



Full paper

Effect of calcination temperature on the electrochemical properties of nickel-rich $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$ cathodes for lithium-ion batteriesJianming Zheng^a, Pengfei Yan^b, Luis Estevez^a, Chongmin Wang^b, Ji-Guang Zhang^{a,*}^a Energy and Environment Directorate, Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99354, USA^b Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99354, USA

ARTICLE INFO

Keywords:

Nickel-rich cathodes
 Calcination temperature
 Cycling stability
 Micro-strain
 Crack formation
 Lithium-ion batteries

ABSTRACT

High energy density, nickel (Ni)-rich, layered $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC, $x \geq 0.6$) materials are promising cathodes for lithium-ion batteries. However, several technical challenges, such as fast capacity fading and high voltage instability, hinder their large-scale application. Herein, we identified an optimum calcining temperature range for the Ni-rich cathode $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$ (NMC76). NMC76 calcined at 750–775 °C exhibits a high discharge capacity ($\sim 215 \text{ mAh g}^{-1}$ when charged to 4.5 V) and retains ca. 79% of its initial capacity after 200 cycles. It also exhibits an excellent high-rate capability, delivering a capacity of more than 160 mAh g^{-1} even at a 10 C rate. The high performance of NMC76 is directly related to the optimized size of its primary particles (100–300 nm) (which constitute the spherical secondary particles of $> 10 \mu\text{m}$) and cation mixing. Higher calcination temperature ($\geq 800 \text{ }^\circ\text{C}$) leads to rapid increase of primary particle size, poor cycling stability, and inferior rate capability of NMC76 due to severe micro-strain and -crack formation upon repeated lithium-ion de/intercalations. Therefore, NMC76 calcined at 750–775 °C is a very good candidate for the next generation of Li ion batteries.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the dominant power sources for consumer electronics and electric vehicles (EVs) because of their high energy density, light weight, and long cycle life [1–4]. Although significant progress has been made, the driving range of EVs using the state-of-the-art LIBs is still far below those of vehicles using internal combustion engines. The energy density and power capability of LIBs must be improved to increase the driving range and decrease the recharging time. To meet these requirements, significant effort has been made in the search of cathode materials with high discharge capacity and high operating voltage [5–8].

Recently, the Ni-rich, layered-structure cathode material $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC, $x \geq 0.6$) has received much attention due to its high discharge capacity (200–220 mAh g^{-1}) [7–10] and its high energy density ($> 800 \text{ Wh kg}^{-1}$) compared to traditional LiCoO_2 ($\sim 570 \text{ Wh kg}^{-1}$) and spinel LiMn_2O_4 ($\sim 440 \text{ Wh kg}^{-1}$). Ni-rich cathode material also has much higher lithium-ion diffusion coefficients, indicating better power capability than other NMC cathodes with lower Ni content [11]. Another advantage of Ni-rich cathode materials is that their lower Co content reduces production cost. Technical challenges that hinder large-scale application of Ni-rich NMC cathode materials

[9,10] include (i) Li/Ni cation mixing due to the difficulty of maintaining all the Ni in the 3+ valence state, (ii) micro-strain and -crack formation caused by significant volume variation during lithium-ion de/intercalation processes, and (iii) safety concern regarding aggressive thermal reactions between the delithiated Ni-rich NMC electrode and the organic carbonate electrolyte.

Significant effort has been dedicated to improving the electrochemical performance and thermal stability of the Ni-rich NMC cathode materials [9]. Representative approaches include lattice doping [12,13], surface treatment/modification [14–17], tuning the material compositions [18], a “smart” design of core-shell or concentration gradient structures [7,8,19], and structural stabilization with low Li_2MnO_3 content [20–22]. Synthetic conditions, such as co-precipitation pH value [23], particle size [23], lithium content [24,25], calcination temperature [26,27], calcination atmosphere (O_2 , air, etc.) [28–30], and heating/cooling rates also are important in determining the material's structural properties and thus influencing the electrochemical performance of as-prepared Ni-rich NMC cathode materials. Although the effect of calcination temperature has been reported, most previous study was performed with a low charge cutoff voltage of 4.3 V, which could not fully exploit the advantages of Ni-rich NMC cathodes.

