

## Supporting Information

### Selective Separation of Li, Ni, Co and Mn from Model Spent Li Ion Battery Cathode by Dry Processing using Combination of Chlorination and Oxidation

Yuuki Mochizuki<sup>1</sup>, Naoto Tsubouchi<sup>1</sup>

*Center for Advanced Research of Energy and Materials, Faculty of Engineering, Hokkaido University,  
Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan*

#### Carbo-chlorination of LNO, LCO and LMO

**Experimental** LNO, LCO, and LMO were used as samples. Furthermore, chlorides of Ni, Co, and Mn were also used. Carbonaceous material originating from phenolphthalein (denoted as PP) (C: 88.3 wt%, H: 3.6 wt%, O: 8.0 wt%-dry) was used as a reducing agent. The PP was prepared by packing phenolphthalein into a fixed-bed reactor, heating to 500°C at 20°C/min in nitrogen gas flow and holding for 10 min, and then crushing and separating using a 200 mesh cloth at room temperature. The carbon in PP was investigated by XRD and found to be amorphous. Unless specifically noted, the PP was mixed with LNO, LCO, and LMO at a mass ratio of 1:1. The LNO, LCO, and LMO after mixing were labeled LNO/C, LCO/C, and LMO/C, respectively.

**Chlorination** experiments were performed in a flow-type fixed-bed reactor. Measurement and control of the reactor temperature was performed using a thermocouple in contact with the outer wall of the reactor tube. In the experiments, 0.1 g of sample was first placed in an alumina boat which was then inserted into the center of the reactor tube, and then the sample was finally heated to 300 to 1000°C at 20°C/min in a Cl<sub>2</sub> (99.99%) atmosphere and then held for 0 to 60 min. Chlorine gas and the volatilization products were completely absorbed by a trap containing NaOH aqueous solution installed at the reactor tube outlet. After the target temperature and target time were reached, the chlorine gas was switched to N<sub>2</sub> (99.9995%) and the oven was cooled to room temperature.

**Temperature dependence of Li, Ni, Co and Mn release** Figure S1 shows the change in the yields of LNO/C, LCO/C, and LMO/C with temperature during chlorination reduction treatment. For LNO/C, the yield reached a maximum value (around 130%) at 600°C, and then decreased significantly with increasing temperature. The yield for LCO/C reached around 160% up to 500°C, and then greatly decreased at over 800°C. For LMO/C, the yield increased to around 140% at 700°C, and then gradually decreased with increasing temperature to reach around 80% at 1000°C.

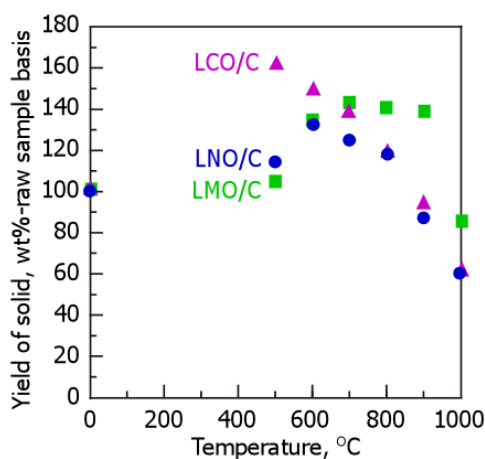
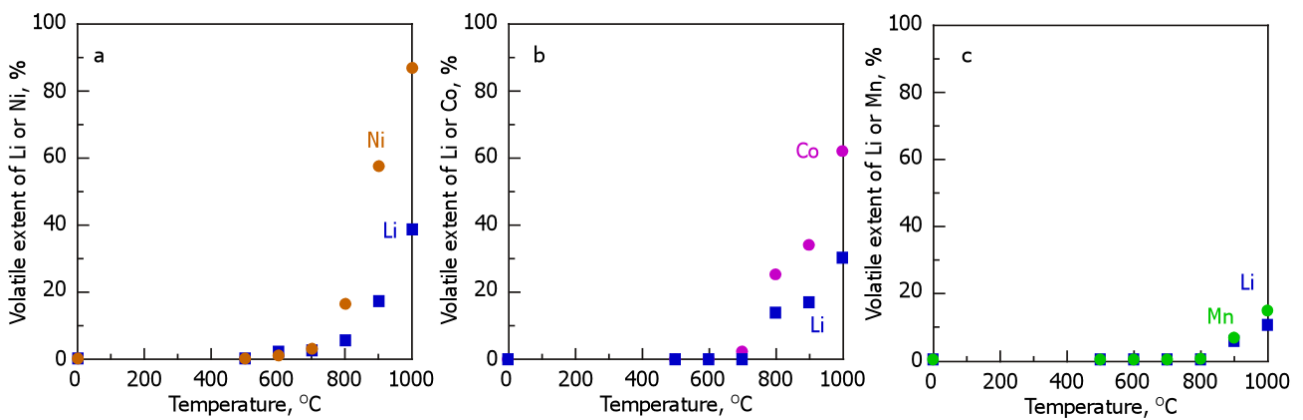


