

Cathode Material for Advanced High-Energy and Safty Rechargeable Lithium Batteries

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Introduction

To reduce the cost of the battery system and increase the driving range for the EVs, batteries with very high energy density and improved safety are needed.[1] In the past, most of the work has been centered on developing high energy layered cathode materials. Among these materials, $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ [2] and $\text{Li}[\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y]\text{O}_2$, where $1 - x - y \geq 0.6$ [3] have been investigated intensely in the past ten years because they offer higher capacity than existing cathode materials. However, they exhibit poor cycling and thermal characteristics, especially at high voltage and elevated temperatures, because of oxygen release from the charged electrode, which oxidizes the electrolyte and leads to a quick capacity fade and, in some cases, severe thermal runaway of the cell.[4]

We report a novel cathode material with full concentration gradients of Ni and Co ions and a fixed composition of Mn (FCG-Mn-F) extending throughout each secondary particle, which has long rod-shaped primary particles that span from the center to the surface. The constant Mn concentration across the particle provides outstanding cycle life and safety, and the linearly decrease in Ni concentration toward the particle outer surface results in high capacity. At the same time, the gradual increase of the Co concentration from the particle center to the surface increases the electronic conductivity, yielding excellent rate capability. This unique FCG-Mn-F morphology, reported here for the first time, could lead to 1) a highly densified particles, which can lead to high volumetric energy density at the cell level, 2) fast lithium diffusion across the particle, which improved the rate capability of the material, especially at low temperature, and 3) high thermal stability because of limited surface reactivity with the electrolyte.

Experimental

The positive electrode material FCG-Mn-F $\text{Li}[\text{Ni}_{0.60}\text{Co}_{0.15}\text{Mn}_{0.25}]\text{O}_2$, a Ni-poor aqueous solution (Ni:Co:Mn = 0.50:0.25:0.25 in molar ratio) from 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 a Ni-rich (Ni:Mn = 0.75:0.25 in molar ratio) stock solution in tank 1, after which the homogeneously mixed solution was fed into a continuously stirred tank reactor (CSTR). During the early stage of coprecipitation reaction, spherical $[\text{Ni}_{0.75}\text{Mn}_{0.25}](\text{OH})_2$ particles were formed first, and a transition-metal-containing hydroxide with different composition gradually accumulated on the surface of the spherical $[\text{Ni}_{0.75}\text{Mn}_{0.25}](\text{OH})_2$ particles via layer-by-layer assembly with a precipitation process. We increased the concentration of the ammonium hydroxide (molar ratio of ammonium hydroxide to transition metal = 1.0) and sodium hydroxide amounts (molar ratio of sodium hydroxide to transition metal = 2.0) to favor the growth the primary particles. The obtained FCG-Mn-F $[\text{Ni}_{0.60}\text{Co}_{0.15}\text{Mn}_{0.25}](\text{OH})_2$ was mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$, and the mixture was calcined at 825 °C for 10 h in air.

To obtain the localized composition of the FCG-Mn-F materials, cross sections of the particles were prepared by embedding the particles in an epoxy and grinding them flat. Mapping of the polished surfaces for the prepared

FCG-Mn-F lithiated $\text{Li}[\text{Ni}_{0.60}\text{Co}_{0.15}\text{Mn}_{0.25}]\text{O}_2$ powders were analyzed via electron probe microanalysis (EPMA) (JEOL, Model JXA-8100). Transmission electron microscopy (TEM) samples were prepared by focused ion beam and examined in a JEOL, Model JEM 2100F instrument.

Results and discussion

Figure 1a shows a cross-sectional scanning electron microscopy (SEM) image of a single lithiated FCG-Mn-F $\text{Li}[\text{Ni}_{0.60}\text{Co}_{0.15}\text{Mn}_{0.25}]\text{O}_2$ oxide particle and the corresponding elemental distribution of Ni, Co, and Mn. The elemental mapping of Mn shows a uniform contrast throughout the entire particle, as expected. The nickel was depleted at the particle surface and became gradually enriched toward the particle center, whereas the opposite concentration gradient was observed for cobalt. Figure 1b shows a TEM image of a single FCG-Mn-F $\text{Li}[\text{Ni}_{0.60}\text{Co}_{0.15}\text{Mn}_{0.25}]\text{O}_2$ particle that had been sectioned with a focused ion beam. Near the center, the particle was composed of equiaxed primary particles, ~200 nm in diameter, from which elongated primary particles whose length reached up to 2.5 μm (~100 nm in width). These long rod-shaped primary particles emanated radially from the center.

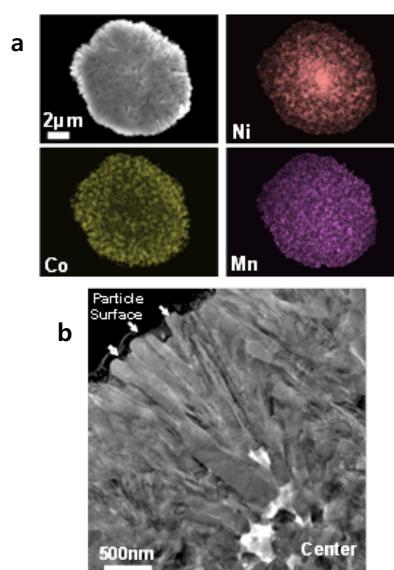


Figure 1. (a) Cross-sectional SEM and EPMA mapping of Ni, Co, and Mn within a single lithiated FCG-Mn-F particle; (b) cross-sectional TEM image of a single FCG-Mn-F particle.

References

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