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**A STUDY ON THE RECOVERY OF LITHIUM AND Ni/Co OXIDE FROM CATHODE ACTIVE POWDER OF
END-OF-LIFE NCA(LiNiCoAlO₂) BATTERY**

This study was attempted to study for recovery of Li as Li₂CO₃ from cathode active material, especially NCA (LiNiCoAlO₂), recovered from spent lithium ion batteries. This consists of two major processes, carbonation using CO₂ and water leaching. Carbonation using CO₂ was performed at 600°C, 700°C and 800°C, and NCA (LiNiCoAlO₂) was phase-separated into Li₂CO₃, NiO and CoO. The water leaching process using the differences in solubility was performed to obtain the optimum conditions by using the washing time and the ratio of the sample to the distilled water as variables. As a result, NCA (LiNiCoAlO₂) was phase-separated into Li₂CO₃ and NiO, CoO at 700°C, and Li₂CO₃ in water was recovered through vacuum filtration after 1 hour at a 1:30 weight ratio of the powder and distilled water. Finally, Li₂CO₃ containing Li of more than 98 wt.% was recovered.

Keywords: Cathode Active Powder, NCA(LiNiCoAlO₂), Li₂CO₃, Nickel Oxide, Cobalt Oxide

1. Introduction

At present, lithium ion batteries (LIBs) are widely used as a main energy source for portable mobile devices such as smartphones and netbooks as well as hybrid vehicles due to high output and high energy characteristics. Lithium ion batteries, which are expected to be used extensively in electric vehicles (EV) and for electric power storage, are capable of storing and using energy through oxidation and reduction reactions that occur in the anode and the cathode [1].

In recent years, lithium ion batteries have been actively studied for their application as a mid-to-large energy source such as for EVs and energy storage systems (ESS) in conventional small electronic devices. For these uses, cathode active material with high energy density, high voltage, charge/discharge efficiency, high stability, and environmentally friendly materials are required [2,3]. For the cathode active material of lithium ion batteries, LCO (LiCoO₂), which has a layered structure with a stable capacity, has mainly been used, but it has limitations such as low capacity, environmental pollution and high cost due to cobalt resource constraints. Therefore, NCA (LiNiCoAlO₂), a cathode active material, came up as an alternative for solving problems such as the high price and low capacity of LCO (LiCoO₂) [4]. With the growth of the electric vehicle battery market, the demand for mid-to-high output batteries has increased, resulting in increased demand for NCA (LiNiCoAlO₂), which is an active material for mid-to-high output. [5].

The market size for lithium-ion batteries reached US\$17.5 billion (about KRW19.3 trillion) in 2013 and is expected to reach US\$76 billion (about KRW83.6 trillion) in 2020 [6]. Demand for lithium ion batteries continues to increase with growing social demand, but the reality is that there is a lack of recycling technology. Most lithium-ion batteries are either buried or disposed of unattended. When such a lithium ion battery is buried, it may cause serious environmental problems when the reactant in the battery is discharged. Therefore, appropriate disposal methods or recycling technology is required [7]. Since many valuable metals such as nickel, lithium, cobalt, and manganese are used to produce the cathode active materials for lithium ion batteries, the recycling technology for waste lithium ion batteries is required more in response to the depletion of resources and for the localization of the valuable metals.

Therefore, many studies have been conducted on a method for recovering valuable metals from the cathode active material in waste lithium ion batteries. Sumitomo Metals Mining Co. has recovered valuable metals by roasting waste lithium ion batteries, followed by crushing-classifying-roasting-acid washing-two-step neutralization (primary pH 4-5.5, oxidizing gas, secondary pH 7 precipitation) [8-9]. Zhang used hydrochloric acid washing and solvent extraction to recover cobalt and lithium from waste lithium ion batteries, and separated cobalt and lithium by solvent extraction after washing the electrode material with hydrochloric acid [10]. KERAM Chemies GmbH (Germany) has developed a technology to recover Ni, Cu, Li, Mn, and Co

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from waste lithium ion batteries through a series of processes: crushing-classifying-acid washing-harvesting electrolytic [11].

In the case of recovering the valuable metal by the above-mentioned wet treatment process, it requires neutralization as a secondary process since an acid solvent is used. As a result, the process is complicated and the washing process must be followed due to the generation of the intermediate product. In addition, since an acid solvent is used, there is the cost of processing acid afterward, resulting in environmental pollution.

