Role of coprecipitation and calcination of precursors on phase homogeneity and electrochemical properties of battery active materials

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ABSTRACT

Coprecipitation has previously been demonstrated to produce diverse compositions of battery precursor particles, frequently under the assumption that the precipitation of transition metals from the solution results in advantages with regards to efficient homogeneous local mixing of transition metal cations within the solid particles. Such mixing is generally considered as an advantage relative to solid state reaction of solid powders with the equivalent starting stoichiometry; however, very few studies have attempted to quantitatively confirm the impact of this local mixing on the resulting final materials. The extent to which local mixing from coprecipitation facilitates the mass transport of transition metals during the calcination process, which would be expected to aid in producing well crystallized single-phase particles, is not clear. Herein, this study will systematically compare the phase purity and crystallinity of oxide powders comprised of a blend of transition metals that were produced from either physical mixture of single transition metal precursors or multicomponent precursors produced via coprecipitation from solution. These experiments provide quantitative support for the role that local mixing, achieved via precipitation, plays in forming high crystallinity final materials with the desired phase. LiMn$_{1.5}$Ni$_{0.5}$O$_4$ was used as a model multicomponent target final material after calcination.

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1. Introduction

Multicomponent transition metal (TM) oxides are the most commonly used cathode active materials in lithium-ion (Li-ion) batteries due to their broad capabilities in power and energy densities that can be tuned depending on the transition metal stoichiometry [1–5]. Many techniques have been developed to synthesize multicomponent TM oxide materials at both research and industrial scales [6–11]. Solid state synthesis is straightforward in that single component powders of each element can be measured at the desired stoichiometry directly and then physically mixed, but high temperature and/or long calcination times are required due to large diffusion distances for ions to form homogeneous final active materials [12–14]. Sol-gel synthesis is a modified solid state method that achieves very good mixing of the constituent elements, but the control over particle morphology is relatively limited [15–18]. Spray pyrolysis, a synthesis route commonly utilized in industry, is very scalable and has local mixing homogeneity but also limited particle morphology control [19–21]. Coprecipitation is another popular method to synthesize precursors for multicomponent TM oxide materials. Mixing between different TMs is assumed to be achieved at the atomic level during coprecipitation reactions, which in principle will reduce the requirement for aggressive firing conditions.

The particle morphologies can be adjusted by tuning the reaction conditions and the particle morphologies can be well retained after the calcination process, which makes particle morphology control possible [22–25]. The method is fast, has low equipment needs, and is scalable. However, there are no reports on quantitative confirmation of the advantages of the assumed local mixing of precursors produced via coprecipitation, or to what extent the mixing facilitates ion diffusion during subsequent calcination. The focus of this study is to understand to what extent coprecipitation provides an advantage with local mixing of transition metals in the precursor particles, and for comparison we will also use solid state synthesis with physical mixing of single transition metal precursors.

LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (LMNO) was chosen as the example final calcined material for this study. LMNO is commonly referred to as high voltage spinel due to its high redox potential at 4.7 V vs. Li/Li$^+$ and because the material forms a spinel crystalline structure [1,26]. Depending on the distribution of Mn and Ni ions, LMNO may form two different crystallographic structures: the ordered P4$_3$32 space group and the disordered Fd-3 m space group [27]. Correct stoichiometry is essential for extracting the maximum capacity from LMNO materials. According to previous reports, either Mn or Ni enrichment relative to the target Mn:Ni 3:1 stoichiometry may cause decreased material capacity and/or material stability during electrochemical charge/discharge [17,26]. The sensitivity of electrochemical properties to stoichiometry necessitates good mixing between Mn and Ni ions in the final active material particles, since localized Mn or Ni segregation will result in phase

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impurities and deteriorate resulting electrochemical properties of the materials. In this study, we will show the influence of local mixing and processing conditions on resulting final material crystal structure and electrochemical properties. The advantage of local mixing via coprecipitation relative to solid state physical blends of precursors is quantitatively characterized.

2. Materials and methods

2.1. Precursor synthesis and calcination

For the coprecipitation reaction, oxalate was used as the precipitation anion for all materials synthesized. Oxalate was chosen because Mn, Ni, and blends of Mn and Ni form stable oxalate dihydrates across the entire range of Mn:Ni ratios [17,28]. Other common precipitation anions, such as hydroxide and carbonate, have challenges with regards to impurity phases in the precipitate within certain stoichiometric ratios of Mn:Ni [10,24]. The dual functions of oxalate ions as both a precipitation reagent and a complexing agent also has the advantage of slowing down the precipitation rate which enables better control over the process within low concentration regimes [29].

The pure Mn and pure Ni TM precursors and the Mn:Ni 3:1 precursors were synthesized using coprecipitation via reaction of TM sulfate solutions with sodium oxalate solution. The synthesis was adapted from a procedure described previously [30]. In brief, a pre-determined amount of TM sulfate salts (containing either Mn, Ni, or Mn:Ni 3:1 feed) was dissolved in 400 mL deionized water (DI water) and heated to 60 °C. Separately, sodium oxalate was dissolved and heated to 60 °C in 400 mL DI water. The precipitation was initiated by pouring the TM sulfate solution into the sodium oxalate solution all at once with vigorous stirring. The solution was assumed to be homogeneous upon mixing, with the total concentrations of TM and oxalate both 0.15 M after the initial mixing step. The reaction was allowed to proceed for 30 min after mixing the two solutions together, at which time the precipitates were filtered and rinsed with DI water. The initial solution concentrations for TM and oxalate were chosen to mitigate the deviation of the precipitate composition relative to the feed conditions for the Mn:Ni 3:1 and to result in high yield of precursor particles [30]. The composition of the resulting precursor from the 3:1 Mn:Ni feed was determined by inductively coupled plasma – optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 8000) to be Mn: Ni 2.82:1. As reported in the literature [31,32], the pure Ni, pure Mn, and 3:1 Mn:Ni precursors all were oxalate dihydrates as determined via thermal gravimetric analysis. After filtration and rinsing, all precursor material powders were dried in a vacuum oven at 80 °C overnight.

