



# Long cycle life lithium ion battery with lithium nickel cobalt manganese oxide (NCM) cathode



Shuang Liu<sup>a,\*</sup>, L. Xiong<sup>b</sup>, C. He<sup>c</sup>

<sup>a</sup> University of Electronic Science and Technology of China, Chengdu 610054, China

<sup>b</sup> Paramount Sciences, Cleveland, OH 44111, USA

<sup>c</sup> Chengdu Yanbai Technology Co. Ltd., Chengdu 610054, China

## HIGHLIGHTS

- Characterized lithium ion batteries under extensive cycling (>3000 cycles).
- Achieved long cycle life (>3000 cycles) with  $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$  cathode.
- Importance of cathode composition and electrode design for long cycle life.
- Possible capacity fade mechanisms were discussed.

## ARTICLE INFO

### Article history:

Received 17 December 2013

Received in revised form

21 February 2014

Accepted 19 March 2014

Available online 26 March 2014

### Keywords:

Long cycle life

Lithium ion

Characterization

Lithium nickel cobalt manganese oxide cathode

## ABSTRACT

Lithium ion batteries with lithium nickel cobalt manganese oxide (NCM) cathode were characterized by extensive cycling (>2000 cycles), discharge rate test, hybrid pulse power characterization test (HPPC), and electrochemical impedance spectroscopy (EIS). The crystal structure, morphology and particle size of cathode materials were characterized by X-ray diffraction and scanning electron microscopy (SEM). It was demonstrated that the rate performance and cycle life of battery are closely related to the cathode material composition and electrode design. With proper selection of cathode composition and electrode design, the lithium ion battery cell achieved close to 3500 cycles with 85% capacity retention at 1C current.

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## 1. Introduction

Lithium ion batteries have drawn a lot of attention as one of the most promising power sources for electric vehicles (EV) or hybrid electric vehicles (HEV), and residential energy storage applications [1–3]. Unfortunately, the high energy density and cycle life requirements for these applications necessitate further improvement of the present lithium ion batteries. Electrode materials play an important role in achieving these requirements, and considerable efforts have been devoted to develop new cathode materials and new structured materials [4,5].

Lithium nickel cobalt manganese oxides (NCM),  $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ , are attractive alternative to  $\text{LiCoO}_2$  as cathode materials for lithium ion batteries due to their relative low cost, high capacity, and better thermal stability [6–10]. The capacity and

thermal stability of NCM strongly depend on composition, especially Ni content. Higher Ni content in NCM is responsible for higher reversible capacity because of the main redox species of Ni. However, high Ni content also leads to lower structural and thermal stabilities when NCM cathode is deeply charged, increasing the solid-electrolyte interfacial impedance. For instance, the  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  cathode has good thermal stability and delivers discharge capacities of 150–160  $\text{mAh g}^{-1}$  when charged to 4.3 V. However, the capacity of  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  is not sufficient for PHEVs application [10]. On the other hand, Ni rich NCM, such as  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  have been intensively investigated as positive electrode materials for EV applications because of their relatively high reversible capacity, about 200  $\text{mAh g}^{-1}$ . Unfortunately, they have shown poor thermal stability and poor cycle life. The thermal instability is due to oxygen release from the highly delithiated NCM, which reacts with the organic electrolyte and causes thermal runaway [11]. Meanwhile, the reduction of  $\text{Ni}^{4+}$  in the delithiated NCM to inactive NiO results in high solid-electrolyte interfacial

\* Corresponding author. Tel.: +86 83208687; fax: +86 83206481.

E-mail address: [shuangliu@uestc.edu.cn](mailto:shuangliu@uestc.edu.cn) (S. Liu).

impedance and poor cycle life of the cell [12]. The compromise between high capacity, cycle life, and thermal stability leads to the development of NCM in which the Ni content is between  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ . It was reported that introduction of stable tetravalent Mn in the layered  $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  reduces the interfacial impedance, leading to a significant improvement of cell cycle life and thermal stability [8].

The relative high energy density, good thermal stability and cycle life of NCM have made it a promising candidate for commercial applications. However, the characterization of NCM cathodes was mainly investigated in coin cells, where typically less than a few hundreds of cycles were conducted [13–16]. For applications such as EV/PHEV and stationary power application, the evaluation of full cells with extended cycle life test is desired. For instance, 5000 charge-depleting cycles and 15 years of calendar life are required for the PHEV application with 40-mile electric drive battery [17]. We present here the characterization of pouch cells with NCM cathode and graphite anode under extensive cycling (>2000 cycles). The effects of cathode composition and electrode design on cycle life were investigated. The possible capacity degradation mechanism was also discussed.

## 2. Experimental

All experiments were performed on lithium ion battery pouch cells that were assembled with lithium nickel cobalt manganese oxides (NCM) as cathode, synthetic graphite as anode, polyethylene as separator, and 1.15 M LiPF<sub>6</sub> in EC/EMC (1:3) as electrolyte. All electrode materials were purchased from commercial suppliers without modification. The cathodes consist of 92% active material, 4% conductive carbon black, and 4 wt% poly(vinylidene fluoride) (PVDF). The anodes consist of 85% active material, 8% conductive graphite, and 7% PVDF. The electrodes were obtained by mixing active materials, conductive additives, and PVDF in NMP, coating the slurry onto a current collect (Al for cathode, Cu for anode), drying the electrodes, and roll pressing to targeted thickness. The porosity of cathodes was kept constant (~30%). The electrodes were finally vacuum dried at 120 °C before cell assembly.