In this study, the authors have studied a new method of separating and recovering Li from the cathode active material (LiNiCoAlO₂) in waste lithium ion batteries by carbonizing it to Li₂CO₃, which is an environmentally friendly and simple process. Through thermal reaction between cathode powder and CO₂ gas, Li₂CO₃, NiO and CoO were formed and Li was also recovered by washing leaching process. The phase of Li after carbonation was analyzed by X-ray diffraction (XRD), and Li content in water was analyzed by inductively coupled plasma (ICP). Li₂CO₃ was recovered in an environmentally friendly manner with only dry heat treatment instead of the conventional wet process using an acidic solution.

2. Experimental

The experimental material used in this study was NCA(LiNiCoAlO₂), which is a composite of cobalt, nickel, aluminum, and lithium among the cathode active materials in waste lithium ion batteries. The components of the raw sample were analyzed by EDS, XRD, and ICP and the results are shown in Figure 1. The results of XRD, EDS, and ICP analyses show that the phase of the cathode active material sample is found to be LiNiCoAlO₂. As a result of EDS analysis, 62.02 wt.% Ni was contained as the main component, followed by Co (10.06 wt.%) and Al (0.6 wt.%). And as a result of ICP analysis, Li content was found to be 7.0 wt.%.

The equipment used for carbonation using CO₂ gas was shown in Fig. 2 (a) that shows a cross section of an electric furnace with a SiC heater inside. (b) is a reactor which controls the temperature and atmosphere so that the sample charged into the reactor can react directly. (c) is an O-ring that seals and covers the electric furnace to maintain the atmosphere inside and shut it off from outside atmosphere. In this experiment, a crucible made of alumina (d) was used. The cover of the electric furnace, which is water-cooled, minimizes the deformation of equipment caused by high temperature.

