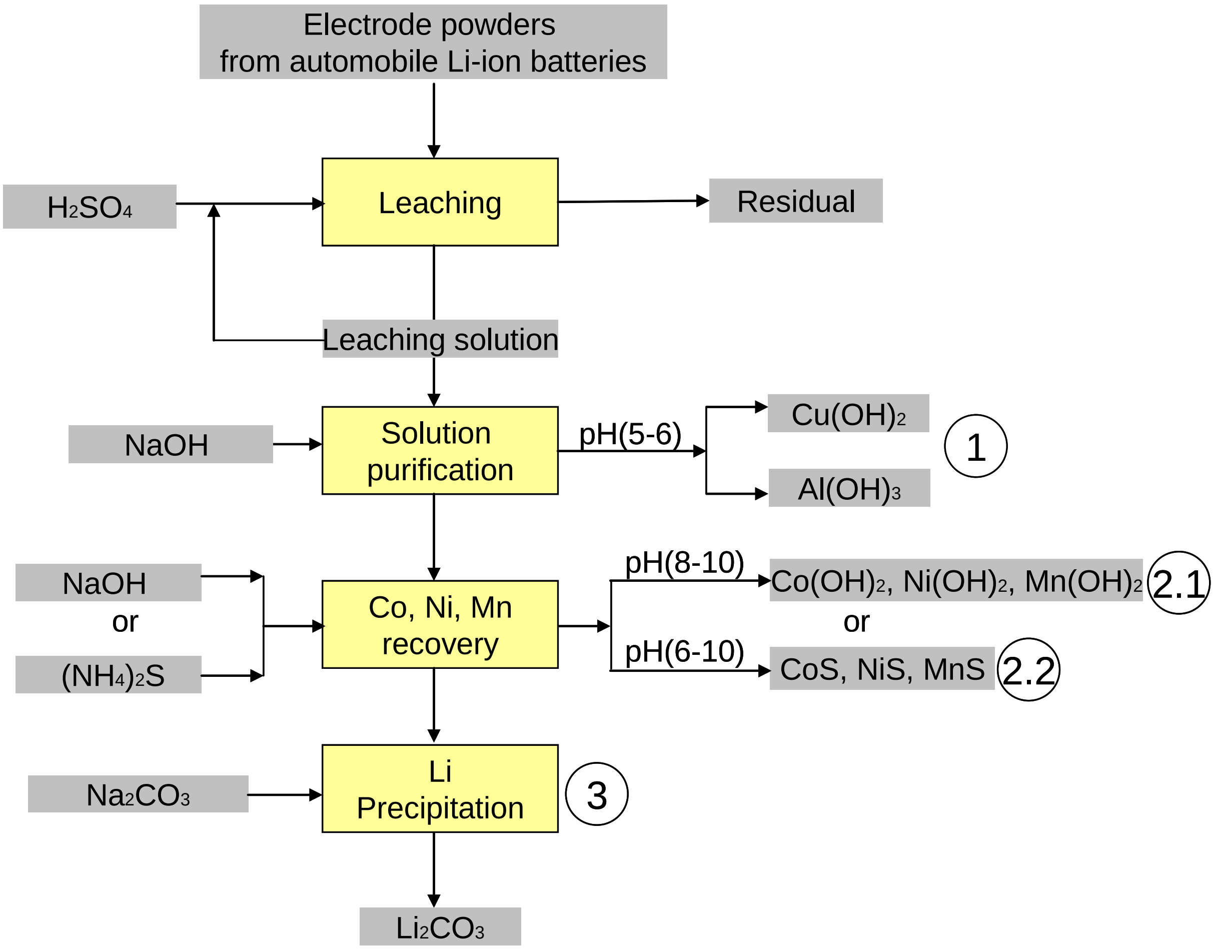

Figure 2: The designed hydrometallurgical recovery process of spent lithium-ion batteries

The leaching process is inevitable for the whole recycling process. Leaching time, temperature, acid concentration and additives are chosen in such a way that the optimum leaching conditions are developed. The valuable metals in the raw material are extracted and dissolved in the leaching solution.

In the solution purification step, copper and aluminium are removed first by hydroxide precipitation. The co-precipitation and adsorption of Co/Ni in the precipitate is tried to be prevented. With an appropriate temperature and reaction time, the equilibrium can be completely reached. The $Cu(OH)_2$ and $Al(OH)_3$ particles can grow and aggregate to a sufficient size. Subsequently, the solution can be filtered and the residual is supplied to copper and aluminium production. At moment, the Al and Cu is precipitated together, it will be tried to remove them from the solution separately in future.

After the step 1 (see Figure 2), Ni, Co and Mn are removed from Li with hydroxide or sulphide precipitation methods. The Ni, Co and Mn containing concentrate is filtered and supplied to other metal recovery process. The step 2.1 (see Figure 2) is the removal of Co, Ni and Mn with hydroxide precipitation method. With sufficient high pH value by adding the neutralisation reagent, the Co, Ni and Mn hydroxide will form in the solution. An alternative of step 2.1 is by using sulphide precipitation, step 2.2 (see Figure 2). Ammonium sulphide solution serves as the sulphide ions supplier. The amount of ammonium sulphide must be precisely controlled otherwise the rest of ammonium sulphide can influence the following lithium recovery process.

In step 3 (see Figure 2), the lithium ions are recovered in the form of lithium carbonate by adding saturated soda solution.

