Short communication

Unconventional irreversible structural changes in a high-voltage Li–Mn-rich oxide for lithium-ion battery cathodes

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HIGHLIGHTS

- Irreversible phase transformation in a high-voltage Li–Mn-rich oxide is demonstrated.
- Magnetization technique is employed to ascertain the major spinel phase.
- A spin-glass type transition is observed, indicating a dominant $LiMn_2O_4$ type spinel.
- Irreversible phase transformation leads to voltage and/or capacity fading.

GRAPHICAL ABSTRACT
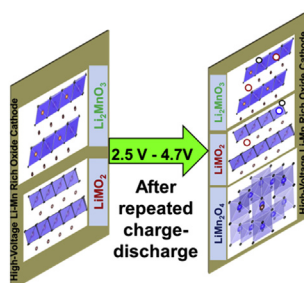
ABSTRACT

Making *all*-electric vehicles (EVs) commonplace in transportation applications will require affordable high-power and high-energy-density lithium-ion batteries (LIBs). The quest for suitable cathode materials to meet this end has currently plateaued with the discovery of high-voltage ($\geq$4.7 V vs. Li$^+$), high capacity (~250 mAh/g) lithium–manganese-rich (LMR) layered composite oxides. Despite the promise of LMR oxides in high-energy-density LIBs, an irreversible structural change has been identified in this work that is governed by the formation of a 'permanent' spin-glass type magnetically frustrated phase indicating a dominant AB_2O_4 (A = Li, B = Mn) type spinel after a short-term lithium deintercalation (charging) and intercalation (discharging) process. Furthermore, reduction of transition metal (Mn) ions from the 4+ state (pristine LMR) to 3+ (cycled LMR), which alters the intercalation redox chemistry and suggests the presence of 'unfilled' lithium vacancies and/or oxygen vacancies in the lattice after cycling, has presented a major stumbling block. These situations result in both loss of capacity and fading of the voltage profile, and these combined effects significantly reduce the high energy density over even short-term cycling.

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1. Introduction

Today's energy storage devices in EVs require advanced high power and high-energy-density lithium-ion batteries (LIBs) [1–3]. LIB energy density is directly proportional to specific capacity and average operating voltage (energy density = specific

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capacity × average operating voltage). Lithium-containing layered metal oxide (ex: $LiMO_2$; M = Ni, Mn, Co or NMC) materials are the state-of-the-art commercial cathode materials in current LIBs. These layered oxides have tremendous capabilities for facile lithium (de)intercalation reactions [4,5]. The charge and discharge processes in a LIB involve deintercalation and intercalation of lithium ions from and to the cathode structure, respectively [6]. Therefore, maintaining the original oxide structure through the repeated charge−discharge cycles is a vital to long-term performance. Current state-of-the-art cathode nickel-−manganese−cobalt (NMC) oxides (such as $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) maintain the original host structure without undergoing alteration after several charge−discharge cycles. Unfortunately, these oxides are limited in energy density because of lower operating voltages (~4.2 V) and lower practical capacity (~160 mAh/g) [7]. However, adding an excess of lithium in place of transition metals (M) in the NMC oxide maintains the layered structure and dramatically increases the capacity and operating voltage [8–12]. For instance, with 20% excess lithium and a stoichiometrically proportionate increase in Mn to $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ (in this study), a remarkable reversible capacity of 250 mAh/g can be achieved at high operating voltage (~4.7 V) [13,14]. These lithium−manganese-rich (LMR) layered oxides are promising cathode candidates for high voltage, high capacity (high-energy-density) LIBs for EV applications, but they are hampered by a layered-to-spinel structural degradation during cycling [15−19].

Here we present that despite these excellent beginning-of-life properties, LMR oxides undergo an unconventional 'irreversible' structural change after minimal numbers of charge−discharge cycles (25 in this study) that severely degrade performance by blocking the ion transport pathways in the oxide lattice. In this study, our inquisition is focused on answering these important questions; i) Is this structural change irreversible? ii) How do these irreversible structural and electronic changes occur? iii) What is the dominant 'spinel' phase formed after structural changes? iv) What is the impact of these irreversible structural changes on the lithium-ion transport phenomena? In order to obtain fundamental insight into these irreversible structural changes, we executed temperature-dependent magnetic susceptibility combined with selected area electron diffraction (SAED) on LMR oxides harvested from *full LIB pouch cells* at different states of charge (SOCs) during early (second) cycle and after short-term (25) cycles (see S1 in ESI). The motivation behind employing the magnetic susceptibility technique [20] was to take advantage of its sensitivity in detecting subtle structural changes, as well as the electronic states of transition metal (M) ions, as compared to other conventional techniques such as diffraction and its ability to distinguish the crystal structure of different types of spinel compound such as tetragonal spinel and cubic spinel.

