From $LiMn_2O_4$ to Partially-Disordered Li_2MnNiO_4: The Evolution of Lithiated-Spinel Cathodes for Li-ion Batteries

Michael M. Thackeray, Eungje Lee, Boyu Shi and Jason R. Croy

Chemical Sciences and Engineering Division, Argonne National Laboratory,
Lemont, Illinois 60439, USA

Abstract

This personal narrative chronicles the discovery in 1981 of LiM_2O_4 spinel electrodes (where M = one or more metal cations) for lithium batteries by the Goodenough group at Oxford University, UK and the subsequent evolution of lithiated-spinel $Li_2M_2O_4$ (or $LiMO_2$) materials such as $Li_2Co_2O_4$, $Li_2Co_{2-2x}Ni_{2x}O_4$, $Li_2Co_{2-2x}Al_{2-2x}O_4$ and Li_2MnNiO_4 at the CSIR, South Africa and Argonne National Laboratory, USA. The competition between layered and lithiated-spinel $LiMO_2$ formation at 400 °C, and the opportunity to strategically design structurally integrated, high-capacity cathodes with partially disordered structures is highlighted. The paper is written in honor of John Goodenough's 100^{th} birthday.

Introduction

The impact of the discovery of the spinel, $LiMn_2O_4$, as an insertion electrode for lithium batteries by the Goodenough group at the Inorganic Chemistry Laboratory, Oxford University in 1981/82 influenced subsequent research on spinel-related materials at the Council for Scientific and Industrial Research in South Africa (1983-1993) and at Argonne National Laboratory in the United States (1994-). These advances in knowledge were documented recently in a review as a tribute to John Goodenough as recipient of the 2019 Nobel Prize in Chemistry [1]. This paper builds on the review, and highlights further advances that have recently been made to exploit lithiated-spinel compositions with partially-disordered configurations, such as Li_2MnNiO_4, in order to increase the operational capacity and the energy density of a Li-ion cell, instead of using stoichiometric spinel cathodes such as $Li_{1-x}Mn_2O_4$ and $Li_{1-x}Mn_{1.5}Ni_{0.5}O_4$. The message emphasizes the possibility and importance of controlling and exploiting structural relationships in integrated and disordered lithium-metal-oxide cathode systems, particularly those with spinel, lithiated-spinel and layered components that contain Mn, Ni and Co.

The Evolution of Spinel and Lithiated-Spinel Electrodes

The early days: layered $LiCoO_2$ and spinel $LiMn_2O_4$

In 1981, a year after Goodenough's seminal announcement of layered $LiCoO_2$ as a cathode for a rechargeable 4 V lithium cell [2], and ten years before the commercialization of the first $C/LiCoO_2$ Li-ion cell by Sony Corporation, his team at Oxford University (Goodenough, Thackeray, David, Bruce) discovered that spinel oxides, such as Fe_3O_4 and Mn_3O_4, with the

general formula $A[B_2]O_4$, in which the A and B cations occupy in tetrahedral and octahedral sites, respectively, could accommodate one lithium ion per formula unit without disturbing the $[B_2]O_4$ spinel framework [3,4]. During these lithiation reactions, the A cations are displaced into neighboring empty octahedral sites, while the inserted Li ions occupy the remaining octahedral sites to generate partially-ordered rock salt structures with lithiated-spinel configurations $LiFe[Fe_2]O_4$ and $LiMn[Mn_2]O_4$. These insertion reactions are inherently irreversible because there are no energetically-favorable pathways in the discharged $LiFe_3O_4$ and $LiMn_3O_4$ cathodes to facilitate fast lithium-ion diffusion during charge when lithium is extracted from the structure. The solution to this dilemma was to replace the A-site manganese cations in Mn_3O_4 with lithium to yield $Li[Mn_2]O_4$, in which the interstitial space of the $[Mn_2]O_4$ spinel framework provides a three-dimensional network of face-sharing tetrahedra and octahedra for lithium ion diffusion during both discharge and charge. This discovery led to the general concept of using the $[B_2]O_4$ spinel framework as an anode or a cathode for a lithium cell in which the voltage of the lithium/spinel cell could be tuned by selection of the B cations. For example, the lithium titanate spinel, $LiTi_2O_4$, accommodates lithium at a potential of ~1.5 V vs. metallic lithium whereas $LiMn_2O_4$ accommodates lithium at 3 V [5-7].

