Innovative recycling of Li-based electric vehicle batteries

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Abstract

The demand for automotive lithium ion batteries will increase dramatically in the foreseeable future. By 2015, about 1.3 million EV batteries will be produced annually in the world and about 80% of them are Li-ion batteries. EV Li-ion battery recycling market is expected to process batteries worth more than $2 billion by 2022 with more than half a million end-of-life EVs' battery packs available for recycling through the waste stream.

Acknowledgement

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1. Reference

[1]

The automobile lithium ion batteries consist of many valuable metals, such as lithium, cobalt, nickel, manganese, copper and aluminium. They need an appropriate circulation to the LIBs production. The new German Battery Law "Batteriegesetz" (BattG) turned into action in December 2009. The BattG is the implementation of the EU directive 2006/66/EC and commits producers and traders of all kind of batteries to take used batteries back and assure a state of art treatment and recycling. The recycling processes for batteries have to reach at least a 50 wt-% recycling efficiency.

This paper has focused on the hydrometallurgical route which is after the pretreatment of batteries. The metal values from the batteries are leached, purified and recovered. The influences of operating parameters have been investigated to obtain the optimum working conditions.

2. Introduction of IME-Accurec Hydro process

The electrode powder from pretreatment was supplied to hydrometallurgical process which is illustrated in Figure 1. In the leaching process, the metal values in the raw materials are extracted from the raw material by the reaction with the sulfuric acid. In the solution refining steps, copper has been firstly cemented by adding iron powder. In the following Al&Fe precipitation step, the iron and aluminum are precipitated by adjusting the pH value. Cobalt, nickel and manganese were subsequently precipitated by adding sodium hydroxide. The lithium was recovered from the solution in the lithium carbonate crystallization step.

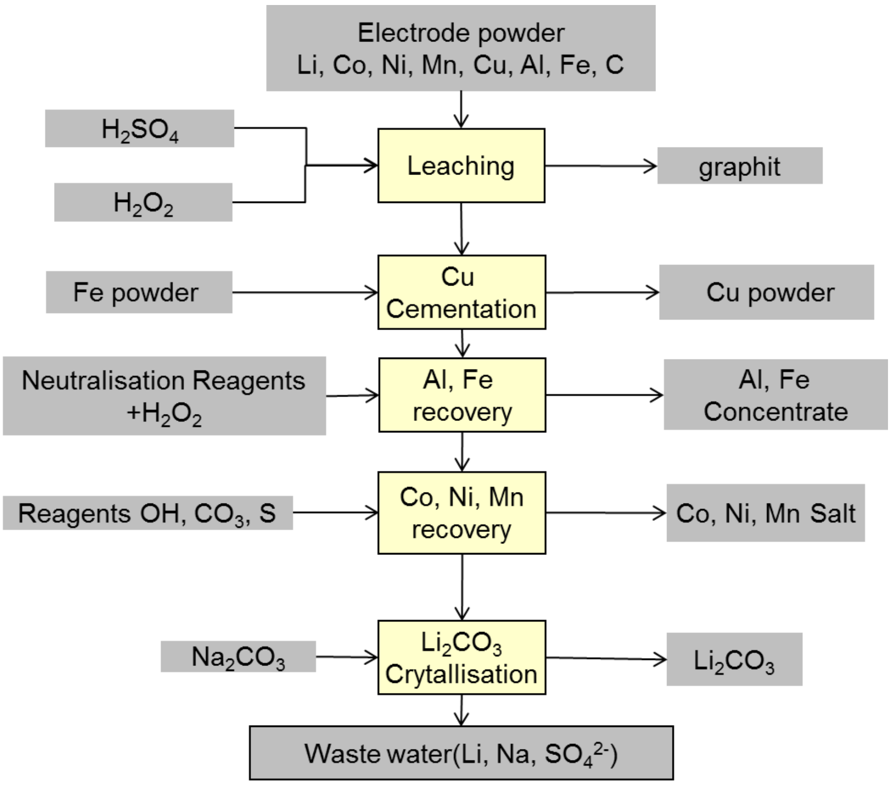

Figure 1 The hydrometallurgical recovery process (IME-Accurec Hydro)

3. Results and discussion

<u>Leaching:</u> The extraction rate of valuable metal has been evaluated in the whole retention time. The extraction rate of lithium has reached 90 % in the first 15 minutes and keeps a high level in the following time. The oxidation potential of solution has critical effect on copper extraction. At the present of hydrogen peroxide, the solution becomes oxidative and the copper metal will be dissolved easily. (s. Figure 2) The final extraction rate of copper in the trail has reached 98 % with a 20 g/L hydrogen peroxide at 60°C. The leaching performance of nickel has been shown in Figure 3. The fastest extraction has been obtained at 80 °C and at the present of hydrogen peroxide. The performances of them are in sequence: 80 °C + H_2O_2 >80 °C > 60 °C+ H_2O_2 > 60 °C. The evaluation of cobalt has shown the similar results but the average speed of leaching is faster the nickel.