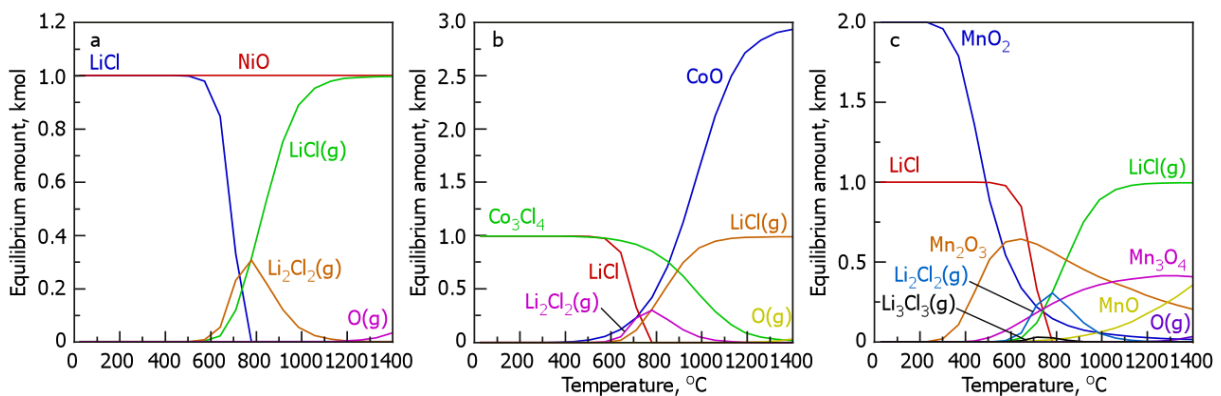
Fig. S1 □ Temperature dependence of yield of LNO/C, LCO/C or LMO/C in Cl<sub>2</sub>.

**Figure S2** shows the change in volatilization rate for Li, Ni, Co, and Mn with temperature during the experiments in **Fig. S1**. In the case of LNO/C (**Fig. S2a**), volatilization of Li occurred at above 600°C, and the volatilization rate was around 40% at 1000°C. Ni also exhibited a temperature dependence similar to that for Li, and exhibited a volatilization rate of around 85% at 1000°C. Volatilization of Li from LCO/C (**Fig. S2b**) occurred at over 700°C, and the volatilization rate at 1000°C was around 30%. The volatilization rate for Co became significant at over 700°C and exhibited a volatilization rate of around 60% at 1000°C. For LMO/C (**Fig. S2c**), Li and Mn desorbed at over 800°C, and the volatilization rate at 1000°C was 10 to 15%. When the results from **Fig. 3** and **Fig. S2** were compared, a trend was found for the volatilization rates of each element to be smaller with addition of carbon compared to without addition of carbon. According to previous research, carbonates form during carbon reduction reactions with LIB. Because of this, it is possible that reactions such as carbonate evolution occur in the presence of carbon, and the volatilization rate decreases as a result. The explanation for this is left as a research topic for the future.



