



Effect of outer layer thickness on full concentration gradient layered cathode material for lithium-ion batteries



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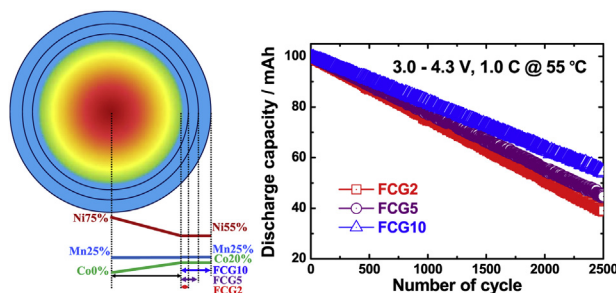
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HIGHLIGHTS

- $\text{Li}[\text{Ni}_{0.6-x}\text{Co}_{0.15+x}\text{Mn}_{0.25}]\text{O}_2$ with full concentration gradient was synthesized.
- Cathodes were coated with different outer layer thickness having a constant composition.
- Thicker outer layer improved cycle performance and thermal stability.
- Thicker outer layer undermined the rate capability.
- Outer layer coating can be selectively used for specific requirements.

GRAPHICAL ABSTRACT



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ABSTRACT

Full concentration gradient (FCG) layered cathode materials $\text{Li}[\text{Ni}_{0.6-x}\text{Co}_{0.15+x}\text{Mn}_{0.25}]\text{O}_2$ ($x = 0, 0.01, \text{ and } 0.04$) with different outer layer thicknesses are synthesized via a specially developed coprecipitation method. In the FCG cathode, the nickel concentration decreases linearly and the cobalt concentration increases from the center to particle surface throughout the particle at a fixed composition of Mn. The thickness of the FCG primary particle increases in the radial direction with an increasing outer layer thickness of the secondary particles and significantly affects the electrochemical performance. An increase in the stable outer layer thickness improves the cycle performance and thermal stability of the FCG materials at the expense of reversible capacity, whereas the rate capability and low temperature performance are significantly deteriorated by increasing outer layer thickness. All of the FCG materials exhibit superior electrochemical and thermal properties compared to the conventional cathode $\text{Li}[\text{Ni}_{0.58}\text{Co}_{0.17}\text{Mn}_{0.25}]\text{O}_2$ due to the unique microstructure of the FCG cathode.

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1. Introduction

Over the past decade, much attention has been paid to layered Ni-rich $\text{Li}[\text{Ni}_{1-x}\text{M}_x]\text{O}_2$ ($M = \text{transition metal}, x \leq 0.2$) as a promising cathode material for lithium-ion batteries because of their potentially high reversible capacity, good rate capability, and relatively low cost [1–4]. However, $\text{Li}[\text{Ni}_{1-x}\text{M}_x]\text{O}_2$ materials suffer from poor

cycling performance and thermal safety because of the high concentration of relatively reactive Ni^{4+} when charged to greater than 4.2 V and the oxygen release from the highly delithiated electrode, especially at elevated temperature [1,2]. To overcome these problems of layered Ni-rich materials, Co and/or Mn and Al have been substituted for Ni to form $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}]\text{O}_2$ and $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$ [3,5–7]. While these materials have shown improved electrochemical properties, the cycling performance and thermal stability should be further improved for practical battery applications.

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It is well-known that an increase in Ni concentration in Li $[\text{Ni}_{1-x}\text{M}_x]\text{O}_2$ increases the reversible capacity, whereas an increase in Mn content yields better cycle life and thermal stability at the expense of reversible capacity [8,9]. We recently reported synthesis of a Ni-enriched cathode material with a layered structure and a full concentration gradient (FCG). The FCG cathode was spherical in shape, with the Ni concentration decreasing gradually from the particle center toward the surface, while the Mn concentration increased linearly from the core. The FCG produced the Ni-enriched particle core and the Mn-enriched outer layer without an abrupt change in composition and imparted both high capacity and outstanding safety performance to the Ni-enriched cathode [10–13]. In addition, FCG material has a unique microstructure composed of long rod-shaped primary particles radiating from the particle center. The rod-shaped primary particles are responsible for the excellent cycle performance, thermal stability, and lower temperature performance by reducing the exposed contact area with the liquid electrolyte due to the lower specific surface area and the enhanced Li^+ diffusion through the material [11,12].

Here, we report the effect of an outer layer with a constant composition encapsulating the FCG cathode, which is schematically described in Fig. 1. The particle center ($[\text{Ni}_{0.75}\text{Mn}_{0.25}](\text{OH})_2$) and outer surface compositions ($[\text{Ni}_{0.55}\text{Co}_{0.20}\text{Mn}_{0.25}](\text{OH})_2$) in the hydroxide precursor are fixed, as shown in Fig. 1. The particle had a linearly decreasing Ni concentration from 75% to 55% toward the particle outer surface, while the Co concentration increased from 0% to 20% at a fixed Mn concentration. The FCG hydroxide particle was encapsulated with an outer layer having a constant composition of $[\text{Ni}_{0.55}\text{Co}_{0.20}\text{Mn}_{0.25}](\text{OH})_2$ with three different thicknesses. The long-term cycling performance and thermal properties of the FCG material with an outer layer were evaluated as a function of the outer layer thickness (0.2, 0.5, and 1.0 μm). Hereafter, the FCG materials with outer layer thickness 0.2, 0.5, and 1.0 μm are denoted as FCG2, FCG5, and FCG10, respectively. For comparison, the electrochemical performances and thermal properties of the conventional cathode (CC, $\text{Li}[\text{Ni}_{0.58}\text{Co}_{0.17}\text{Mn}_{0.25}]\text{O}_2$) without a concentration gradient were also evaluated.

