

Influence of Processing Route and Chemical Composition on Capacity/Fading of Layered Oxide Cathodes

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Abstract

In Li ion batteries; oxide cathode with layered structure still remain the ones that provide higher capacities. However, higher charging capacity means the creation of more ionic/electronic defects in both cation and/or anion sublattices of layered structure. Higher defect concentration tend to destabilize its crystal structure. As a result, the phase change may be observed in cycled cathode. Furthermore, the phase-changing layered cathode tends to show the capacity fading after cycling. In this study, the electrical/electrochemical/structural properties of NMC 811 and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ were investigated. Since Ni content is fixed at 80% in the transition metal ion layers in these oxides, the variation in electrochemical properties will be caused by the minor elements/dopants such as Mn and Al. First, the electrical measurement of NMC 811 and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ are conducted. Assembled cells using above-mentioned cathode and Li anode with desired liquid electrolyte were tested and cycled. SEM and XRD analyses were conducted on assembled and cycled cells. The results were illustrated based on the chemical characteristics of doping ions and their defects created

1. Introduction

Li ion batteries using layered-structured cathode still the one remain attractive. Recently, cathode materials with high capacity and high Ni content such as $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM-811) have received great attention due to high price of cobalt. However, capacity fading in high Ni containing cathode still remain to be the problems to be overcome. In this study, the dependence of processing routes on electrochemical/structural properties NCA are investigated. In additions, the capacity fading of cycled NCA and NCM 811 are investigated. Since Ni content is fixed at 80% in the transition metal ion layers, the variation in electrochemical properties will be caused by the minor elements/dopants such as Mn and Al. SEM and XRD analyses will be conducted on as-assembled and cycled cells. The analyzing results will be illustrated based on the chemistry of doping ions and accompanying defects created.

2. Method of approach.

Ni-based layered oxides were prepared by co-precipitation process. Metal hydroxides were first co-precipitated by controlling proper pH value using NaOH and NH_3OH . After centrifugation and washing, precursors were then slowly heated at various temperatures. Co-precipitation method is known to be a feasible method to fabricate layered oxides with adequate properties. For comparison, a solid state reaction based on mixture of nickel/cobalt oxides, Al salt, and $\text{LiOH}\cdot\text{H}_2\text{O}$ were also prepared by wet-milling. After precursors and powder mixture preparation, samples from both co-precipitation and solid state reaction were processed under the same conditions at various temperatures and followed by careful weight measurement, XRD, electrochemical testing.

3. Significant results

Effect of Processing Route on weight changes

Fig.1 (a) and (b) show the weight changes of precursors and powder mixtures after heating at various temperature up to 750°C . For co-precipitated precursors, the final weight loss reached about 40% of dried counterparts before heating. Based on the dehydration of transition metal hydroxides, Al salts, and LiOH, the estimated weight loss is about 30%. The additional weight loss may be contributed from absorbed moisture on the powder surface. For powder mixture prepared by solid state reaction, the final weight loss reached about 30%. Most of the weight change is contributed from the conversion of LiOH to Li_2O . During the heating or calcination process, the accompanied crystallization process were also investigated using XRD. Fig. 2(a)(b) show the XRD pattern of powder mixture from solid state reaction heated at 550°C , 650°C , 750°C respectively. Up to 650°C , reflections from hexagonal layered structure were not noticeable. After heating at 750°C , strong reflections such as (003), (104) were clearly observed. For precursors from co-precipitation, weak reflections from layered structure started to appear after heating at 650°C . (Fig. 2(b))

Further heating at 750°C , all reflections corresponding to a typical layered structure were clearly observed. The splitting of (006)/(012) and (018)/(110) suggests that samples prepared by co-precipitation method give better crystallization in NaFeO₂ structure. It is believed that nanosized Ni/Co hydroxide particles were able to precipitate simultaneously and homogeneously and reached desired mixing. With penetration of Al and Li-containing solution into nanosized mixture of Ni/Co(OH)₂, better crystallization may be reached at lower

temperature. Regarding to solid state reaction, we believe that homogeneity of Ni/Co/Al ions distributed in cation sublattice tend to need longer time or higher temperature although layered structure was also observed in microscale. It is worth of noting that crystallization of layered oxides seems to occur at temperature greater than 700. It is due to the decomposition of LiOH/Li₂CO₃ into Li₂O for better/faster reaction kinetics

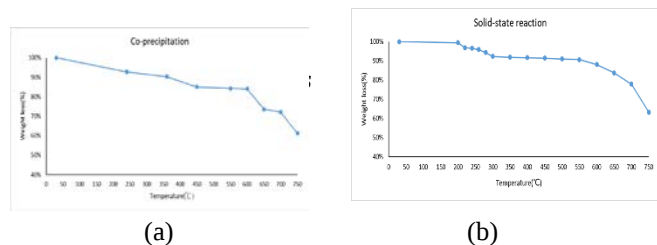


Fig. 1. Weight change on heating to 750°C for NCA prepared from (a) Co-precipitation (b) Solid-State Reaction