3. Description of prepared electrode powder from automobile lithium-ion batteries

The electrode powder is a mixture of metal oxide compound and metal scrap particles which comes from different cathode types of automobile batteries. The spent lithium-ion batteries are dismantled to separate plastic, steel casing and electronic scrap from the cell. In the following deactivation step, the cells are treated for five hours at temperature 500 °C. The electrolyte in the cell will degrade and volatile. The deactivated cells are sent to crushing and sieving processes. Ferrous scrap is subsequently magnetically separated. The non-ferrous metals, such as Copper and Aluminium scraps are obtained by sieving.

The chemical composition of obtained powder is shown in Table 1. In the electrode powder, nickel and cobalt are 17.9 wt-% and 4.15 wt-% respectively. Lithium has taken 3.95 wt-% of the whole electrode powder. Even though copper, aluminium and iron can be separated mechanically, they can still intermingle into the prepared electrode powder. The rest of electrode powder is carbon which is about 36 wt-% of the powder.

Table 1: Chemical composition of prepared electrode powders

Element	Li	Ni	Co	Mn	Cu	Al	Fe	C
Composition (%)	3.95	17.9	4.15	15.2	0.95	1.14	<0.1	36.6

4. Leaching of electrode powder from automobile batteries

In the leaching process, the valuable metals in the raw materials can be extracted from the raw material to the solution. The leaching experiments will be carried out in various conditions. Each influence factor, such as leaching time, acid concentration, temperature, additives will be investigated respectively.

4.1 The influence of leaching time

The leaching reaction is carried out at the conditions: 60 °C, 2 mol/L H_2SO_4, 20 g/L H_2O_2, 50 g/L solid liquid ratio. The concentrations of extracted metals are tested by the Inductively Coupled Plasma (ICP-OES). The metal extraction changing with different leaching time is shown in Figure 3.

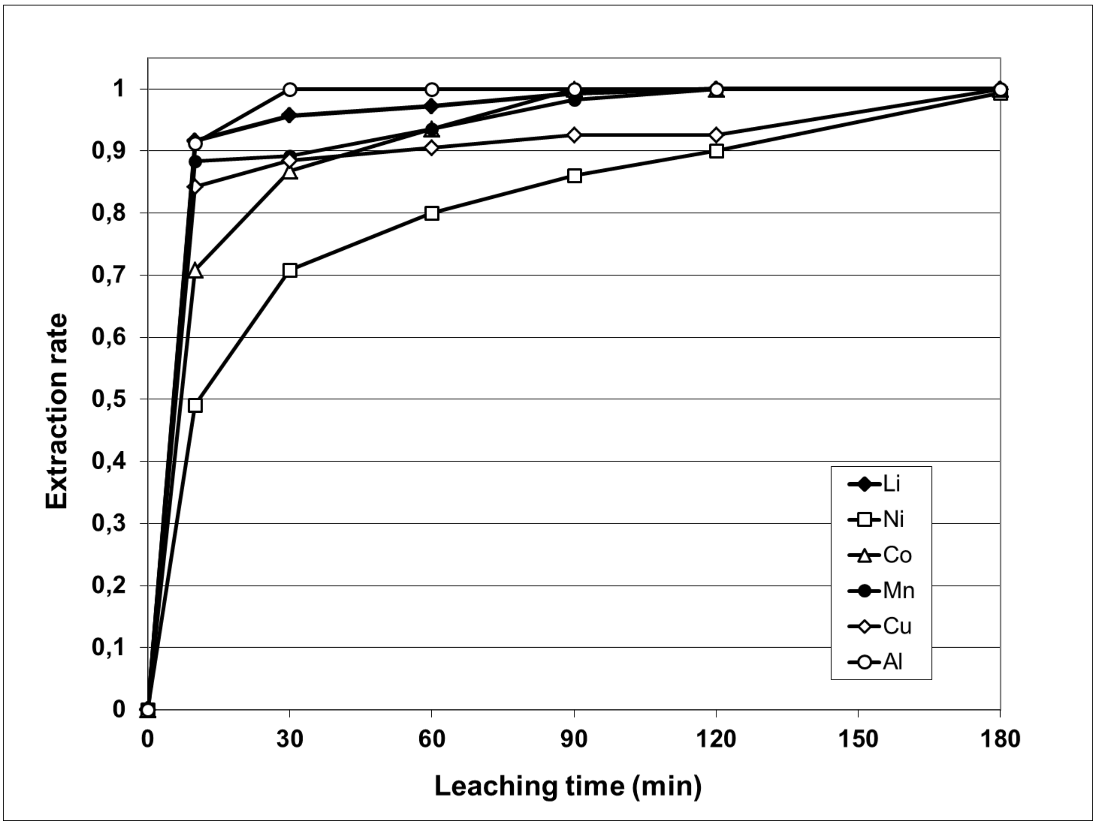

Figure 3: The influence of leaching time on the extraction of metals. (60 °C, 2 mol/L H_2SO_4, 20 g/L H_2O_2, 50 g/L)

