

Chemical Changes in $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Lithium-Ion-Battery Cathodes During Electrochemical Cycling

Hanshuo Liu,¹ Mark J.R. Dunham,² Kristopher J. Harris,²
Jian Liu,³ Xifei Li,³ Xueliang Sun,³ Meng Jiang,⁴ Yan
Wu,⁴ Gillian R. Goward,² and Gianluigi A. Botton¹

¹*Dept. of Materials Science and Engineering, and
²Dept. of Chemistry, McMaster University, 1280 Main St.
W. Hamilton, ON, L8S 4M1 Canada*

³*Dept. of Mechanical and Materials Engineering,
Western University, London, Ontario, N6A 5B9*

⁴*GM R&D Center, Chemical and Materials Systems Lab,
30500 Mound Rd, Warren, MI 48090, USA*

Increased use of lithium ion batteries in hybrid electric vehicles and other automotive applications has driven the need for batteries which are capable of high discharge rates and long cycling lifetimes. The necessity of high ion mobility without loss of structural integrity places stringent demands on the crystalline structures of cathodes.¹ Detailed understanding of the modes of structural breakdown in cathode materials is of paramount importance to the design of better battery materials.

$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, NMC, is well known as a promising cathode material because of its high capacity (190-220 mAh g⁻¹), excellent charge-discharge efficiency of 99% and an almost zero volume change under cycling with 2/3 lithium extraction.² However, it suffers from transition metal diffusion: both Mn²⁺ diffusion into the electrolyte and Ni²⁺ diffusion into the Li layer. These structural instabilities play an important role in reducing the lifetime of NMC cells.²

In order to understand, and ultimately improve, the electrochemical performance of such materials, it is important to study NMC materials using a range of characterization techniques. In this work we therefore provide a detailed structural characterization using scanning and transmission electron microscopy (SEM and TEM) as well as nuclear magnetic resonance (NMR) methods. The morphology of the NMC-based cathode material (Figure 1) is complex with agglomeration of elongated particles, approximately 0.1 μm in size, forming 10 μm size clusters when deposited on a cathode substrate. The distribution of such particles is, however, not uniform

over the cathode (Fig. 1). Given the size of the particles, further studies with TEM have been carried out. Using electron energy loss spectroscopy in the TEM, we have been able to identify the valence of Ni, Mn, and Co in this compound and study the evolution of valence and structure of NMC following electrochemical cycling.

Further complementary information on the Li atoms, however, needs to be obtained to fully understand the charge and discharge process. The low atomic mass of Li makes it challenging to study with X-ray methods. However, ⁷Li and ⁶Li are highly receptive nuclei in NMR spectroscopy. Solid-state NMR can be effectively employed to elucidate the position and distribution of Li atoms, as well as to evaluate energy barriers involved in Li ion mobility.³ We have previously shown that solid-state NMR provides unique insight into the modes of disorder in pristine NMC.⁴ Here, we extend these methods of ultra-fast sample spinning at low applied magnetic fields to study changes in NMC-based cathodes under electrochemical cycling. The state of the cathode at various points in the electrochemical cycle provides a detailed picture of the charge/discharge process and should provide insight into the capacity change of NMC over time.

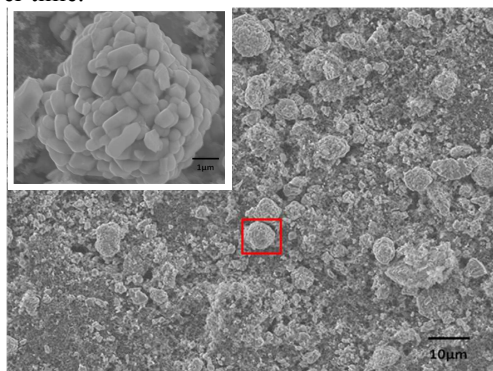


Figure 1 SEM micrographs of NMC-based cathode; insert is a detailed image of the red-highlighted area.

References:

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