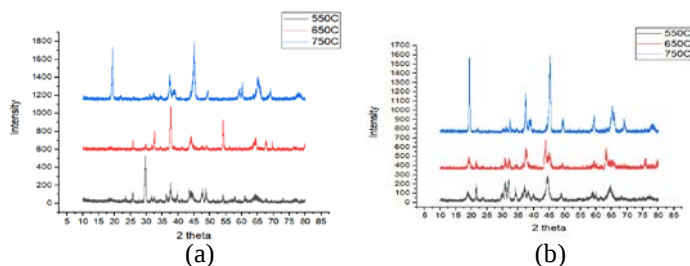


Fig. 3. XRD pattern for NCA processed different routes (s) solid state reaction (right) co-precipitation upto 750°C

In high Ni-based cathodes, both NCA and NCM-811 contain 80% Ni in transition metal layer. Its capacity may be estimated based on numbers of the transition metal ions that act as electron acceptors or donors. Using NCA as an example, the theoretical capacity for one mole of NCA is $26.8 \times 0.95 = 25.46 \text{ Ah}$ assuming Ni ions are in trivalent state since Al being a non-active cation. In the case of NCM-811, Mn tends to be in its tetravalent state. Thus, the substitution of Mn⁴⁺ for a trivalent site in cation sublattice of layered structure will induce a negative charged e⁻ based on charge-compensation theory. These e⁻s tend to associate with Ni³⁺, and then it will be reduced to Ni²⁺ according to defect reaction:

Thus, NCM-811 may be expressed as LiNi_{0.1}²⁺Co_{0.1}³⁺Mn_{0.1}⁴⁺O₂. As a result, electron donation in NCM-811 may come from Ni²⁺ to Ni⁴⁺, Ni³⁺ to Ni⁴⁺, Co³⁺ to Co⁴⁺. For one mole of LiNi_{0.1}²⁺Co_{0.1}³⁺Mn_{0.1}⁴⁺O₂, the theoretical capacity becomes 26.8 Ah which is higher than NCA. After reviewing published data [1,2], it is found that the initial capacity of NCM-811 reached over 210 mAh/g specific capacity under C/10 rate as seen in Fig. 3. In comparison to NCA, its initial capacity is about 185 mAh/g. Followed by charging/discharging cycling tests, fast capacity fading was observed in results of NCM-811 cells. After 50 cycles, only 125 mAh/g capacity remained with nearly 40% loss. On the contrary, NCA still retained 90% of its initial capacity after 50 cycles testing. It is believed that the difference in capacity fading in both NCM-811 and NCA is strongly related to the presence of Al and Mn ions. Al is known to be an excellent stabilizing agent, due to its very stable valence state and strong bonding with oxygen ions. Hexagonal LiAlO₂ is an

good example. In NCM, Mn ions exhibit several problems that may result in fast capacity fading in NCM-811. First, the presence of Ni²⁺ may form rock-salt structure domain and slow down Li transport. Secondly, the multiple-valency of Mn ions may form spinel structure easily after cycling. Moreover, the dissolution of Mn in liquid may further degrade the performance of NMC.

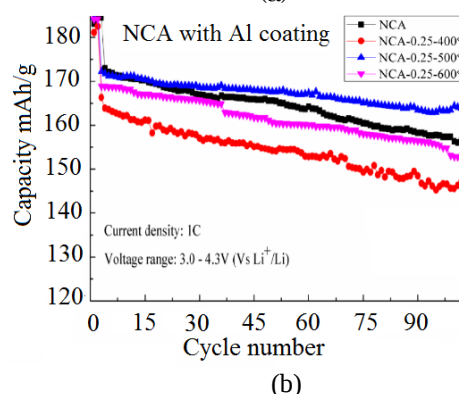
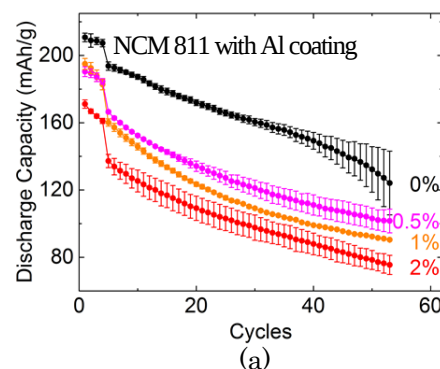


Fig. 4. Effect of Al doping on cycling Behavior for (a) NCM-811 and (b) NCA.

3. Conclusions

1. NCA processed by Co-precipitation shows better crystallization due to nanoscale mixing in precipitates;
2. NCM-811 shows higher initial capacity than NCA due to charge compensation of Mn⁴⁺ substitution resulting more Ni²⁺;
3. Al seems to be a better stabilizing agent than Mn for high Ni cathode. Homogeneous distribution of Al is crucial.

Acknowledgements

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