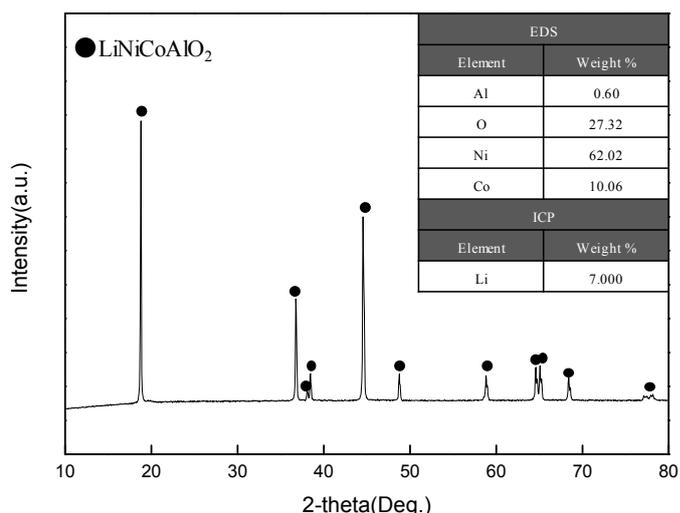


Fig. 1. XRD pattern and ICP analysis, EDS analysis of NCA

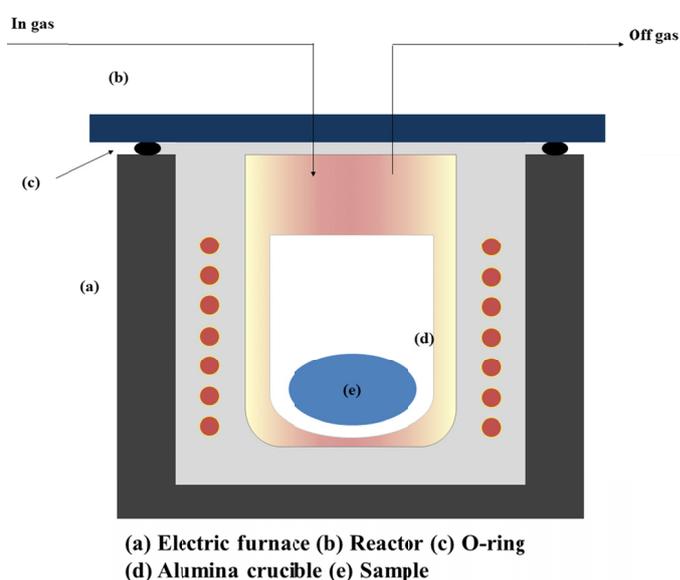


Fig. 2. Schematic diagram of experimental apparatus

The overall process of recovering Li₂CO₃ from NCA(LiNiCoAlO₂) is shown in Fig. 3. This experiment consists of two processes: phase separation through the reaction between CO₂ gas and raw sample, and extraction of Li₂CO₃ using vacuum filtration after washing through distilled water. In the first process of phase separation, a certain amount of raw sample NCA(LiNiCoAlO₂) put in the alumina crucible is charged into the furnace and is heated by blowing argon gas up to target temperatures while maintaining the inert atmosphere. After that, CO₂ gas is injected

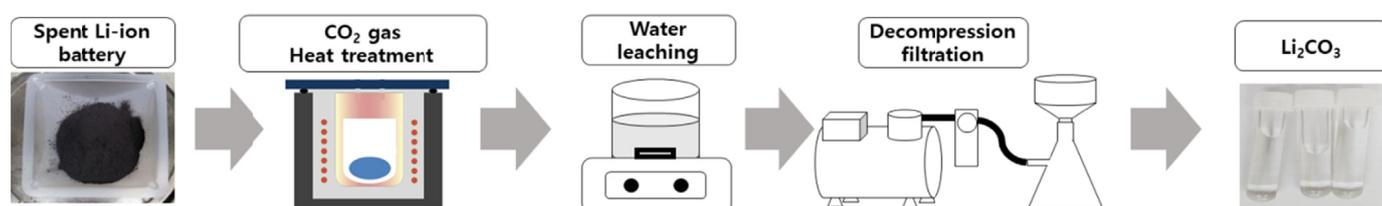


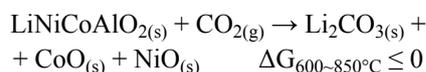
Fig. 3. Schematic diagram of experimental process

into the reactor for carbonation process. After thermal treatment, the sample is recovered, which is found to be phase-separated from LiNiCoAlO_2 into Li_2CO_3 , CoO and NiO . After that, Li_2CO_3 and CoO , NiO are separated by washing with water and Li can only be recovered through vacuum filtration due to solubility of water. To observe the results of the experiment, phase change and Li content were analyzed by X-ray diffraction (XRD) or inductively coupled plasma (ICP) for each process.

3. Results and discussion

3.1. Phase separation through reaction between $\text{NCA}(\text{LiNiCoAlO}_2)$ and CO_2 gas

To extract Li from $\text{NCA}(\text{LiNiCoAlO}_2)$, new solid-gas reaction was proposed that LiNiCoAlO_2 reacts with CO_2 gas and it is separated into Li_2CO_3 , CoO and NiO as expressed in the following reaction formula.



Prior to the phase separation, the above reaction was confirmed using a thermogravimetric apparatus. And weight change was observed by heating LiNiCoAlO_2 from room temperature to high temperature in a CO_2 gas atmosphere. The temperature was raised from 25°C to 990°C at a rate of $5^\circ\text{C}/\text{min}$, and the gas injection rate was constantly maintained at 500 cc/min. The results are shown in Fig. 4, and analysis was performed three times.