The leaching reaction at the beginning ten minutes proceeds very fast. After evaluation of extraction rate, more than 90 % of Li and Al are already dissolved. The Mn and Cu extraction rates also reach a high level. Cobalt and nickel are relatively nobler than other metals. Nickel dissolves slowest and only 49.05 % has been dissolved at the beginning ten minutes. The complete extraction requires 3 hours. Cobalt dissolves not so fast and has only 70.84 % extraction rate after 10 minutes. After 90 minutes almost all the cobalt has been leached. The nearly complete dissolution of all metals can be finished in 3 hours leaching time. The leaching reaction of $LiCoO_2$ with sulphuric acid is:

$$6H_2SO_4 + 4LiCoO_2 \rightarrow 4CoSO_4 + 2Li_2SO_4 + O_2 + 6H_2O \qquad (3)$$

The leaching reaction of $LiCoO_2$ of lithium-ion batteries in H_2SO_4 with the addition of hydrogen peroxide is as following [3]:

$$2LiCoO_2 + 6H^+ + H_2O_2 \rightarrow 2Co^{2+} + O_2 + 2Li^+ + 4H_2O \qquad (4)$$

In the first hour, the chemical reaction proceeds very fast. In the aspect of continuous operation, the suitable leaching time: 1 hour. After 1 hour, the new acid and the new material are added into the reactor to keep a high efficiency.

4.2 The influence of H_2O_2 during leaching

Hydrogen peroxide (H_2O_2) has a high oxidation potential and can oxidise some relative noble metals. The effect of H_2O_2 during leaching has been shown in Figure 4. The extraction of nickel has decreased from 0.9 (without H_2O_2) to 0.7 (with 10 g/L H_2O_2). There is no large difference with further adding H_2O_2. The concentration of cobalt also decreases a little at the present of H_2O_2. Copper extraction has increased from 44.21 % (without H_2O_2) to 88.62 % (with 10 g/L H_2O_2). All the copper has been leached at the H_2O_2 content of 20 g/L. For other metals, such as aluminium, manganese and lithium, there are no significant influences.

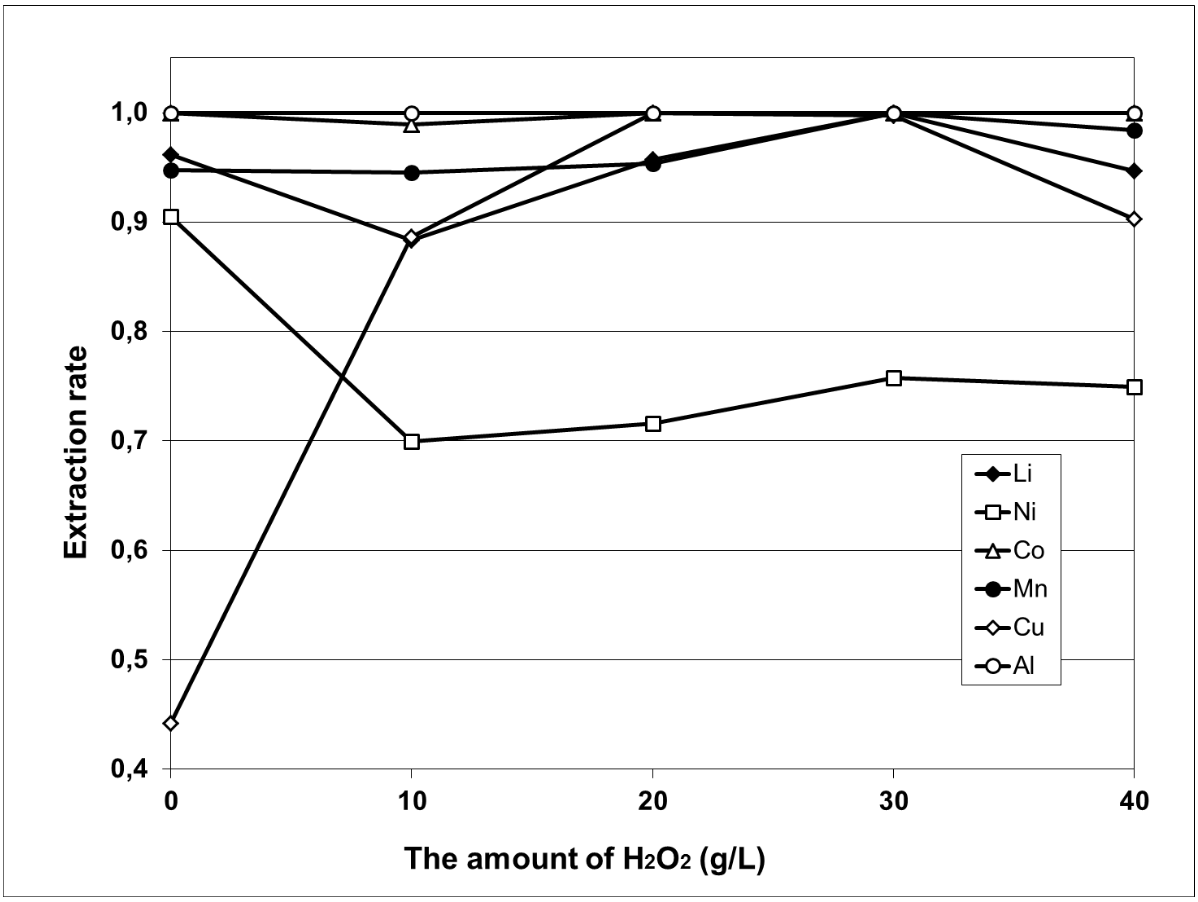

Figure 4: The influence of hydrogen peroxide (H_2O_2) on the extraction of metals (60 °C, 2 mol/L H_2SO_4, 1 h, 50 g/L)

It is evident that the nickel extraction has been hindered with adding H_2O_2 in the 1 hour's reaction time, while copper extraction has been increased significantly up to completely dissolution because of the high oxidation potential of H_2O_2. The residual of the leaching without H_2O_2 has been washed to remove the carbon particles. Certain amount of copper has been observed on the bottom of the glass beaker, as copper has a larger density than carbon. However, no copper has been observed in the other residuals from leaching experiments with H_2O_2. Figure 5 shows the copper particles in the residual. With presence of H_2O_2, the extraction of copper can be improved and meantime the dissolution of nickel is relatively hindered in the limited reaction time (1h).