Lithium insertion into cubic $Li[Mn_2]O_4$ (space group Fd-3m) at 3 V yields the lithiated-spinel structure, $Li_2[Mn]_2O_4$ [4]. The reaction fully reduces the manganese ions in the $[Mn]_2O_4$ spinel framework to the trivalent state, inducing a damaging Jahn-Teller distortion and a reduction of crystal symmetry to tetragonal symmetry ($F4_1/ddm$). In $Li_2^{+}[Mn_2^{3+}]O_4$, the *c/a* axial ratio of the unit cell, 1.16, represents a 16% expansion along the *c* direction, as it also is in the tetragonal spinel, Mn_3O_4 ($Mn^{2+}[Mn_2^{3+}]O_4$). The structural damage that occurs on cycling the cell over this compositional range harms the reversibility of the reaction, thereby inhibiting the commercial use of 3 V $Li/Li_{1+x}Mn_2O_4$ ($0 \le x \le 1$) spinel cells and batteries.

Electrochemical extraction of lithium from $LiMn_2O_4$ was first demonstrated in 1983 by the Thackeray team at the Council for Scientific and Industrial Research (CSIR) in South Africa [8]. In this case, extraction and reinsertion of lithium occurs at ~4 V vs. metallic lithium while maintaining cubic symmetry. Despite capacity loss effects due to manganese dissolution, cation-stabilized $LiMn_{2-x}M_xO_4$ (LMO) spinel cathodes ($M=Li^{+}$, Ni^{2+}, Al^{3+}) have played a small, yet significant role in high-power Li-ion batteries relative to higher capacity layered analogues, such as $LiCoO_2$ (LCO), $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $LiNi_{1-y-z}Mn_yCo_xO_2$ (NMC) systems [6].

The spinels $Li_4Ti_5O_{12}$ and $LiMn_{1.5}Ni_{0.5}O_4$

The electrochemical properties of the lithium titanate spinel, $Li_4Ti_5O_{12}$ (LTO) when used as a cathode in rechargeable $Li/Li_4Ti_5O_{12}$ cells, were first reported in 1989 by Colbow et al. at the University of British Columbia, Canada [9]. In the early 1990's, after the concept of a rocking chair 'Li-ion' battery had been introduced by Sony Corporation and CSIR's earlier spinel-anode/spinel-cathode patent [5], $Li_4Ti_5O_{12}$ was proposed, almost simultaneously by Matsushita in Japan and CSIR as a Li-ion battery anode when coupled to a high-potential cathode material

[7]. Since then, $Li_4Ti_5O_{12}$, which operates as a 'zero-strain' electrode with minimal volume change during charge and discharge [10], has been coupled with various cathode materials (with spinel, layered and olivine structures) to yield Li-ion battery products with voltages that range between 2.0 and 3.2 V [7].

All Li-ion cells are assembled in a safe, discharged state in which the anode, such as graphite and $Li_4Ti_5O_{12}$, and the cathode, such as layered $LiCoO_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiNi_{1-y-z}Mn_yCo_xO_2$, the spinels $LiMn_{2-x}M_xO_4$ and $LiMn_{1.5}Ni_{0.5}O_4$, (LMNO-sp) and olivine $LiFePO_4$ (LFP) are stable materials that are prepared at elevated temperatures. In practice, $LiMn_{2-x}M_xO_4$ and $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathodes offer only one half of their theoretical electrochemical capacity (<150 mAh/g) because their fully lithiated (discharged) compositions, namely $Li_2Mn_{2-x}M_xO_4$ and $Li_2Mn_{1.5}Ni_{0.5}O_4$ respectively, have crystallographically-distorted, lithiated-spinel $LiMO_2$ structures. These materials are unstable in air and are also difficult to prepare, requiring unconventional and costly synthesis techniques; the same is true for the lithiated-spinel $Li_7Ti_5O_{12}$, which represents a fully charged anode. Furthermore, lithium insertion into $LiMn_{2-x}M_xO_4$ and $LiMn_{1.5}Ni_{0.5}O_4$ cathodes occurs at 3 V, i.e., at a substantially lower voltage than lithium extraction at 4.1 and 4.7 V, respectively, thereby complicating the electronic control and delivery of energy and power from Li-ion cells over an extended voltage range [4,11-13]. In contrast, lithium insertion and extraction reactions with layered $LiMO_2$ cathodes, notably Ni-rich $LiNi_{1-y-z}Mn_yCo_xO_2$ (NMC) materials, tend to provide Li-ion cells with gradually sloping voltage profiles, typically between 4.3 and 3.0 V, yielding significantly higher capacities that approach or exceed 200 mAh/g [14].