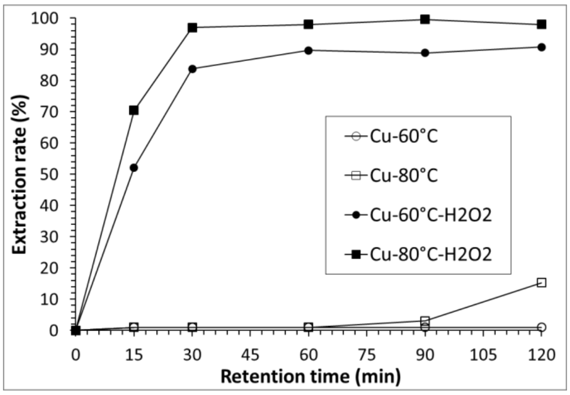

Figure 2 The extraction rate of copper

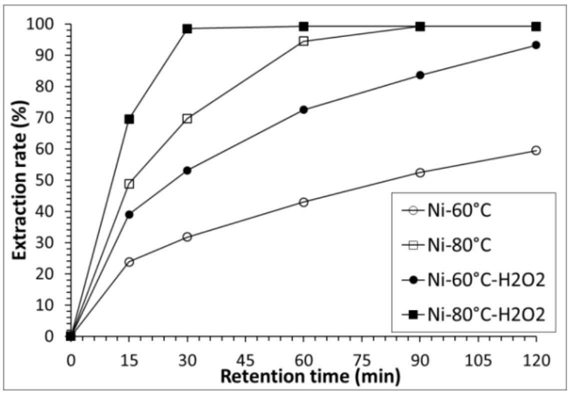

Figure 3 The extraction rate of nickel

<u>Copper cementation:</u> The time dependent copper concentration with different temperature has been shown in Figure 4. The process proceeds fast and 94% the copper has been cemented in 30 minutes. High temperature has a positive effect on copper cementation. Table **1** shows the chemical composition in a validation experiment. The composition of copper has reached 90 °%, which is highly marketable for cooper industry.

Table 1 The chemical composition of cemented copper powder

Element	Al	Co	Cu	Fe	Li	Mn	Ni
Composition (%)	0.017	0.05	90	0.013	0.17	0.1	0.03

<u>Aluminium & Iron precipitation:</u> Iron and aluminium precipiation have been investigated by adjustment of pH.

Figure 5 shows the aluminium concentration at different pH at different temperatures. It is clear that the aluminium are very sensitive to pH value. The concentration decrease very significantly since pH 2.5 and nearly to zero until 3.5. The same situation happens also with the iron precipitation. The effeciency of iorn and aluminium recovery is more than 97 %.

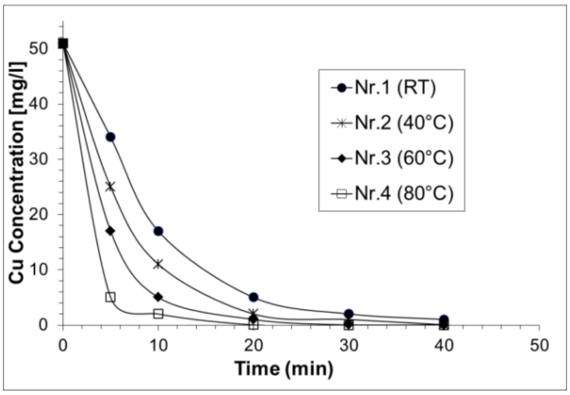

Figure 4 Copper cementation at different temperature

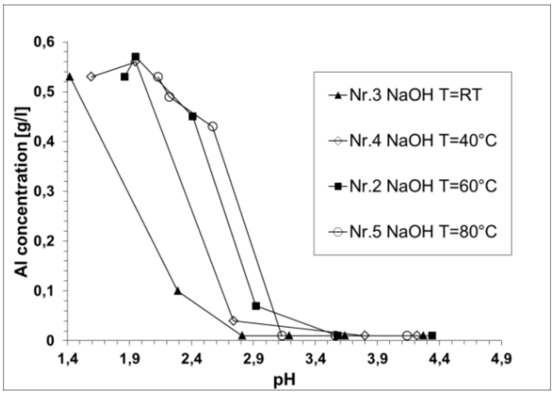

Figure 5 The aluminium concentration at different initial pH solution.

Co, Ni and Mn precipitation and Li_2CO_3 crystallization: Since there are many types of batteries, the contents of cobalt, nickel and manganese vary a lot. They can be recovered together and serve as the raw material of new electrode powder production. After adding sodium hydroxide solution, the solid has been formed in the liquid. Table 2 shows the chemical composition of the powders.

Table 2: The chemical composition of precipitated Co, Ni and Mn hydroxide

Element	Co	Ni	Mn	Fe	Li	Al	Cu
Composition (%)	5,47	21,1	26,1	<0,05	0,5	0,16	<0,05

The solution after filtration is ready for the lithium carbonate crystallization. The solution was boiled at 90 °C to concentrate the lithium. The soda solution is filled and the temperature was kept at 95 °C. The crystallized lithium carbonate is shown in Table 3.

Table 3: The chemical composition of precipitated Li_2CO_3 powder

Element	Li_2CO_3	Al	Co	Cu	Ni	Mn	Fe	Na
Composition (%)	95.1	0.02	1.36	<0.01	0.04	<0.01	<0.01	3.39

4. Conclusion

The IME-ACCUREC hydrometallurgical process has been demonstrated to be capable to recover the valuable metals. Leaching in the sulfuric acid media at 80 °C, 20 g/L hydrogen peroxide has the highest recovery rate. The copper cementation has been demonstrated very efficient. The qualified products, such as iron and aluminum hydroxide, cobalt, nickel and manganese salts, and lithium carbonate are also recovered from the solutions.

5. 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).

6. Reference

[1] Reuse and Recycling to Ensure the Completion of the "Green Car" Publication of "Frost & Sullivan"