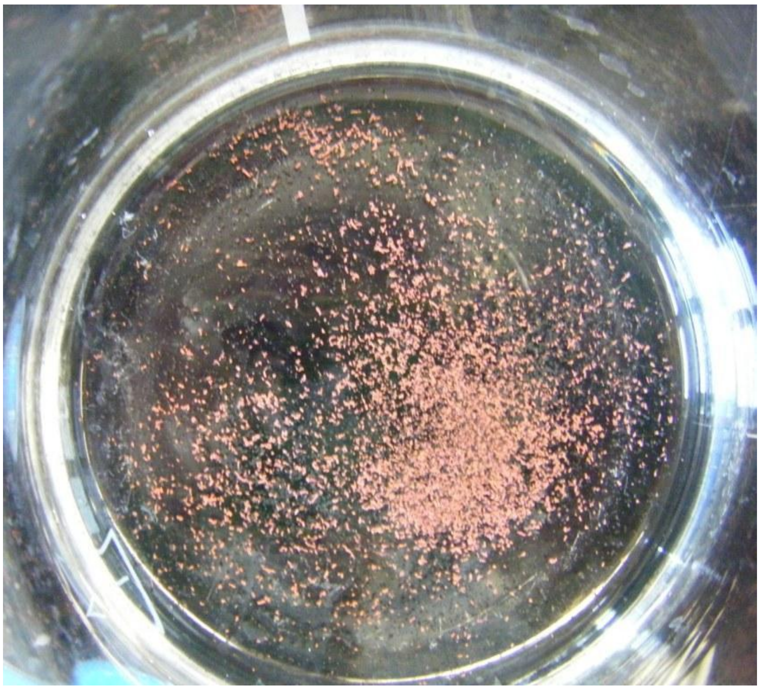

Figure 5: Copper particles from the residual of leaching experiment without H_2O_2

4.3 Leaching with different acid concentration

Figure 6 shows the leaching experiments with different acid concentrations. In the case of leaching with water (acid 0 mol/L), 35.44 % lithium has dissolved. The solution appears to be an alkaline solution (pH>7). From acid content 0.5 to 2.5 mol/L, the extraction of metals increases slightly. For cobalt extraction, high sulphur acid concentration is more effective. The extraction of cobalt has increased from 0.91 (0.5 mol/L H_2SO_4) to 0.99 (2 mol/L H_2SO_4). For nickel, cobalt and manganese, higher acid contents promote their extraction rate. Lithium and aluminium are relatively easier soluble elements, which can reach a high extraction level at a lower acid concentration. The copper extraction stays between 40 % and 50 %. It is not significantly influenced by acid content. According to the above discussion, the suitable H_2SO_4 concentration is 1-2 mol/L to maintain a high leaching efficiency.