Electrochemical tests were conducted on Maccor testers. Five pouch cells were prepared for each test to ensure the reproducibility of the results. For discharge rate test, the pouch cells were charged at 0.5C rate to 4.2 V, kept at 4.2 V until current decreases to 0.05C (CC-CV protocol), and discharged at various C rates to 2.7 V. The cycling test was conducted at 1C current for both charge and discharge between 4.2 V and 3.0 V at 25 °C. The impedance change during cycles was monitored by electrochemical impedance spectroscopy (EIS), which was performed in the frequency range from 1 kHz to 50 mHz with ac amplitude of 10 mV. The pouch cells were also characterized by the application of the hybrid pulse power characterization (HPPC) test following the FreedomCAR battery test manual for plug-in hybrid vehicles [18].

XRD patterns were collected on a Phillips X-ray diffractometer with Cu K $\alpha$  radiation. Data were collected between 15° and 90° at a scan rate of 0.01°/s. The lattice constants a and c and the fraction of transition-metal atoms (assumed to be Ni) in the lithium layer were determined using Rietveld refinements with Reitica software. The morphology and composition of the cathode powders were also examined by scanning electron microscopy (SEM, Hitachi S-900) and energy dispersive spectroscopy (EDS) attached to the SEM.

## 3. Results and discussion

Fig. 1 shows the XRD patterns and Rietveld fit of two commercial NCM materials that were employed as cathodes. The two NCM cathode powders has atomic ratio of Ni, Co, Mn close to 50:20:30

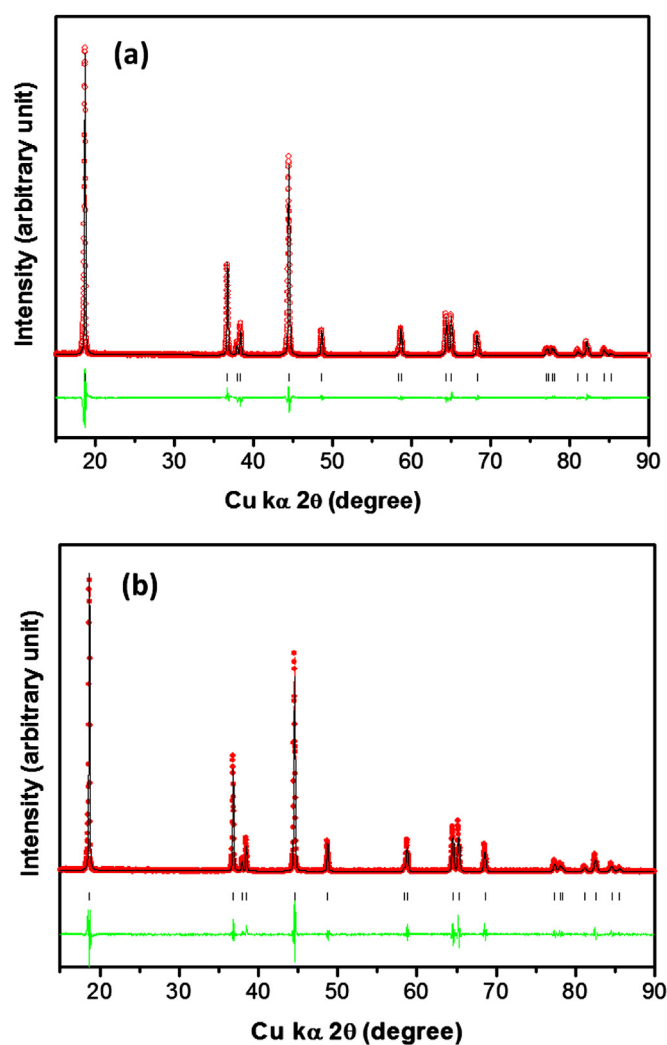


Fig. 1. XRD pattern and Rietveld refinement of cathode powders: (a) NCM523, (b) NCM433. Circles and lines correspond, respectively, to the observed and calculated intensities. The difference between the observed and calculated patterns and the peak positions corresponding to the O3 type phase are also shown.

and 40:30:30, respectively, according to EDS analysis (Table 1), and therefore is referred to as NCM523 and NCM433, respectively for simplicity. The XRD patterns of NCMs in Fig. 1 can be well fitted by the  $\alpha$ -NaFeO<sub>2</sub> structure with space group R-3m. The refined lattice constants and the fraction of transition-metal atoms in the lithium layer for the cathode samples were also listed in Table 1. For the refinements, it was supposed that Ni<sup>2+</sup> ions located with the 3b site can be exchanged with Li<sup>+</sup> occupied at the 3a site due to similarity of their ionic radii (Li<sup>+</sup> = 0.76 Å, Ni<sup>2+</sup> = 0.69 Å). The NCM433 exhibits lower degree of cation mixing and smaller lattice parameter compared to NCM523 (Table 1). The reduced degree of cation mixing is largely due to increased Co content, because Co<sup>3+</sup> has

Table 1  
Crystal structural parameters and compositions of cathode powders.

Cathode	Crystal structural parameters from XRD				Composition from EDS		
	a (Å)	c (Å)	Volume (Å <sup>3</sup> )	Cation mixing (%)	Ni (%)	Co (%)	Mn (%)
NCM 523	2.868	14.234	101.421	3.6	49.7	20.1	30.2
NCM 433	2.855	14.202	100.244	2.1	38.2	28.5	33.4

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