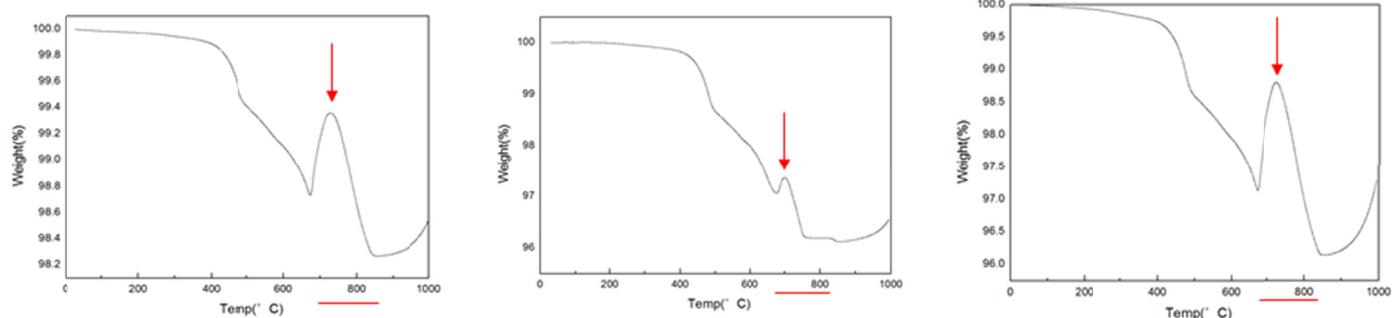


Fig. 4. Weight change of LiNiCoAlO_2 in CO_2 atmosphere through TGA

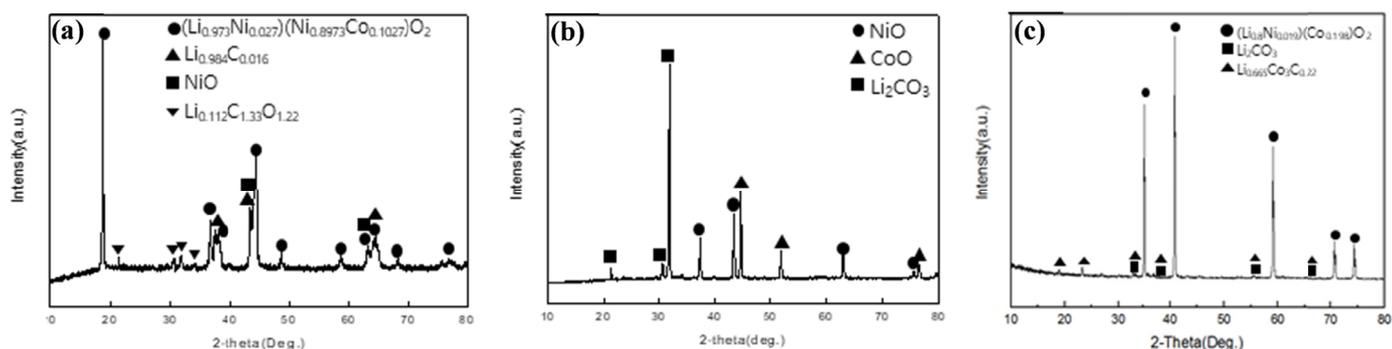


Fig. 5. XRD pattern of heat-treated LiNiCoAlO_2 at (a) 600°C , (b) 700°C , (c) 800°C

The results of TGA analysis show that the weight of LiNiCoAlO_2 gradually decreases with increasing temperature, and increases sharply at $650\sim 750^\circ\text{C}$, which implies that there might be a phase change of LiNiCoAlO_2 in this temperature range.

Based on the above results, the experiment was performed at 600°C , 700°C and 800°C in CO_2 atmosphere for phase separation of LiNiCoAlO_2 and phase change was observed by XRD analysis. The heating and cooling rate was $5^\circ\text{C}/\text{min}$, the same as that in TGA analysis. During the heating process, the temperature was raised in an inert atmosphere by blowing Ar gas and carbonation was performed while maintaining the amount of CO_2 gas injection constantly at 0.5L/min for 3 hours. As shown in Fig. 5, LiNiCoAlO_2 was separated into various phases such as NiO and $\text{Li}_{0.984}\text{C}_{0.016}$ at 600°C , and LiNiCoAlO_2 was carbonated to Li_2CO_3 and completely separated into CoO and NiO at 700°C . At 800°C LiNiCoAlO_2 phase such as $(\text{Li}_{0.8}\text{Ni}_{0.019})(\text{Co}_{0.198})\text{O}_2$ was observed together with Li_2CO_3 , which was expected to be a phase generated by the re-synthesis of Li_2CO_3 and CoO/NiO above this temperature. Therefore, it was confirmed that the optimal temperature for the carbonization and phase separation into Li_2CO_3 , CoO and NiO was found to be 700°C .