**Fig. S2** □ Temperature dependence of volatile extent for Li, Ni, Co and Mn from (a) LNO/C, (b) LCO/C and (c) LMO/C in  $\text{Cl}_2$ .

**Equilibrium calculation results for LiCl and Ni, Co, Mn oxides in  $\text{N}_2$  atmosphere** **Figure S3** shows the results of thermodynamic investigation of LiCl and the oxides of Ni, Co, and Mn. For LiCl/NiO (**Fig. S3a**), evolution of Ni chlorides was not found, and NiO was thermally stable. The same result was also found for Co (**Fig. S3b**) and Mn (**Fig. S3c**). These results indicate that reactions with LiCl evolved by the chlorination reaction of LIB at up to 600°C and the oxides of Ni, Co, and Mn formed during the subsequent oxidation process, did not proceed under the conditions in this experiment.



**Fig. S3** □ Equilibrium calculation results for LiCl (a-c) and Ni (a), Co (b), Mn (c) oxides in  $\text{N}_2$  atmosphere.

**Oxidation temperature dependence of XRD profile for LNO, LCO or LMO after chlorination at 600°C and subsequent H<sub>2</sub>O treatment** Figure S4 shows XRD profiles for solid samples after performing water treatment on samples of LNO, LCO, and LMO chlorinated at 600°C that had been oxidized at 600°C to 1200°C in the experiments. Diffraction peaks attributable to oxide species appeared in all cases. Furthermore, in the case of Mn, a phase change from Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub> was observed at over 1000°C (Fig. S4c). These results indicate that oxides of Ni, Co, and Mn exist in the solid phase in a thermally stable form under the experimental conditions.

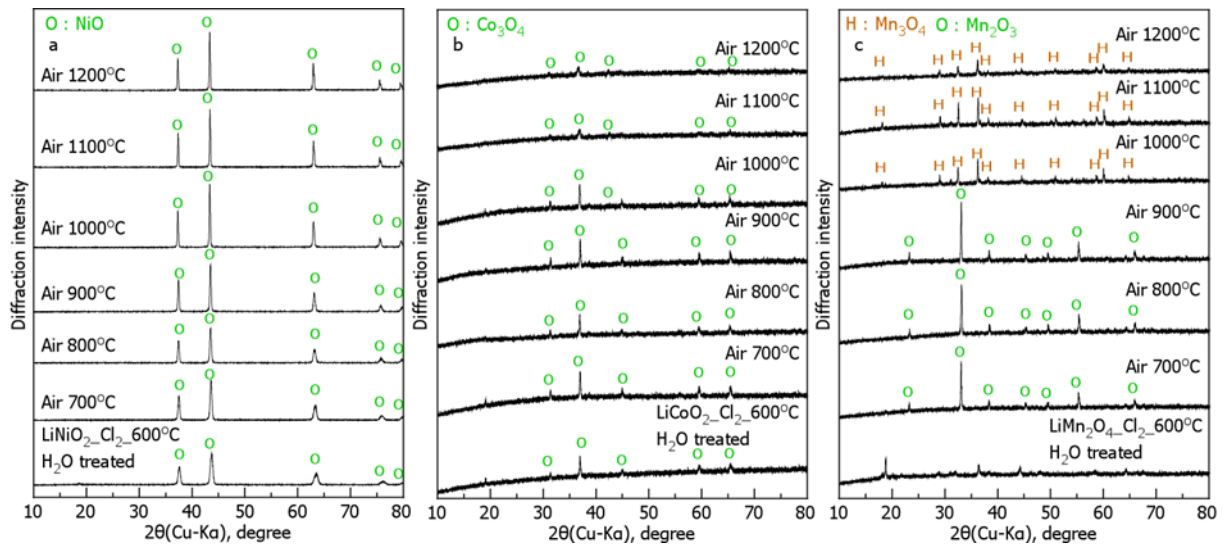


Fig. S4 □ Oxidation temperature dependence of XRD profile after chlorination at 600°C and subsequent H<sub>2</sub>O treatment for (a) LNO, (b) LCO and (c) LMO.