We systematically investigated the effect of calcination temperature

* Corresponding author.

E-mail addresses: xmzhjm@126.com (J. Zheng), jiguang.zhang@pnnl.gov (J.-G. Zhang).

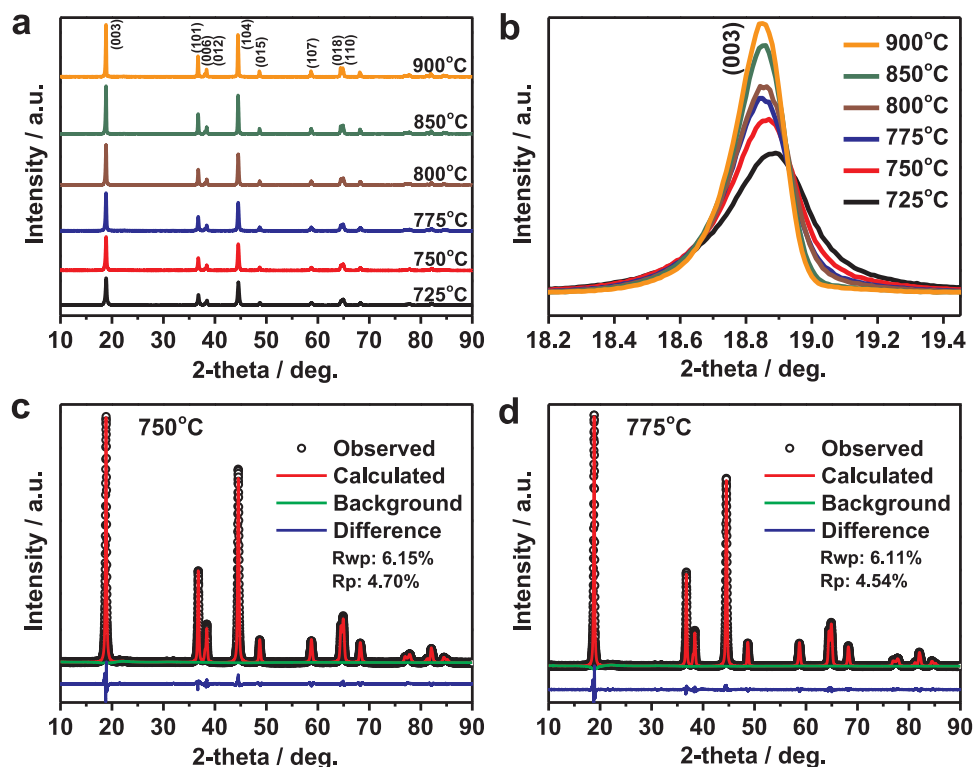


Fig. 1. (a) XRD patterns and (b) (003) diffraction peaks of the $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$ cathodes calcined at different temperatures. (c, d) Rietveld refinement results of $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$ cathodes prepared at (c) 750 °C and (d) 775 °C.

on the primary particle size, cation mixing, and electrochemical performance of a Ni-rich cathode material, $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$, with a large secondary particle size ($> 10 \mu\text{m}$), which is required to reach a high volumetric density. To obtain high energy density, the $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$ materials, calcined at temperatures ranging from 725 to 900 °C, were cycled with a high charge cutoff voltage of 4.5 V. Observations of the structural and interfacial changes in these materials provided insight into the capacity fading mechanism and the relationship between primary particle size and micro-strain generation inside secondary particles of Ni-rich cathode materials.