3.2. Water leaching and filtration

After heat treatment with CO_2 , Li was carbonated to Li_2CO_3 , and Co and Ni were transformed into CoO and NiO . To separate only Li_2CO_3 from the specimen, water leaching was performed using the difference in solubility between Li_2CO_3 and CoO and NiO . The differences in solubility between Li_2CO_3 ,

CoO and NiO are listed in Table 1. Li_2CO_3 is very water soluble, but NiO and CoO are insoluble when water is used as a solvent. Therefore, when the sample heat-treated with CO_2 is leached through distilled water, only Li_2CO_3 can be dissolved into the water. After the water leaching, Li_2CO_3 , CoO and NiO were separated by vacuum filtration at 2×10^{-2} torr $\sim 6 \times 10^{-2}$ torr.

TABLE 1

Solubility of Li_2CO_3 , NiO and CoO in water

Molecular formula	Solubility in Water
Li_2CO_3	1.54 g/100 mL (0°C)
	1.32 g/100 mL (20°C)
	1.00 g/100 mL (60°C)
	0.72 g/100 mL (100°C)
NiO, CoO	Insoluble

The water leaching was performed according to the amount of distilled water and the water leaching time. The Li content in the distilled water according to the water leaching time is listed in Table 2 below. The water leaching time was 1 hr, 3 hr, and 5 hr, and it was performed under the condition of 1: 5 weight ratio of sample and distilled water. Li content was 2343 ppm after water leaching for 1 hr and 2377 ppm after water leaching for 5 hours.

TABLE 2

Lithium content of distilled water with water leaching time

Washing time, hour	Li content, ppm
1	2343
3	2338
5	2377

Therefore, water leaching was performed according to the amount of distilled water by fixing the water leaching time to 1 hr. Water leaching was performed at 1: 5, 1:10, and 1:15 weight ratio of the sample heat-treated with CO_2 and distilled water, and the content of Li in distilled water is listed in Table 3 below. Even if the amount of distilled water increased, the amount of

Li_2CO_3 dissolved in the distilled water did not change much, which is probably due to the distilled water reaching the saturated solution Li_2CO_3 .

TABLE 3

Lithium content according to amount of distilled water during water leaching

Weight ratio between sample and distilled water	Li content, ppm
1:5	2343
1:10	2338
1:15	2377

Given that the Li content in the raw sample is 7 wt.% and the analyzed solution is 10 ml, it can be predicted that Li_2CO_3 of the heat-treated sample will be completely dissolved in water when the weight ratio of the CO_2 heat-treated sample and the distilled water is 1:30. Fig. 6 shows the results of XRD analysis of a sample that was not dissolved after water leaching at the 1:30 weight ratio of the CO_2 heat-treated sample and the distilled water. Table 4 shows the results of ICP analysis indicating the elements contained in distilled water after vacuum filtration. In the case of water leaching at the 1:30 weight ratio of the CO_2 heat-treated sample and distilled water, Li_2CO_3 was completely removed after water leaching and only NiO and CoO peaks were observed. In the case of the solution where Li_2CO_3 was dissolved after water leaching at the weight ratio of 1:30, trace amounts of impurities such as Al, Co and Ni were observed. And finally, Li_2CO_3 , where Li of more than 98 wt.% was dissolved could be recovered.