2. Experimental

The LMR oxide powder used in this study was synthesized by TODA America, Inc., (alternate name:HE5050) and the composition, *ex and in situ* XRD, particle morphology, selected area electron diffraction (SAED), high-resolution transmission electron microscopy (HR-TEM) images, and electrochemical performance data can be found in earlier report [16]. LMR electrode and pouch cell fabrication was reported previously [21]. All full cells (with ConocoPhillips A12 graphite anodes) underwent formation cycling following a procedure reported elsewhere [13] and were cycled between 2.5 and 4.7 V for 26 cycles at a rate of 20 mA/g. Cathode samples were collected at different SOCs (3.2, 3.5, 4.1, and 4.5 V) during the second and 26th charge−discharge cycles. All pouch cells were disassembled in an argon-containing glove box, washed

with dimethyl carbonate (DMC), and dried for several hours in the glove box. Cycled LMR oxide powder materials were removed from the Al current collectors after being dried for selected area electron diffraction (SAED) experiments. For temperature dependent magnetic susceptibility experiments, half-inch diameter specimens were punched from the cycled LMR oxide electrodes. These specimens contained LMR active oxides, PVDF binder, carbon black, and Al foil. A Quantum Design Magnetic Property Measurement System was used to measure the DC magnetization of the specimens. Each sample was first cooled to 5 K in zero field (zero-field cooling mode, represented as ZFC). Then a field of 100 Oe was applied, and data were collected from $T = 5$ K−300 K. The samples were also cooled in the applied field from 300 K down to 5 K while magnetization was measured (field cooling, represented as FC). The experimental effective magnetic moment was obtained from a linear fit of the plot of inverse molar magnetic susceptibility vs. temperature between 150 and 300 K using the Curie−Weiss equation $\chi_m = C_m(T - \theta)$, where χ_m is the molar magnetic susceptibility, C_m is the Curie constant, and θ is the Curie−Weiss temperature. For SAED experiments, the harvested cycled powder was dispersed in ethanol and few drops of the solution were added to a holey Cu grid. A Hitachi HF3300 TEM at 300 kV was used to collect SAED patterns.

3. Results and discussion

The structure of $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ (LMR here onward) oxide is a composite of layered $xLiMO_2$ (Phase I) and layered $(1 − x)$ Li_2MnO_3 (Phase II)composition ($x = 0.5$ in this study). $LiMO_2$ attains a typical α-$NaFeO_2$ type structure having a trigonal lattice, where the transition metal (M; Co, Mn, Ni) ions are freely occupied in octahedral metal sites, so magnetic moments are non-interacting and are not aligned in a regular pattern (randomly oriented) such that Curie−Weiss (CW) paramagnetic behavior (Fig. 1 and Fig. 2e) is expected. The excess lithium ions present in the LMR structure occupy the M layer, filling all the octahedral sites of cubic close-packed (*ccp*) oxygen arrays. The presence of lithium ions in the M
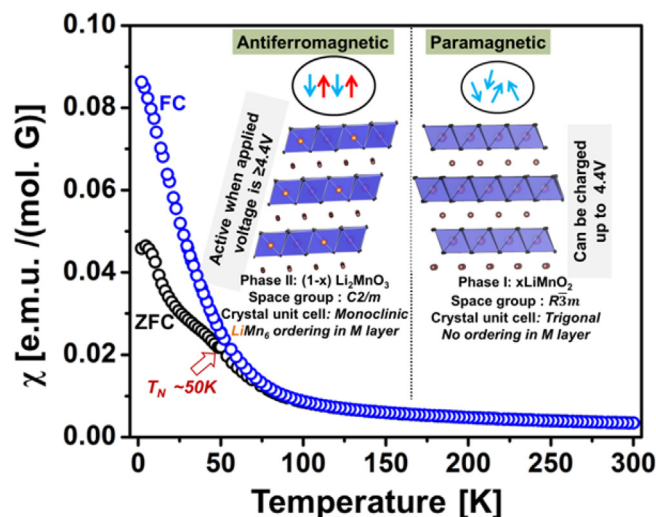

Fig. 1. Temperature dependent magnetic susceptibility data from pristine LMR oxide at field cooling (FC) and zero field cooling (ZFC) modes. At higher temperature paramagnetic nature is observed indicating presence of trigonal $LiMO_2$ lattice (Phase I) and at low temperature antiferromagnetic transition occurs at T_N ~ 50 K indicating a second monoclinic Li_2MnO_3 phase (Phase II) where lithium is present in the M layer ($LiMn_6$ ordering) in pristine LMR oxide. Lithium intercalation from Phase II occurs beyond 4.4 V charging. Adapted (modified) with permission from *Chem. Mater.*, 2013, 25 (20), pp 4064−4070. Copyright 2013 American Chemical Society [23].