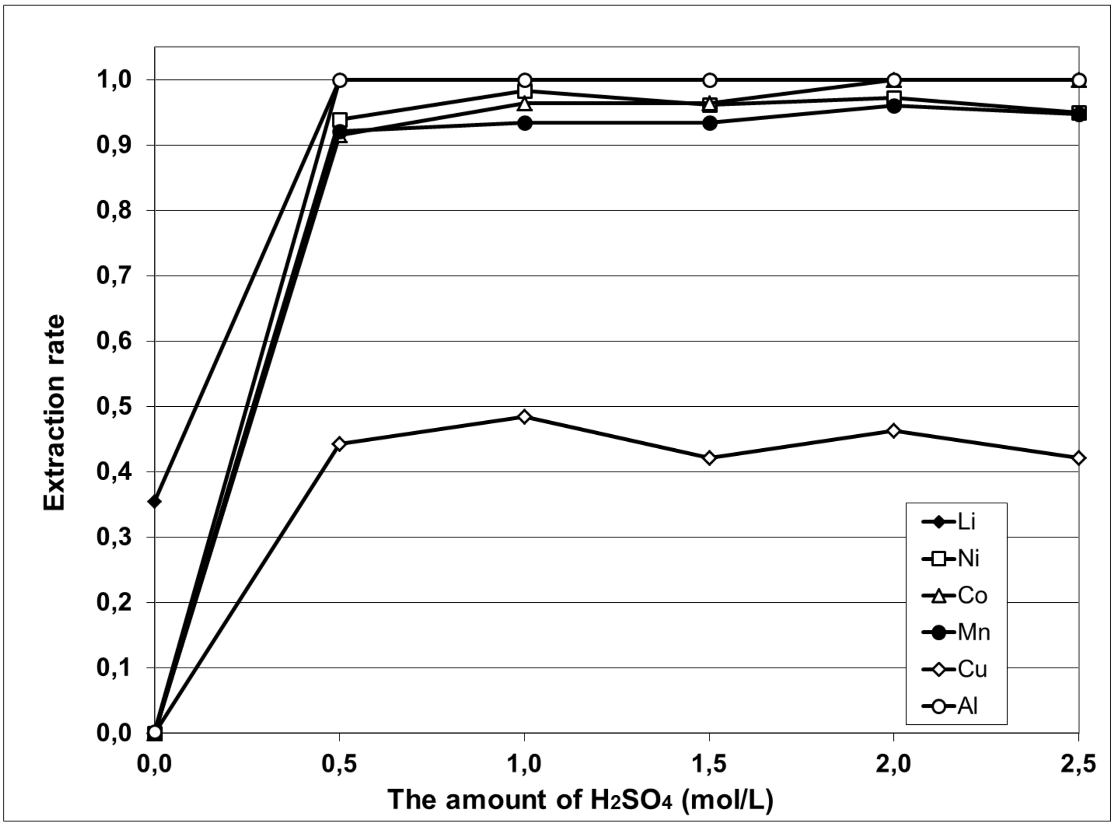

Figure 6: The influence of sulphuric acid concentration on the extraction of metals (60 °C, 1 h, 50 g/L)

4.4 Leaching with different temperature

As the leaching of electrode powder belongs to the diminishing particles model, the reaction temperature plays an important role in the leaching process. Figure 7 shows the leaching performance from 40 °C to 80 °C. At 40 °C, the extraction of cobalt and nickel are lowest in comparison with other temperatures. A little foam is formed at the beginning of the leaching experiment. In addition the exothermal effect is not significant. It implies that a very low temperature can hinder the reaction kinetics.

The increasing of temperature is favoured by leaching of metals. The nickel extraction has increased steadily with increasing the leaching temperature. The copper, aluminium and lithium extraction are slightly influenced by temperature. At higher temperature high leaching efficiency was obtained but also caused high energy consumption. According to the above discussion, the suitable leaching temperature is 60~80 °C to maintain a fast leaching reaction.

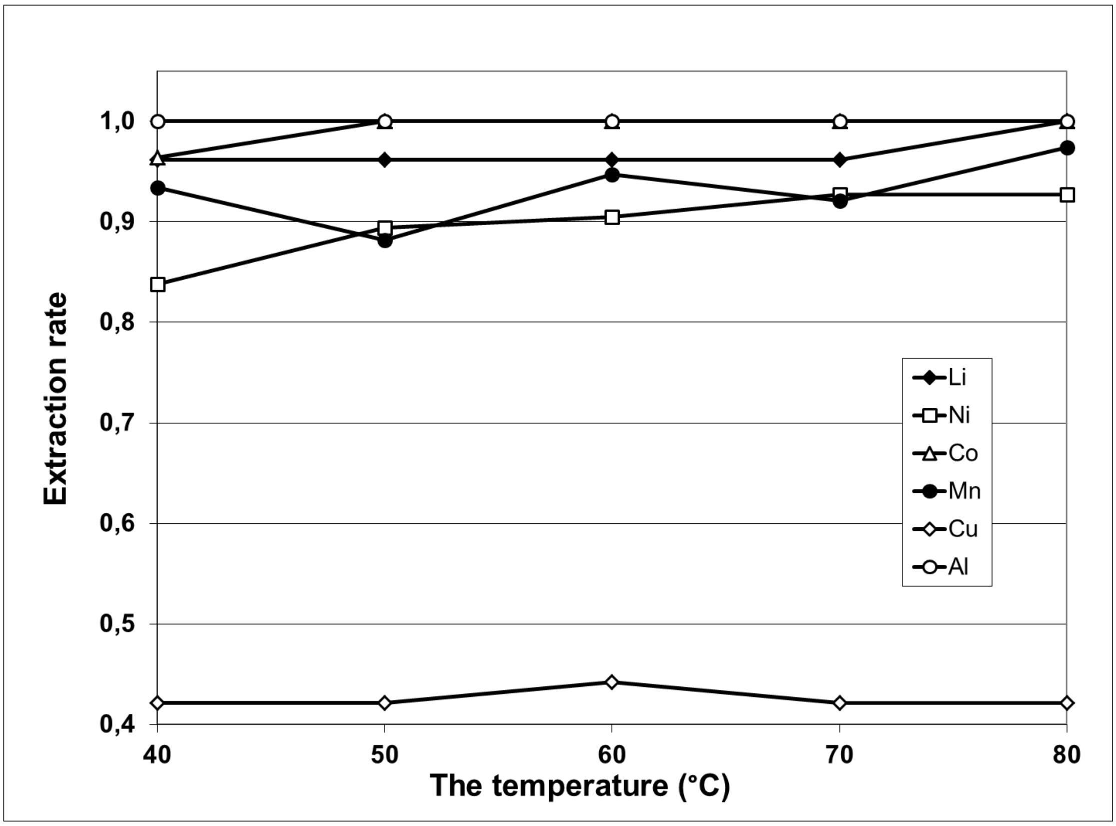

Figure 7: The influence of temperature on the extraction of metals (2 mol/L H_2SO_4, 1 h, 50 g/L)

5. Solution purification and metal recovery

5.1 Solution purification step (Al, Cu and Fe precipitation)

The solution purification process proceeds with changing pH values of the solution at 40 °C. With adding the sodium hydroxide solution, the pH of the solution increases slowly. Solid particles are formed in the solution. The sampling of the solution is taken at equilibrium pH of 1.39, 1.92, 2.88, 4.33, 5.07, 5.56, 6.00, and 6.93 in the whole solution purification process. The effect of pH on the precipitation of metals has been illustrated in Figure 8. This chart has revealed aluminium, iron and copper are successfully precipitated from the solution.