Lithiated spinels LT-$LiCoO_2$ and LT-$LiCo_{1-x}Ni_xO_2$ ($0<x<0.2$)

In 1989/90, Nohma et al. at Sanyo Corporation, Japan, reported a 'composite-dimensional-manganese-oxide' cathode, Li_xMnO_y, that contains uni-dimensional and two-dimensional pathways for lithium-ion transport [15,16]. When prepared at a relatively low temperature (LT) of 375 °C, a CDMO electrode with a Li:Li+Mn ratio between 0.3 and 0.5 works well in 3 V lithium cells. In 1992, following this synthesis approach at the CSIR, Gummow et al. initially reported that LT-$LiCoO_2$, when synthesized at 400 °C, yielded a slightly disordered layered structure in which the oxygen ions were essentially cubic-close packed (*c/a*=4.91) [17] in stark contrast to Goodenough's layered, high-temperature analogue (HT-$LiCoO_2$, 850-900 °C) with trigonal symmetry (R-3m, *c/a*=4.99), which deviates substantially from ideal cubic-close-packing (*c/a*=4.90) [18]. While approximately one-half of the Li^+ ions can be extracted from HT-$LiCoO_2$ between 3.0 and 4.3 V, Gummow et al. showed that Li is extracted electrochemically from LT-$LiCoO_2$ at a constant 3.6 V, and that a chemically-delithiated sample, LT-$Li_{0.5}CoO_2$, has strong, spinel-like features [18]. Subsequent analyses of LT-$LiCoO_2$ by Gummow et al. [19] and Rossen et al. at Simon Fraser University, Canada [20] confirmed that the LT-$LiCoO_2$ had an atomic configuration that was more lithiated-spinel-like, rather than layered-like, in character.

In clarifying the structure of LT-$LiCoO_2$, Rossen et al. recognized a remarkable structural anomaly that would exist between layered and lithated-spinel $LiCoO_2$ materials *but only if*

both structure types were ideally cubic-close-packed, i.e., with a *c/a* ratio of 4.90 [20]. In such a hypothetical situation, the layered and lithated-spinel configurations in $LiCoO_2$ would have exactly the same atomic environments, thereby yielding identical powder X-ray diffraction patterns and making it impossible to distinguish one structure type from the other (Figure 1); it also explained Gummow et al.'s initial interpretation that LT-$LiCoO_2$ had a disordered, layered structure. In this instance, note that the *a* lattice parameter of the cubic lithiated-spinel LT-$LiCoO_2$ structure (8.000 Å [20]) would correspond to *a* and *c* lattice parameters of 2.828 Å and 13.856 Å, respectively, in an ideal cubic-close-packed, layered structure with trigonal symmetry, R-3m (*c/a*=4.90). In practice, a single-phase, lithiated-spinel $LiCoO_2$ product is difficult to prepare at 400 °C; it often contains a minor amount of layered $LiCoO_2$, which is challenging to quantify and qualify. In such an instance, structural refinement with powder X-ray diffraction data would yield a cation distribution that is intermediate between the two structure types. Nevertheless, these two components can be readily identified from one another by other techniques, for example, by high-resolution transmission electron microscopy or by their significantly different electrochemical profiles.

In subsequent work at the CSIR, Gummow et al. demonstrated that by substituting 10-20% of the cobalt ions by nickel it was possible to counter the formation of the layered component and to produce a single-phase, lithiated-spinel product, LT-$LiCo_{1-x}Ni_xO_2$ ($0<x<0.2$) [21]. However, both LT-$LiCoO_2$ and LT-$LiCo_{1-x}Ni_xO_2$ electrodes were unstable to electrochemical cycling, so interest in these materials waned.

