



High-performance lithium-rich layered oxide materials: Effects of chelating agents on microstructure and electrochemical properties



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ABSTRACT

The mechanisms and effects of three typical chelating agents, namely glucose, citric acid and sucrose on the sol-gel synthesis process, electrochemical degradation and structural evolution of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (LLMO) materials are systematically compared for the first time. X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy analysis indicate that the sample synthesized from sucrose owns well structure, homogenous distribution, low Ni^{3+} concentration and good surface structural stability during cycling, respectively. Electrochemical tests further prove that the LLMO material obtained from sucrose maintains 258.4mAh g^{-1} with 94.8% capacity retention after 100 cycles at 0.2C. The superior electrochemical performance can be ascribed to the exceptional complexing mechanism of sucrose, compared to those of the glucose and citric acid. Namely, one mole sucrose can be hydrolyzed into two different monosaccharides and further chelates three M (Li, Ni, Co and Mn) ions to form a more uniform ion-chelated matrix during sol-gel process. This discovery is an important step towards understanding the selection criterion of chelating agents for sol-gel method, that chelating agent with excellent complexing capability is beneficial to the distribution, structural stability and electrochemical properties of advanced lithium-rich layered materials.

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1. Introduction

Lithium-ion batteries (LIBs) are indispensable for everyday life as power sources for laptops, cellphones, e-book readers, digital cameras, and a variety of other portable devices, with the characteristics of high open-circuit voltage, large discharge capacity and environmental friendliness [1,2]. The performance of LIBs is highly related to the properties of the active cathode materials. A typical LIB is composed of a graphite anode and a layered transition metal oxide cathode active material, exemplified by LiCoO_2 , or one of its congeners obtained by substituting some of the Co with Ni and/or Mn [3–5]. Nevertheless, all of their available discharge capacities approach their limitations ($<200\text{mAh g}^{-1}$), thus the development of cathode materials with higher capacities

are urgently needed to meet the demand for the larger energy densities of LIBs.

In this regard, a class of layered transition metal oxides, namely, the lithium-rich layered oxides (shorted as LLMO) of the general formula $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (M=Mn, Ni, Co) have attracted much attention, which are reported to deliver $230\text{--}285\text{mAh g}^{-1}$ reversible capacity, reaching nearly the theoretical one e^-/metal capacity of the transition metal dioxide [6–12]. The electrochemical performance of the LLMO materials is strongly dependent on the synthesis technique [13,14]. It is reported that the particle size of LLMO and the stoichiometry of Li and O elements are very sensitive to synthesis processes [15,16].

Nowadays, solid-state and co-precipitation et al. approaches have been applied to prepare the LLMO materials [4,6–7,14–18]. However, these methods cannot build high quality complex metal oxide cathodes with homogenous distribution. It is noted that the M ions distribute randomly in precursor, which leads to cation mixing and formation of impurity phases in the prepared cathode materials, and further affecting the electrochemical performance of LLMO [15,16].

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The sol-gel method, which possesses high possibility to synthesize homogeneous and stoichiometric nano-sized particles via binding the transition metal ions at sub atomic levels in starting sol, has been adopted as the preferred technique to produce LLMO [18–21]. Shen et al. investigated the effect of Ni/Mn content on the structural and electrochemical properties of LLMO by using a citric acid-assisted sol-gel method [20]. Manthiram et al. prepared LLMO by a sol-gel method using EDTA/citric acid as chelating agent that plays an important role in preventing phase separation and improving homogeneity of the products [19]. The effects of reaction temperatures of single chelating agent on structure and electrochemical properties of LLMO have also been investigated.

However, to the best of our knowledge, all of these available reports are confined to single chelating agent. The comparison about the effects of different chelating agents on the properties of LLMO materials, and the discussion of various complexing mechanisms of chelating agents have not been reported. The selection criterion of chelating agents for synthesizing high performance cathode materials is still fuzzy. Considering that the chelating agents are responsible for highly homogeneous distribution of metal ions and play a vital role in the sol-gel process, a systematical study for different chelating agents and corresponding complexing mechanism is imperative.

In this work, we first compare the effects of three typical chelating agents, namely glucose, citric acid and sucrose on the physical and electrochemical performance of LLMO materials. The mechanisms of these chelating agents are also revealed. It is found that glucose monomer can only chelate one M ions ($M = \text{Li}^+, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$), while citric acid monomer owns enhanced complexing ability and can chelate three M ions. Interestingly, sucrose can also chelate three M ions and exhibits exceptional complexing ability by a unique synergistic effect of two different monosaccharides, to form a more homogeneous ion-chelated matrix. As anticipated, the sample synthesized from glucose exhibits the poorest electrochemical performance among the three chelating agents. The sample synthesized from sucrose, on the other hand, owns well distribution, less Ni^{3+} ions, and better surface stability during cycling compared to those of the citric acid and glucose. The optimized LLMO (sucrose) delivers a high discharge capacity of 258.4 mAh g^{-1} (0.2 C) with 94.8% capacity retention after 100 cycles at a cut-off potential of 4.8 V.

