

## Hydrothermal leaching of commercial and spent lithium-ion battery cathode materials with citric acids employing batch and continuous flow system

Qingxin Zheng <sup>a</sup>, Kensuke Shibazaki <sup>b</sup>, Seiya Hirama <sup>a</sup>, Tetsufumi Ogawa <sup>a</sup>, Akitoshi Nakajima <sup>a</sup>, Yuya Hiraga <sup>a</sup>, Atsushi Kishita <sup>a</sup>, Masaru Watanabe <sup>a,c</sup>

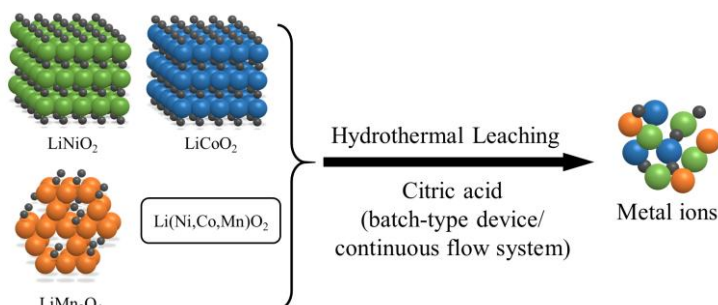
<sup>a</sup>: Research Center of Supercritical Fluid Technology, Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, 6-6-11 Aoba, Aramaki, Aoba-ku, Sendai 980-8579 Japan;

<sup>b</sup>: Faculty of Environmental Studies, Tohoku University, 6-6-11 Aoba, Aramaki, Aoba-ku, Sendai 980-8579 Japan;

<sup>c</sup>: Environment Conservation Center, Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, 6-6-11 Aoba, Aramaki, Aoba-ku, Sendai 980-8579 Japan.

Efficient recovery of valuable metals (e.g., Li, Co, Ni, Mn) from spent lithium-ion battery (LIB) cathode materials under a mild condition is becoming an urgent topic in the world and will be essential to conserve natural resources, reduce environmental problems, keep resource stability and security, and bring economic benefits. As one of the conventional recovery methods, hydrometallurgy consists of two steps: acid leaching and separation. In a traditional acid leaching process, metal ion solutions were leached into non-pressurized hot water using various inorganic or organic acids in the presence of reductants such as  $H_2O_2$ . Due to the drawbacks in terms of high-concentration inorganic acids, large consumption of reductants, and long reaction time, the traditional acid leaching process always brings serious environmental pollution and economic burden, and the device is limited to be the batch-type apparatus. Recently, a method of hydrothermal leaching was proposed for leaching Li and Co from  $LiCoO_2$  using citric acid ( $H_3Cit$ ) as the leachant.<sup>1</sup> Even without the use of inorganic acids and the consumption of reductants, hydrothermal leaching can achieve high efficiencies of over 90% for both Li and Co. Additionally, the reaction temperature in the hydrothermal leaching process is not limited to be lower than the boiling point of water at 100 °C, which greatly shortened the reaction time, decreased the required concentration of acid, and make the continuous leaching possible.

Here, hydrothermal leaching of commercial and spent LIB cathode materials was performed with  $H_3Cit$  employing a batch-type device and a specifically-designed flow system. First, the metal components were leached from ternary ( $LiCoO_2/LiNiO_2/LiMn_2O_4$ ) and binary oxides ( $LiCoO_2/LiNiO_2$ ) employing a batch-type apparatus.<sup>2</sup> High



leaching efficiency was achieved for each metal component. A shrinking unreacted-core model was adopted to predict reaction behavior, the controlling step was estimated by fitting kinetic parameters with the experimental data, and the activated energy for leaching each metal was calculated. Then, the first running of continuous hydrothermal leaching of  $LiCoO_2$  was performed with  $H_3Cit$  employing the flow system.<sup>3</sup> At 60 min after the start of slurry feeding, the leaching efficiency of Li and Co reached 81.3% and 92.7%, respectively, and is expected to continue to increase with the extension of time. Finally, the method of hydrothermal leaching with  $H_3Cit$  was applied to spent LIB cathode materials,  $Li(Ni,Mn,Co)O_2$  (NMC), employing both the batch-type device and flow system in turn. Before the leaching, NMC cathode materials were pretreated and characterized. Based on the results of using the batch-type device, the preliminary conditions for the hydrothermal leaching using the flow system were determined and pre-set; then, the leachate was continuously leached from NMC cathode materials, and after 65 min of feeding the slurry, the leaching efficiency of Li, Co, Ni, and Mn reached to 96%, 91%, 98%, and 94%, respectively.

Reference:

1. a) Aikawa, T. et al., *Kagaku Kogaku Ronbunshu* 2017, 43 (4), 313-318; b) Azuma, D. et al., *Kagaku Kogaku Ronbunshu* 2019, 45 (4), 147-157; c) Shibazaki, K. et al., *Kagaku Kogaku Ronbunshu* 2020, 46 (5), 167-175.
2. Zheng, Q. et al., *The Journal of Supercritical Fluids* 2020, 165, 104990 (1-10).
3. Zheng, Q. et al., *Reaction Chemistry & Engineering* 2020, 5 (12), 2148-2154.