Iron is the earliest metal to precipitate. It has a two-step precipitation. From pH 1 to pH 3, almost half of the iron has entered into solid form. From pH 4 to pH 5, the rest of iron precipitates. Aluminium is also very easily precipitated from the solution. From pH 1.92, the amount of aluminium in the solution decrease steadily. The aluminium is completely removed from the solution at pH 6. Different from iron and aluminium, the precipitation of copper is in a shorter pH-range. The precipitation of copper starts at pH higher than 5 and already at a pH 6 all of the copper has been precipitated.

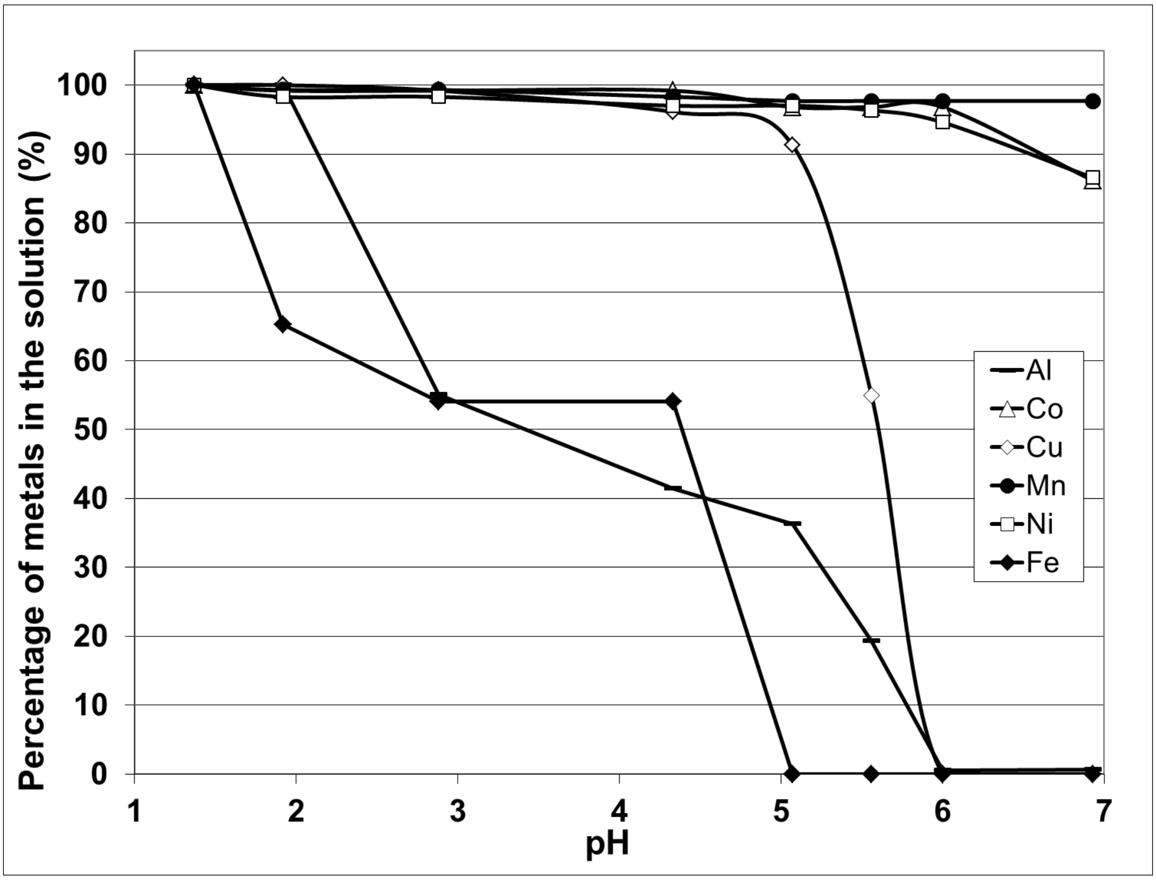

Figure 8: Effect of pH on the removal of impurity metals from the Li-rich leaching solution

The co-precipitation of cobalt, nickel and manganese cannot completely be avoided. At lower pH value, these three metals stay in the solution. At pH 6, the loss of cobalt, nickel and manganese are 3.2 %, 5.4 % and 2.3 % respectively. Once the pH increases further to 6.93, more cobalt and nickel hydroxide has been formed. The cobalt and nickel losses have increased to 13.8 % and 13.4 % respectively. According to the above discussion, the optimum pH for the solution purification is about 5.5 (40 °C). In this pH range, nearly all the aluminium, copper and iron can be successfully separated from the solution. The co-precipitated cobalt, nickel and manganese are in a very low level. In Principle, Lithium cannot form any compounds with other ions. The loss of lithium is usually caused by sampling and absorption, therefore lithium is not included in this diagram.

5.2 Co-Ni-Mn recovery through hydroxide precipitation

The cobalt, nickel and manganese have been successfully removed from the solution after adding 6 ml NaOH solution (1 mol/L). The remaining aluminium and copper have also co-precipitated at the same time. There is only Li left in the solution. The obtained solution can be directly supplied to the lithium recovery process. Figure 9 shows the mass flow of the whole process. Table 2 shows the metal concentrations before and after the precipitation process.

