



# Revealing the mitigation of intrinsic structure transformation and oxygen evolution in a layered $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ cathode using restricted charging protocols



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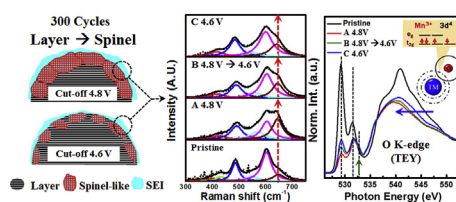
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## HIGHLIGHTS

- The structural evolution of layered Li-rich cathode during cycling is studied.
- Long-term galvanostatic charging/discharging up to 300 cycles is investigated.
- Superior capacity retention of 91.6% is achieved by restricted cycling protocol.
- Mitigated intrinsic structure decline is shown by soft XAS and Raman studies.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Li-rich cathode materials have attracted substantial attention because of their high energy density, but they still suffer from structural instability and voltage decay in cycling. Herein, a dynamic observation of the initial structural conversion and transformation is achieved by *in situ* Raman spectroscopy, and the effect of cut-off voltage on the intrinsic structure transformation is investigated by the using of three strategic charging protocols. The clear peak evolution related to the post-discharge spinel transformation is found that more obvious for the higher cut-off (4.8 V) protocol than for the lower cut-off (4.6 V) one after 300 cycles. In soft X-ray absorption spectroscopy, as demonstrated by the Mn L-edge spectra, more surface spinel-like  $\text{Li}_{1-x}\text{MnO}_{2-\delta}$  ( $\text{Mn}^{3+}$ ) structure is formed as the cycle number and cut-off voltage increased, whereas the Ni L-edge spectra exhibited the same features throughout the cycling. The significant variations in the O K-edge also provide evidence distinguishing the structure transformation from the surface to the bulk material and the change in the lower cut-off protocol. Such spectroscopic analysis clearly confirm how the protocol control with an overall restricted charge cut-off voltage of 4.6 V significantly reduces the adverse effects of cycling on the oxygen plateau of the  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  cathode.

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## 1. Introduction

With the rapid increase in consumer demand for mobile devices, portable electronic products, and electric vehicles, high-energy secondary Li-ion batteries (LIBs) with long cycle lives and good power performance are needed in the current and near-future markets. A series of Li-rich cathode materials with the  $\alpha$ -NaFeO<sub>2</sub>-type layered structure composed of LiMO<sub>2</sub> (space group  $R\bar{3}m$ ) and Li<sub>2</sub>MO<sub>3</sub> (space group  $C2/m$ ) phases (M = Ni, Co, Mn, etc.) were created [1–3] that can be expressed using the solid solution notation—Li[Ni<sub>x</sub>Li<sub>(1-2x)/3</sub>Mn<sub>(2-x)/3</sub>]O<sub>2</sub> ( $0 \leq x \leq 0.5$ ) [4] or composite notation—xLi<sub>2</sub>MnO<sub>3</sub>·(1-x)LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> [5,6]. Li-rich cathode materials with layered structures have attracted significant attention and represent some of the most promising candidates for high-energy rechargeable LIBs because of their high reversible capacities (>250 mAh g<sup>-1</sup>) and potential windows (>4.2 V vs Li/Li<sup>+</sup>) relative to those of conventional cathode materials, such as LiCoO<sub>2</sub>, LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, LiFePO<sub>4</sub>, and LiMn<sub>2</sub>O<sub>4</sub> [7–12]. However, some significant challenges still limit their cycle lives and commercial applications, including structural instability, voltage fading, and long-term cycling decay. During the initial charging process, the activation of Li<sub>2</sub>MnO<sub>3</sub> contributes to an anomalous charge capacity (>300 mAh g<sup>-1</sup>) via extraction of the excess Li ions concomitant with the unconventional participation of the oxygen anion in the redox reaction; as a result, a characteristic extended voltage plateau of 4.4 V–4.8 V can be observed [13–17]. In the end-of-plateau region for Li<sub>2</sub>MnO<sub>3</sub> activation, a large amount of oxygen vacancies are formed by oxygen loss, inducing the migration of transition metal (TM) ions and resulting in remarkable structural reorganization. Meanwhile, the activation of oxygen causes electrolyte degradation and irreversible chemical reactions on the electrode/electrolyte interface [17–21]. Because of this structural reorganization and the lattice instability, the structural transformation of the layered structure to a defect-spinel structure is initiated from the surface region during the charge/discharge process. This transformation leads to deterioration of the surface structure and gradual voltage fading during cycling, and the average voltage fade over several cycles leads to a severe drop in the energy density [22–28]. The extensive side reactions between the extracted oxygen species and the decomposed electrolyte give rise to the continuous accumulation of a thick surface electrolyte interphase (SEI) layer on the electrode surface [29]. The acidic byproducts (e.g., HF) attack the electrode surface and cause surface damage and Mn dissolution, resulting in rapid impedance rise and drastic capacity loss [30–32]. Direct observation of the Li-rich cathode surface during electrochemical cycling would facilitate clarifying the surface degradation mechanisms involved in the structural transformation and interfacial reactions. Recently, Raman spectroscopy and soft X-ray absorption spectroscopy (XAS) have been determined to be effective tools for investigating the mechanisms underlying the local structural transformation and electronic structural changes [33–37]. Indeed, soft XAS can be used to elucidate each element's role during the structural transformation because the total electron yield (TEY) mode is surface sensitive (within ~5 nm), whereas the fluorescence yield (FY) mode is suitable for probing the bulk material (~more than 300 nm) [36,38]. In contrast, Raman spectroscopy is sensitive to the structural symmetry of metal oxides and can be used to probe the atomic arrangement in terms of the specific vibrational modes [39,40]. These techniques are useful for studying the structural changes in cycled electrodes. Previously, Hy et al. reported evidence of the differences between surface and bulk structural changes in the first cycle and observed the migration of transition metals from the surface to the bulk when the voltage reaches the oxygen plateau region of 4.55 V and the growth of the characteristic spinel structure during cycles using soft XAS and

