

Coprecipitation and Characterization of Nickel-Cobalt-Manganese Hydroxides Precursor for Battery Cathode Materials

H.-J. Kim,^{1,#} K.-M. Nam,^{1,#} E. J. Lee,¹
Y.-S. Kim,² D.-H. Kang,² S.-W. Song^{1,*}

¹Dept. of Fine Chemical Engineering & Applied Chemistry,
Chungnam National University, Daejeon, 305-764,

²EMT, Co. Ltd., Chungju, 380-871, Korea

[#]These authors contributed equally.

There has been an increasing demand for the development of high-voltage and high-capacity cathode materials for higher energy density lithium-ion batteries than current ones, which are being adapted in electric vehicles and energy storage systems. The Ni-rich materials of $\text{Li}[\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y]\text{O}_2$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$) (NCM) have been extensively studied as attractive cathode materials, due to their large reversible capacity of approximately 200 mAh/g^{1,2} and high operation voltage upto 4.6 V. For the synthesis of NCM active materials, the use of coprecipitate precursor, which possesses homogenous elemental distribution and specific particle morphology for high tap density, is one of the most efficient routes. Preparation of three-components hydroxide coprecipitate is not a difficult process, but a number of parameters are known to affect its physical properties. Although ammonia water is widely used as a coprecipitating agent, it is ill-smelling and produces environmentally unfriendly nitrogen-containing chemical wastes. Coprecipitation without the use of ammonia water is highly desirable. Here, we report a novel non-ammonia coprecipitation method for hydroxide precursor using a new chelating agent.

The pH for the precipitation of metal-hydroxide was calculated based on the chemical species present in water with respect to pH and metal ion concentrations and their thermodynamic equilibrium constants.³ Then the pH for anion-exchange and hydroxide coprecipitation was determined by finding the optimum pH region of coprecipitation as revealed in Fig. 1. The precursor of NCM-hydroxides (Ni:Co:Mn=5:2:3) coprecipitate was synthesized at pH 10.5 using a chelating agent and 0.1M NaOH. First, metal-complex forms and hydroxide was produced by anion-exchange. The separated coprecipitate was dried at 110 °C. NCM active material was synthesized by solid-state synthesis with NCM coprecipitate precursor and LiOH at 900 °C. Energy dispersive X-ray spectroscopy was used for composition analysis, and X-ray diffraction for crystal structure. Cyclic voltammetry (CV) was conducted to evaluate the electrochemical activity of NCM cathode using a three-electrodes lithium cell with 1M $\text{LiPF}_6/\text{EC}:\text{EMC}$ based electrolyte. The CV was performed at 3.0 - 4.6 V vs. Li/Li^+ at the scan rate of 0.05 mV/s using a potentiostat (CHI 633C).

Fig. 1 shows the pH diagrams for precipitation of $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$. Overlapping the diagrams finds the coprecipitation pH of metal-hydroxides by anion-exchange to be 10.5 - 11.

Fig. 2 shows cyclic voltammogram of the lithium cell with NMC cathode. In the first cycle, the anodic peak due to $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple by Li^+ -deintercalation is observed at 3.99 V, and the cathodic peak of $\text{Ni}^{4+}/\text{Ni}^{2+}$ by Li^+ -intercalation at 3.57 V. In the next cycles, a reversible cycling proceeds. Further discussion regarding material characterization and cycling ability of cathode would be

presented.

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References

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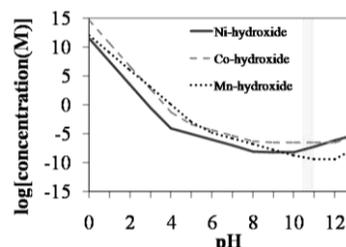


Fig. 1. pH diagram for coprecipitation of Ni-Co-Mn hydroxides.

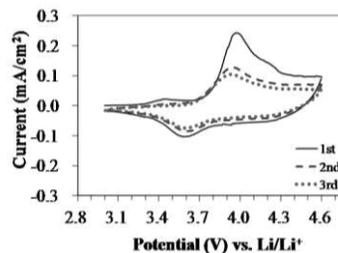


Fig. 2. Cyclic voltammogram of the lithium cell with NMC cathode at 3.0 - 4.6 V; scan rate = 0.05 mV/s.