Table 2: The experimental result of Co-Ni-Mn hydroxide precipitation from purified Li-solution

Concentration of metal ions	Al	Co	Cu	Fe	Li	Mn	Ni
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Purified solution	6.6	589	4.57	<1	583	1077	2446
Li-ion solution	<1	<1	<1	<1	620	<1	<1

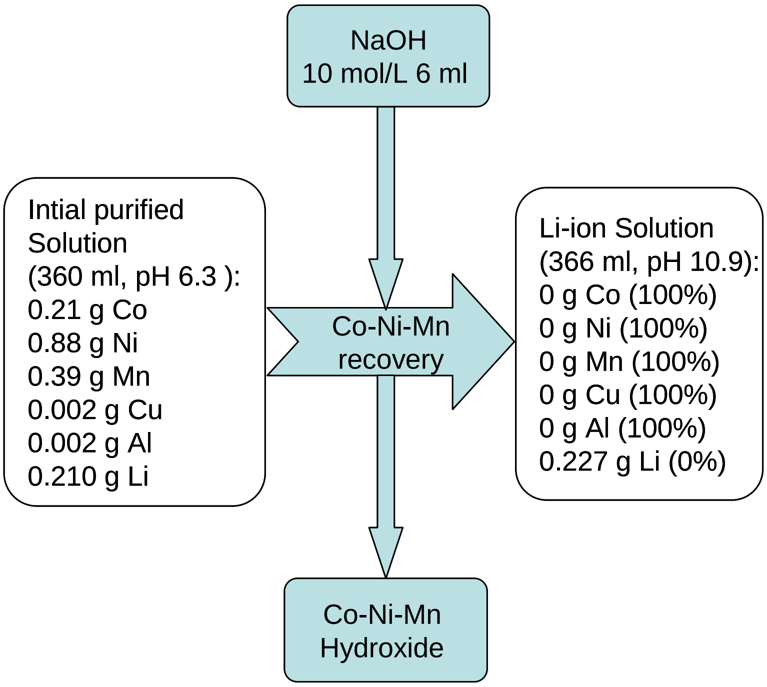

Figure 9: The analysis of the experimental results of Co-Ni-Mn hydroxide precipitation process (the percentage in bracket is the precipitated amount of metals)

The experimental result has demonstrated that the hydroxide precipitation at pH>10 can recover Co, Ni and Mn as a valuable mixture of three metals. The chemical composition is shown in Table 3.

Table 3: Chemical composition of Co-Ni-Mn mixture

Element	Li	$Ni(OH)_2$	$Co(OH)_2$	$Mn(OH)_2$	Cu	Al	Fe
Composition (%)	0.5	33.3	8.63	42.3	<0.05	0.16	<0.05

5.3 Co-Ni-Mn recovery through sulphide precipitation

The mass flow of all the metals during Co-Ni-Mn sulphide precipitation is shown in Figure 10. At this step, cobalt, nickel and manganese have been removed again nearly to 100 %. Only a trace content of Mn and Al stay in the solution. Manganese has a concentration of only 10.5 mg/L. Aluminium has a rather low concentration of 1.5 mg/L. (s. Table 4) Cobalt, nickel, copper and iron are completely removed. The obtained Li-ion solution can directly be used for lithium recovery.

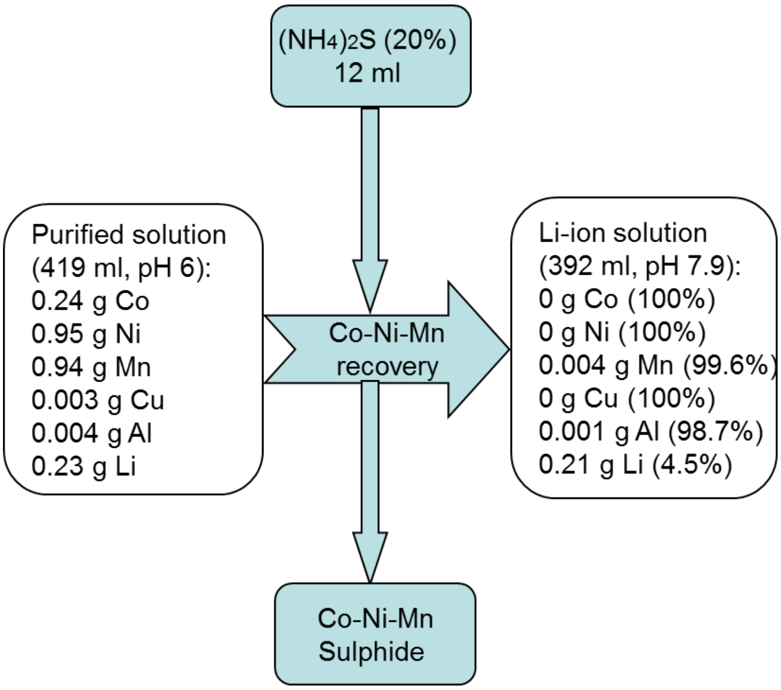

Figure 10: The analysis of Co-Ni-Mn sulphide precipitation process (the percentage in bracket is the precipitated amount of metals)

Table 4: The experimental result of Co-Ni-Mn sulphide precipitation from purified Li-solution

Concentration of metal ions	Al	Co	Cu	Fe	Li	Mn	Ni
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Purified solution	9	592	7.38	<1	559	2248	2266
Li-ion solution	1.5	<1	<1	<1	540	10.5	<1

6. Lithium carbonate precipitation

The solution after Co-Ni-Mn recovery process is tempered on a heating plate at 95°C and subsequently treated with a soda solution to precipitate lithium carbonate. During heating, the lithium containing solution is concentrated by the water evaporation. The crystallisation of lithium carbonate occurs immediately after addition of sodium carbonate. Because the lithium carbonate in the solution has reached the supersaturated state, the lithium carbonate will automatically crystallise. The concentration changing of different metals and detailed data are shown in Table 5. The lithium concentration is decreased from 4.4 g/L to 1 g/L after adding excessive sodium carbonate solution. The raffinate is gathered and purified for the further lithium recovery.