Lithiated-spinel stabilizers for high capacity Li- and Mn-rich $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M=Ni, Mn, Co) electrodes

The discovery in the early 2000s that Li- and Mn-rich layered electrodes could provide an anomalously high capacity of 250 mAh/g or more, if charged to a high potential (>4.5 V vs. Li), heralded the start of an intense international effort to develop a low cost, Mn-rich cathode for the Li-ion battery industry [22]. It is now generally accepted that these materials can be described as having a complex intergrown structure comprising two layered components, formulated $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M = Ni, Mn and Co), rather than the generalized, layered designation $Li_{1+x}M_{1-x}O_2$ [23]. Unfortunately, these Li- and Mn-rich electrodes suffer from hysteresis, voltage fade and impedance rise during cycling, thereby reducing energy and power output and inhibiting their entry into the Li-ion battery market [24,25]. Slight improvements in performance have been achieved by adding a third, spinel component to the composite structure [26], with evidence that the spinel component likely acts predominantly as a stabilizer at the electrode surface [27].

High capacity $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes in their fully discharged state have two integrated layered components, each of which has a rock salt stoichiometry. It stands to reason, therefore, that it would be beneficial to use a lithiated spinel, such as LT-$LiCoO_2$ or LT-$LiCo_{1-x}Ni_xO_2$ ($0<x<0.2$) described above, which also has a rock salt stoichiometry, to stabilize the bulk structure of 'layered-layered' $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes, and to use a stoichiometric spinel component to stabilize the surface. This approach is currently being

pursued at Argonne National Laboratory to engineer stabilized Mn-rich oxide electrode structures for the Li-ion battery industry. To this end, in 2016, Lee et al. repeated Gummow et al.'s experiments on LT-$LiCoO_2$ or LT-$LiCo_{1-x}Ni_xO_2$ ($0<x<0.2$) to confirm their data [28]. Subsequent research at Argonne opened the door to the discovery of several new lithiated-spinel compositions, while also revealing the impact of partial disorder and the structural-integration of layered and lithiated-spinel components on electrochemical behavior, as described in the next two sections.

Lithiated-spinel LT-$LiCo_{1-x}Al_xO_2$

Although partial substitution of nickel for cobalt in LT-$LiCo_{1-x}Ni_xO_2$ suppresses the formation of a layered component and yields a single-phase, lithiated-spinel product, it does not overcome the electrochemical instability and capacity loss of the electrode on repeated cycling [28]. Therefore, instead of using an electrochemically-active ion, such as Ni^{3+}, as a stabilizing agent, Lee et al. probed electrochemically-inactive ions, such as Al^{3+} and Ga^{3+}, as alternative substituents to nickel. This approach had a profound effect on the structural and electrochemical properties of lithiated-spinel electrodes, notably those in the LT-$LiCo_{1-x}Al_xO_2$ system [29]:

1. Exchange of Co^{3+} by Al^{3+} occurs over a wide compositional range, $0<x\leq0.3$, during which the LT-$LiCo_{1-x}Al_xO_2$ structure maintains cubic symmetry;
2. Lithium extraction and reinsertion reactions occur with virtually no change to the unit cell parameter and volume; LT-$LiCo_{1-x}Al_xO_2$ is the best 'zero-strain' cathode reported to date. For x=0.15, the unit cell volume expands and contracts by only 0.02%, i.e., a 10-fold reduction in the volume change observed in a 'zero-strain' $Li_4Ti_5O_{12}$ anode [29]; A $Li_4Ti_5O_{12}$/LT-$LiCo_{1-x}Al_xO_2$ couple therefore constitutes a 'zero-strain' 2.1 V spinel/lithiated-spinel cell, which augurs well for the viable development of an all-solid-state battery system.
3. Lithiated-spinel structures in the system LT-$LiCo_{1-x}Al_xO_2$ (space group Fd-3m) are slightly disordered. For x=0.15, the structurally-refined, rock salt configuration is $[Li_{1.96}Al_{0.04}]_{16c}[Co_{0.85}Al_{0.11}Li_{0.04}]_{16d}O_4$, in which 2% of the Al ions are located on the octahedral (16c) sites, predominantly occupied by lithium;
4. The slight disorder in Al-substituted electrodes changes the voltage profile of the Li/LT-$LiCo_{1-x}Al_xO_2$ cells. Whereas Li/LT-$LiCoO_2$ and Li/LT-$LiCo_{1-x}Ni_xO_2$ cells operate at constant voltage (~3.6 V) consistent with a two-phase reaction involving a lithiated-spinel to spinel transition, Li/LT-$LiCo_{1-x}Al_xO_2$ cells operate by an apparent single-phase process, which is characterized by a sloping voltage profile between 3.5 and 4.2 V, and with improved cycling stability (Figure 2); and
5. Like LT-$LiCoO_2$ and LT-$LiCo_{1-x}Ni_xO_2$ ($0<x<0.2$) systems, LT-$LiCo_{1-x}Al_xO_2$ ($0<x<0.2$) electrodes provide an electrochemical capacity corresponding to the extraction and reinsertion of approximately 0.5 Li per formula unit, or 134-148 mAh/g depending on the value of x. Note, for example, that the electrode composition LT-$LiCo_{0.8}Al_{0.2}O_2$ contains 20% of electrochemically inactive Al^{3+} ions. In this case, the Co redox