TABLE 4

Chemical composition of solution after water leaching

Element	ICP, wt. %
Li	98.69
Al	0.34
Co	0.26
Ni	0.71

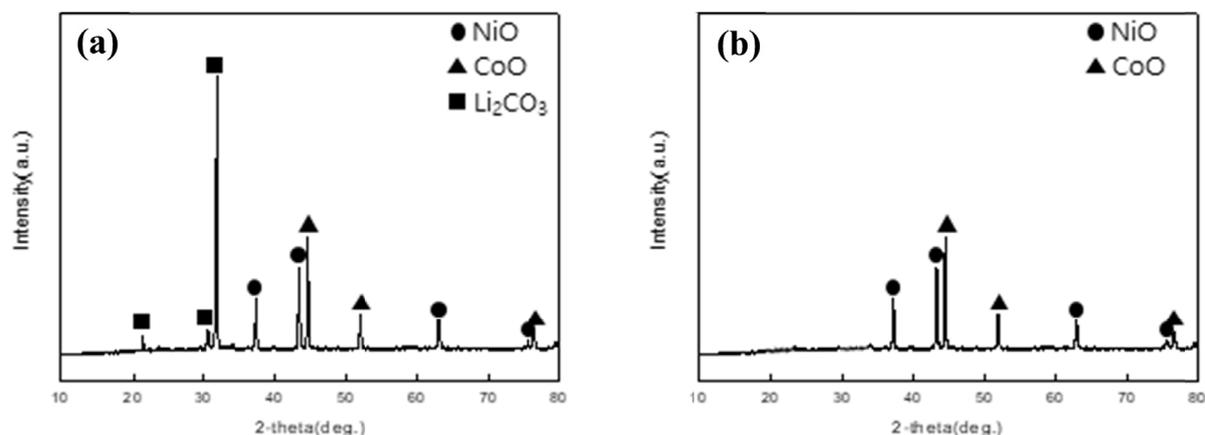


Fig. 6. XRD pattern of Li_2CO_3 and NiO, CoO powder after water washing (a) : Raw sample, (b) Weight ratio of CO_2 heat-treated sample and distilled water (1 : 30)

4. Conclusions

In this study, carbonation and water leaching processes were conducted to separate Li_2CO_3 , NiO and CoO from spent cathode active material, $\text{NCA}(\text{LiNiCoAlO}_2)$, in end-of-life lithium ion battery.

- (1) $\text{NCA}(\text{LiNiCoAlO}_2)$ reacts to CO_2 gas leads to phase transformation at $600^\circ\text{C} \sim 800^\circ\text{C}$, and the optimum temperature was found to be 700°C . Phase separation is not sufficient at 600°C , and the separated phase is recombined again over 800°C to form a nonstoichiometric phase such as $(\text{Li}_{0.8}\text{Ni}_{0.019})(\text{Co}_{0.198})\text{O}_2$.
- (2) Through carbonation at 700°C , Li of $\text{NCA}(\text{LiNiCoAlO}_2)$ was carbonated and formed as Li_2CO_3 . Co and Ni were also formed as CoO and NiO , resulting in phase separation into Li_2CO_3 , CoO and NiO .
- (3) Water leaching was performed to separate Li_2CO_3 and CoO/NiO using the differences in solubility. In the water leaching process, when the weight ratio of the CO_2 heat-treated sample and distilled water was 1:30, complete separation and recovery could be achieved.
- (4) Finally, a Li_2CO_3 solution where Li with more than 98 wt.% could be obtained through this process.

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REFERENCES

- [1] D.G. Hwang, N.H. Cho, H.S. Lee, M.Y. Choi, N.G. Eom, O.G. Jong, K.H. Kim, S.G. Shin, Study on Recycling of Waste Lithium Ion Battery, National Institute of Environmental Research, 1-2 (2016).
- [2] K.Y. Kang, M.G. Choi, Y.G. Lee, K.M. Kim, Phase Change of Nanorod-Clustered MnO_2 by Hydrothermal Reaction Conditions and the Lithium-ion Battery Cathode Properties of LiMn_2O_4 Prepared from the MnO_2 , Korean Chem. Eng. Res. **49** (5), 541-547 (2011).
- [3] H. Y. Lee, J. D. Lee, Electrochemical Performance on the H_3BO_3 Treated Soft Carbon modified from PFO as Anode Material, Korean Chem. Eng. Res. **54** (6), 746-752 (2016).
- [4] D. L. Vu, J. W. Lee, Properties of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ as a High Energy Cathode Material for Lithium-ion Batteries, Korean J. Chem. Eng. **33** (2), 514-526 (2016).
- [5] H.D. Lee, Surface Product and Thermal Safety of Cathode Active Material (NCA) in Lithium Ion Batteries, Korea University Graduate School 2-4 (2015).
- [6] Frost and Sullivan. "Analysis of the Global Lithium-ion Battery Market, Supply Chain Management. ND02-07, (2014).
- [7] C.G. Lee, D.H. Ynag, Recovery of Valuable Metals from Waste Lithium Ion Batteries, Korean Chemical Society Journal **4**, 12.8 (2001).
- [8] Sumitomo Metals Mining Co., JP 06,322,452 (1994. 11.).
- [9] Sumitomo Metals Mining Co., JP 07,207,349 (1995. 8.).
- [10] Pingwei Zhang, Toshiro Yokoyama, Osamu Itabashi, Toshishige M. Suzuki, Katsutoshi Inoue, Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries, Hydrometallurgy **47**, 259-271 (1998).
- [11] Keramchemies GMBH, EP 650,290 (1995. 4).