Table 5: The data of metal concentration at different step in recycling process

Concentration of metal ions	Al	Cu	Li	Co	Ni	Mn
	mg/l	mg/l	g/l	mg/l	mg/l	g/l
Lithium-ion solution	<1	<1	4.4	<1	<1	0.345
Raffinate	<1	<1	1.0	<1	<1	0.267

Based on the information of Table , the lowest lithium concentration to precipitate lithium carbonate at 100 °C is 1.4 g/L and at 20 °C is 2.5 g/L. The higher the temperature, the less lithium carbonate remains in the solution. That's why the lithium precipitation process is always carried out at nearly 100 °C. The lithium cannot be 100% precipitated because of the solubility of Li at 100 °C is still 1.4 g/L. The possibility of formation of other crystals should be considered. There are also sodium and sulphate ions in the solution. (s. Table) The materials which reach supersaturated state first can crystallise from the solution. Thus the formation of Na_2SO_4 even after cooling down of the rest solution is impossible.

Table 6: Solubility of all possible crystallisation products at 25 °C, 90 °C and 100 °C [7]

Solubility (g/L)	Li_2CO_3 (Li)	Na_2CO_3	Li_2SO_4	Na_2SO_4
	g/L	g/L	g/L	g/L
20 °C	13.3 (2.5)	215	348	195
90 °C	---	439	309	427
100 °C	7.2 (1.4)	---	---	425

Table shows the chemical composition of the Li_2CO_3 powder. It is evidently that manganese is also co-precipitated into the lithium carbonate solids. $MnCO_3$ has a much lesser solubility than Li_2CO_3. Manganese in the solution can be removed by addition a small amount of Na_2CO_3. Therefore, the Li-rich solution must be completely purified before Li_2CO_3 crystallisation.

Table 7: The chemical composition of precipitated Li_2CO_3 powder

Element	Li_2CO_3	Ni	Co	Mn	Cu	Al	Fe
Composition (%)	93.6	0.21	0.032	2.16	<0.05	0.024	<0.05

7. Conclusions and prospect

A hydrometallurgical recycling process of Li-ion batteries has been developed and evaluated. In the leaching step, the suitable leaching temperature to obtain a higher leaching efficiency: 60~80 °C;

The suitable sulphuric acid concentration: 1~2 mol/L; The suitable leaching time: 1 hour. With presence of H_2O_2, the extraction of copper can be improved from 40 %-50 % to almost 100% and meantime the dissolution of nickel is relatively hindered in the limited reaction time (1h). The obtained Cu-C leaching residual is suitable for copper production. In the solution purification step, the optimum final pH for the solution purification is about 5.5 (40 °C) to precipitate aluminium, copper and iron. Meanwhile the co-precipitated cobalt, nickel and manganese are no more than 3%. The precipitated residual can be gathered and supplied to further separation process. Cobalt, nickel and manganese have been successfully recovered from the solution by hydroxide precipitation method. The Co-Ni-Mn mixture is available for the new batteries electrode powder production or further hydrometallurgical separation processes. Even though sulphide precipitation can also recover Co, Ni and Mn at a high degree, the remained NH_4^+ and the bad smell of ammonium gas have a negative effect. The lithium recovery from spent Li-ion batteries has been successfully demonstrated.

For the further study, oxidative precipitation of manganese to insoluble manganese oxides (MnO_2/Mn_2O_3) gets also attention for removal of manganese impurity from the leaching solution. Various oxidants for Mn^{2+}, such as ozone (O_3), $KMnO_4$, SO_2/O_2 are interested to be applied. The carbonate precipitation of cobalt, nickel and manganese with soda ash (Na_2CO_3) at the present of lithium is recommended.

Acknowledgement

The authors are thankful to the German Federal Ministry of Education and Research BMBF (Bundesministerium für Bildung und Forschung) for the financial support in the project “LiVe!” (Lithiumbatterie-Verbundstrukturen).

Reference

[1] Status Overview of Hybrid and Electric Vehicle technology (2007)
URL:http://www.ieahev.org/pdfs/annex_7/annex7_hev_final_rpt_110108.pdf

[2] Electrification of transport: Hybrids, Plug-in Hybrids and return of the EV
URL: http://hydrogen.its.ucdavis.edu/workshops/TRB_Brief/PHEV

[3] Xu, “A review of processes and technologies for the recycling of lithium-ion secondary batteries”, Journal of Power Sources, Volume 177, P. 512–527, 2008.

[4] Nishi: “Lithium ion secondary batteries; past 10 years and the future”; Journal of Power Sources; Volume 100; P.101–106; 2001.

[5] Costs of Lithium-Ion Batteries for Vehicles, URL: http://www.transportation.anl.gov/pdfs/TA/149.pdf

[6] Winter. M; Brodd, R.J. Chemical Reviews, 2004, 104, 4245-4270

[7] Dean: Lange’s handbook of chemistry, ISBN 0-07-016384-7, 1999