2. Experimental

2.1. Preparation of lithium-rich layered oxide

$0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, labeled as GLLMO (glucose), CLLMO (citric acid) and SLLMO (sucrose) were prepared by sol-gel method with different chelating agents. Required amounts of lithium acetate (Sinopharm Chemical Reagent Co, 99% pure), manganese acetate (Sinopharm Chemical Reagent Co, 99% pure), nickel acetate (Sinopharm Chemical Reagent Co, 99% pure) and cobalt acetate (Sinopharm Chemical Reagent Co, 99% pure) were first dissolved in deionized water and mixed with an aqueous solution of 0.5 mol L^{-1} chelating agent to give the metal/chelating agent ratio equal to 1.5. The pH-value was adjusted to 5.0 by addition of nitric acid, during which nitrate ion provided an in situ oxidizing environment for sugar being hydrolyzed and converted into carboxylic acids, glucose being oxidized into gluconic acid and the nitrates themselves decomposed to give out brown fumes of nitrogen dioxide (Fig. 1). The resulting solution was stirred at 80°C for 6 h to obtain a clear viscous gel. The gel was dried in an oven at 120°C for 12 h. The dried powder were ground and precalcined at 450°C for 6 h in air to eliminate the organic substances and to obtain the precursors, which is labeled as GL (glucose), CL (citric acid) and SL (sucrose), respectively. A crystalline sample was formed by heating the precursor at 900°C for 12 h in air.

2.2. Characterizations

The crystallographic structure of LLMO powders was examined by using a Rigaku D/Max 200PC X-ray diffractometer (XRD) with a graphite monochromator and $\text{Cu K}\alpha$ radiation at a scan rate of 5° min^{-1} . The morphology of the powders was determined by scanning electron microscopy (SEM). For high resolution transmission electron microscopy (HRTEM) analysis, the active materials were dispersed in dimethyl carbonate (DMC). Then a droplet of the powder was deposited on a copper micro-grid for the observation. To investigate the microstructure and morphology changes of cathode materials after long-term cycles, the fully discharged electrodes (2.0 V) were first disassembled from coin cells and rinsed with dimethyl carbonate (DMC) several times in the glove box, and then dried at room temperature. The dried electrodes were applied for HRTEM analysis, the active materials

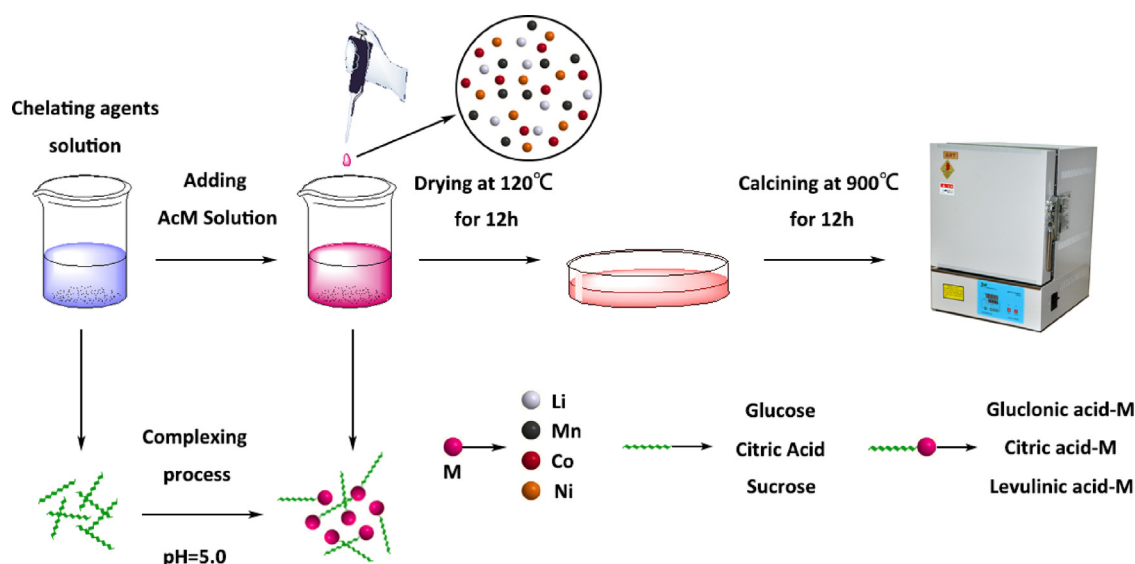


Fig. 1. Schematic view of the sol-gel process and the formation of metal-chelated complexes.

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