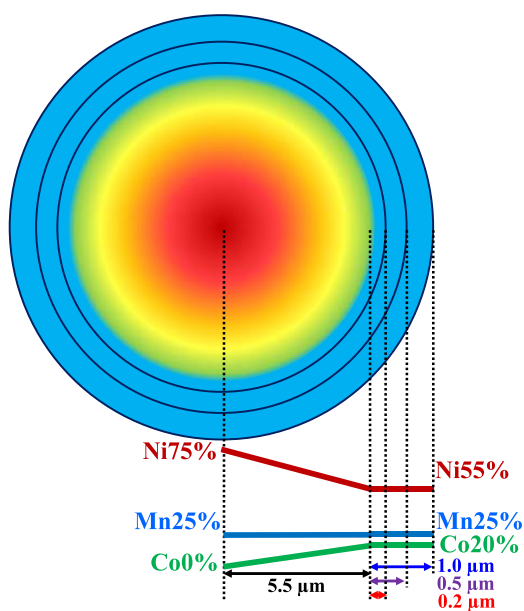


Fig. 1. Schematic diagram of the FCG hydroxide precursor with different outer layer thicknesses. The variation in concentration within the FCG hydroxide precursor with different outer layer thicknesses.

2. Experimental

2.1. Synthesis of CC $\text{Li}[\text{Ni}_{0.58}\text{Co}_{0.17}\text{Mn}_{0.25}]\text{O}_2$

The $[\text{Ni}_{0.58}\text{Co}_{0.17}\text{Mn}_{0.25}](\text{OH})_2$ precursor was synthesized via co-precipitation of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (58:17:25 in molar ratio) as starting materials. Details of the preparation procedures are given in a previous report [14]. The obtained $[\text{Ni}_{0.58}\text{Co}_{0.17}\text{Mn}_{0.25}](\text{OH})_2$ hydroxide precursor was mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$ and calcined at 870 $^\circ\text{C}$ for 10 h in air.

2.2. Synthesis of FCG2, FCG5, and FCG10

To prepare the FCG2, FCG5, and FCG10, at the starting of a continuously stirred tank reactor (CSTR, 4L) operation, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (Ni:Mn = 0.75:0.25 in molar ratio) solution (1.2 mol L^{-1}) from a tank 1 was slowly pumped into the CSTR. Concurrently, a Ni-deficient aqueous solution (Ni:Co:Mn = 0.50:0.25:0.25 in molar ratio) from a tank 2 made of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ was slowly pumped into the Ni-rich (Ni:Mn = 0.75:0.25) stock solution in the tank 1, after which the homogeneously mixed solution was fed into the CSTR [10–12,15]. Simultaneously, a 4.0 mol L^{-1} NaOH solution (aq) (molar ratio of ammonium hydroxide to transition metal = 1.0) and the desired amount of a NH_4OH (2.0 mol L^{-1} solution (aq), molar ratio of sodium hydroxide to transition metal = 2.0) were pumped separately into the reactor. After the composition of tank 1 reached the desired surface composition, the feeding of tank 2 was stopped, and a controlled surface composition from tank 1 was continuously pumped to CSTR for 2 h, 4 h, or 8 h. The co-precipitated hydroxide precursor powders were filtered, washed with deionized water, and dried at 110 $^\circ\text{C}$. The obtained FCG2, FCG5, and FCG10 hydroxide precursors were mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$, and the mixtures were calcined at 825, 845, or 875 $^\circ\text{C}$ for 10 h in air, respectively.

2.3. Material characterizations

The chemical compositions of the prepared powders were determined by atomic absorption spectroscopy (AAS, Vario 6, Analyticjena). The morphology of each powder was observed with scanning electron microscopy (SEM, JSM 6400, JEOL). To obtain the localized composition of the materials at particle level, cross-sections of the particles were prepared by embedding them in an epoxy and grinding them flat. Line scans of the polished surfaces for the prepared FCG hydroxide precursors and lithiated oxides were analyzed by an electron probe micro-analyzer (EPMA) (JXA-8100, JEOL).

2.4. Electrochemical test

For fabrication of the cathodes, the synthesized powders were mixed with carbon black and polyvinylidene fluoride (85:7.5:7.5) in *N*-methylpyrrolidinone. The obtained slurry was coated onto Al foil and roll-pressed. Fundamental cell tests were performed with a 2032 coin-type cell using Li metal as the anode cycled from 2.7 to 4.4 V. Long-term cycle-life tests were performed in a laminated-type full cell (36 mAh) wrapped with an Al pouch. Mesocarbon microbead graphite (MCMB, Osaka Gas) was used as the anode. The electrode size of the full cell was 3 cm \times 5 cm. The electrolyte solution was 1.2 M LiPF_6 in ethylene carbonate–ethyl-methyl carbonate (3:7 in volume). The cells were charged and discharged at 25 $^\circ\text{C}$ and 55 $^\circ\text{C}$, respectively, between 3.0 and 4.3 V by applying a constant 1C current (36 mA corresponds to 200 mA g^{-1}).

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