Raman spectroscopy [26]. Oishi et al. investigated the charge compensation process of TM and oxygen ions and obtained evidence of reversible peroxide phase formation in charged/discharged states using soft XAS spectroscopy [35]. Although the evolution of the layered-to-spinel structural transformation and the electronic structure during the charge/discharge process of Li-rich cathodes have been characterized in the literature [37,41,42], studies of crystal structure decline and the related electronic structure evolution after 200 cycles using various cycling protocols remain rare. The application of a suitable cycling strategy would contribute to mitigating the structural transformation and decelerating the performance decay during long-term cycling [43,44].

In this study, we perform a spectral study to investigate the variation in the structural decline and electronic structure transformation of a Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> Li-rich layered cathode using cycling protocols with restricted charge cut-off voltages. The dynamic observation of the structural conversion and layered-to-spinel structural transformation of a Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> cathode during the first complete charge/discharge process (open-circuit voltage [OCV]—4.8 V—2.5 V) was achieved by *in situ* Raman spectra. Additionally, the long-term galvanostatic charging/discharging (300 cycles) of a Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> Li-rich cathode was performed to elucidate the differences in the structural transformation using three strategic cycling protocols. The soft XAS spectra and Raman studies after extended cycling provide direct information about the local structural decline and electronic structural variation in the electrode that occurred as the cycle number increased.

## 2. Experimental section

### 2.1. Synthesis of the Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> cathode material

The Li-rich cathode materials (Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub>) synthesized by a modified solid-state reaction route were supplied by Advanced Lithium Electrochemistry (Cayman) Co., Ltd. (Taoyuan, Taiwan). Stoichiometric amounts of Li<sub>2</sub>CO<sub>3</sub>, Mn<sub>2</sub>O<sub>4</sub>, and NiCO<sub>3</sub> (mole ratio of 3:1:1) were stirred and ball-milled in aqueous solution (500 ml) to obtain a well-mixed precursor solution, and then fed into a spray dryer. The micron-sized spherical precursor powder was produced by the spray drying process at 200 °C. Next, the precursor powder was placed into a furnace to pre-calcine at 650 °C for 5 h, followed by calcination at 900 °C for 10 h under the air atmosphere with a heating rate of 2 °C/min. The powder was then quenched to room temperature to obtain the final Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> powder.

### 2.2. Characterization

The phase purity of the as-synthesized Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> material was confirmed by X-ray powder diffraction (XRD) using a Bruker D2 phaser diffractometer equipped with a Cu K $\alpha$  radiation source and a LynxEye detector. Scanning electron microscopy (SEM, JEOL, JSM 6500) was conducted to observe the surface morphologies and particle sizes of the synthesized powders. The structural characterization was performed with Raman micro-spectroscopy (ProMaker System) utilizing a green-light laser with an excitation wavelength of 532 nm, and the power was set to 2 mW to avoid degradation with 10 s exposure times and 10 accumulations [31,45]. The attenuation depth of Raman probing for Li-rich electrode is estimated about ~200 nm [39,46]. *In situ* Raman spectra of the Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> cathode were collected during charging and discharging using an Autolab potentiostat operating galvanostatically over the voltage range of 4.8 V—2.5 V at a rate of 0.1 C. Upon the expected voltage, the voltage was held for several minutes to observe the structural evolution. A 2032-type coin cell was assembled inside Ar-filled glovebox with O<sub>2</sub> and H<sub>2</sub>O level lower

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