2. Experimental

2.1. Material preparation and characterization

Spherical, Ni-rich $\text{Ni}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}(\text{OH})_2$ precursor was prepared by a mixed hydroxide co-precipitation method, using a continuously stirred tank reactor (CSTR) under N_2 atmosphere. Initially, the CSTR of 5 L capacity was filled with 1.5 L distilled water. Then, an aqueous solution composed of NiSO_4 , MnSO_4 , and CoSO_4 with a total concentration of 2.0 mol L^{-1} was continuously pumped into the CSTR. At the same time, NaOH solution (8.0 mol L^{-1}) (as the precipitation reagent) and NH_4OH solution (10 mol L^{-1}) (as chelating agent) were also fed into the CSTR separately. The pH value ($\text{pH} = 11.5$), stirring speed (1000 rpm), and temperature (50 °C) were carefully controlled during the precipitation reaction. The precursor was filtered, thoroughly washed with distilled water, and dried overnight at 110 °C. $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}\text{O}_2$ cathode materials were prepared by mixing the $\text{Ni}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}(\text{OH})_2$ precursor with LiOH , followed by precalcining at 500 °C for 10 h and then calcining at temperatures ranging from 725 to 900 °C for 20 h in ambient air atmosphere. 3 mol% excess Li was used to compensate the loss of Li during calcination at high temperatures. The ramping rates were 3 °C for heating and 2 °C for cooling. Calcination is performed in ambient air atmosphere and 5 g of sample material was prepared for each calcination temperature.

Powder X-ray diffraction (XRD) was performed on a Rigaku MiniFlex II apparatus with $\text{Cu K}\alpha$ radiation operated at 30 kV and 15 mA. Data were collected in the 2θ range of 10–90° at 0.1° per min. Lattice parameter were refined by the Rietveld method with the General Structure Analysis System (GSAS program, Los Alamos National Laboratory, USA). The refinement was performed on the basis of the $\alpha\text{-NaFeO}_2$ -type hexagonal structure (R-3m) where the Li ions occupy the 3a (0, 0, 0.5) sites; Ni, Mn, and Co occupy the 3b (0, 0, 0) sites; and O is at the 6c (0, 0, z_{oxy}) sites ($z_{\text{oxy}} \approx 0.25$). The morphology of the prepared materials was characterized using a dual focused ion beam (FIB) scanning electron microscope (SEM) (FEI Quanta environmental). Part of the particle was removed by FIB to observe the cross-sectional morphology of Ni-rich NMC materials before and after cycling. Surface areas of the samples were determined with the Brunauer, Emmett, and Teller (BET) method using N_2 adsorption/desorption data collected with a Quantachrome Autosorb 6-B gas sorption system. Scanning transmission electron microscope (STEM) observations were implemented on a probe-aberration-corrected FEI Titan STEM and image-corrected FEI environmental transmission electron microscope (ETEM) at 300 kV. The image intensity of each atomic column reflects the related average atomic number ($\sim Z^{1.5}$ to $Z^{1.8}$) [31], enabling us to visually observe the atomic level structural characteristics.

2.2. Electrochemical measurements

Electrochemical performance measurements were conducted using R2032 coin-type cells. The electrodes were prepared by casting a slurry containing 80% active material, 10% polyvinylidene fluoride binder (PVDF, Kureha L#1120), and 10% Super P onto an Al current collector foil. A typical loading of the electrodes was about $4\text{--}5 \text{ mg cm}^{-2}$. Thick electrodes with high areal capacity of 2.5 mAh cm^{-2} ($\sim 12 \text{ mg cm}^{-2}$) were also prepared, by coating a slurry mixture containing 92% active material, 4% PVDF, and 4% Super P binder onto Al foil. After drying, the electrodes were punched into disks with area of 1.27 cm^2 . Electrochemical cells were assembled with the cathodes as prepared,

Download English Version:

<https://daneshyari.com/en/article/7952571>

Download Persian Version:

<https://daneshyari.com/article/7952571>

[Daneshyari.com](https://daneshyari.com)