All precursor materials were calcined with a lithium salt to form lithium transition metal oxides. The obtained blend or pure precursor powders were mixed with 5% stoichiometric excess of LiOH for a target stoichiometric ratio of Li:TM 1.05:2. The mixing was conducted by hand using mortar and pestle for 10 min, and the mass of the powder for each batch of material mixed was kept around 3 g for consistency. The powder mixtures were then transferred into crucibles and put into a furnace (Carbolite CWF 1300 box furnace) and fired under an air atmosphere. All the calcination processes used 1 °C/min ramping rate for heating and the materials were held at the target top temperature for a specified period of time followed by naturally cooling down to room temperature. The top temperature and hold time were parameters that were varied and are specified in the manuscript text for a given material.

2.2. Materials characterization

Powder morphologies were characterized using a scanning electron microscope (SEM, FEI Quanta 650). Over 100 particles from SEM images were counted to determine the average particle size and standard deviation. The SEM was also equipped with energy-dispersive X-ray spectroscopy (EDS), which was used to identify elemental composition

and distribution in the particles. The crystal structure of precursors and calcined materials was determined using powder X-ray diffraction (XRD, PANalytical X'pert ProMPD). Thermal gravimetric analysis (TGA, TA Q50) was performed to determine the water stoichiometry in the precipitates and to locate the temperatures where decomposition processes occurred for the precursors. All the TGA tests were conducted in an air atmosphere with the ramping rate of 10 °C/min.

Electrochemical characterization of the final calcined active materials was conducted by using the calcined powders as the cathode active material in Li-ion battery cells paired with lithium metal anodes. The CR2032-type cells were fabricated with cathodes comprised of a blend of 80 wt% active materials, 10 wt% acetylene black, and 10 wt% polyvinylidene difluoride binder (dissolved in N-methyl-2-pyrrolidone). The electrode was cast from a slurry onto aluminum foil with a doctor blade set at a gap height of 250 μm. The electrode was first dried in air at 80 °C for 24 h, and then subsequently further dried under vacuum at 70 °C for 3 h. From the electrode foil, smaller disks with 1.6 cm^2 area were punched to be used as cathodes in the coin cells. The cells, with the composite cathodes paired with lithium metal foil anode, were assembled inside an argon-filled glove box with polymer trilayer membrane as separators and LiPF$_6$ dissolved in 3:7 vol% ethylene carbonate: ethyl methyl carbonate as the electrolyte. The cells were cycled within a voltage window of 3.6–4.9 V at room temperature using a MACCOR multichannel battery cycler. The cells were cycled galvanostatically at C/10, which corresponded to 14.67 mA g^{-1} of active material powder in the electrode, and the total charge/discharge current was adjusted by the amount of active material within a given electrode. The discharge profiles and dQ/dV profiles reported in this manuscript were from the fourth charge/discharge cycle, after the capacity stabilized from material structural activation during the first few cycles [33,34].

3. Results and discussion

3.1. Experimental results

Thermal gravimetrical analyses (TGA) were conducted on the pure manganese and nickel oxalates and the blend (3:1 Mn:Ni) oxalate. The TGA profiles can be found in the Supplementary Information, Fig. S1. Two peaks in differential mass loss were observed for all precursors, one at lower temperature corresponding to structural water loss, and a peak at higher temperature which resulted from decomposition of the oxalate structure during formation of oxide. Even with the fast ramping speed (10 °C/min) in TGA, the dehydration and decomposition processes were completed below 350 °C for all oxalate compounds. The melting point of LiOH is 450–471 °C from ICSC data (CAS #: 1310-66-3), thus above this temperature the liquid LiOH should obtain good contact and distribution with the resulting TM oxide particles. Based on the TM oxalate decomposition temperatures and LiOH melting temperature, we chose a lowest target calcination temperature of 500 °C. The highest calcination temperature was 850 °C, which was a common calcination temperature for similar materials and has been reported to result in good crystallinity while producing desirable primary particle size [14,33,35]. An intermediate calcination temperature of 700 °C was chosen because this temperature has been reported to promote formation of the ordered phase of LMNO [27,36]. The holding time at the target temperature of 700 °C was also varied to understand how the hold duration impacts the crystallinity of the product materials, with the extended hold being expected to facilitate more significant ion diffusion which could help to anneal out metastable phases and enable improved crystallinity. The product samples were named in the format of M-T-t, where M designates the mixing method which was either physically mixing of the two precursors (P, which stands for 'physical' mixing the two TMs) or coprecipitation of the blend TM solution (S, which stands for 'solution' mixing the TMs); T represents for the target top temperature in degrees Celsius, and t is the holding time at the target temperature in hours. For example, the sample referred to as S-500-