utilization (x=0.2; 63%) is therefore significantly higher than it is for unsubstituted LT-$LiCoO_2$ (x=0; 50%), thereby reflecting the greater electrochemical stability of the oxidized cobalt ions in the Al-substituted electrodes.

Although the results above offer a new approach to design and stabilize lithiated-spinel electrodes, the LT-$LiCo_{1-x}Al_xO_2$ system is unattractive because cobalt is an expensive element and low in abundance in the earth's crust. The challenge is therefore to identify a viable high-potential, lithiated-spinel cathode that has minimal cobalt or is, at best, cobalt-free.

Layered and lithiated-spinel $LiMn_{0.5}Ni_{0.5}O_2$

The discovery of the lithiated spinel, LT-$LiCo_{1-x}Al_xO_2$, with its unique, slightly disordered structure, led immediately to the identification of several other substituted, Co-based, lithiated-spinel compounds. For example, gallium-substituted LT-$LiCo_{1-x}Ga_xO_2$ electrodes, synthesized at ~400 °C, were found to behave in a similar manner to Al-substituted analogues, while high resolution scanning transmission electron microscopy (STEM) images of manganese-substituted LT-$LiCo_{1-x-y}Ni_xMn_yO_2$ electrodes, such as LT-$LiCo_{0.333}Ni_{0.333}Mn_{0.333}O_2$, provided evidence of an intergrown structure composed of layered and lithiated-spinel components in which the cobalt ions are predominantly trivalent, the manganese ions tetravalent, and the nickel ions divalent [30].

The latter finding had immediate implications: intuitively, it suggested that it might be possible to synthesize a Co-free lithiated-spinel at ~400 °C, LT-$LiMn_{0.5}Ni_{0.5}O_2$ (or alternatively, in lithiated-spinel notation, LT-Li_2MnNiO_4), in which the manganese and nickel ions would be tetravalent and divalent, respectively, as they are in the partially-disordered (~11%) layered, high-temperature analogue HT-$LiMn_{0.5}Ni_{0.5}O_2$ [31]. This instinct proved to be at least partially correct. Structural refinement of LT-$LiMn_{0.5}Ni_{0.5}O_2$ with high-quality, synchrotron X-ray diffraction data obtained at Argonne's Advanced Photon Source revealed that the oxygen array of LT-$LiMn_{0.5}Ni_{0.5}O_2$ was cubic-close packed ($c/a \approx 4.90$). An essentially identical fit to the data was obtained using either a lithiated-spinel or layered structural model in which there was approximately 16% (~1/6) disorder between the lithium and the transition-metal ions (Figure 3) [32]). This observation therefore mimics, in reality, the hypothetical anomaly described earlier that would exist between lithiated-spinel and layered LT-$LiCoO_2$ if both structure-types were ideally cubic-close-packed [20]. Furthermore, high-resolution STEM images of LT-$LiMn_{0.5}Ni_{0.5}O_2$ clearly showed evidence of both layered and lithiated-spinel configurations, beautifully integrated with one another [32].

The electrochemical profile of a Li/LT-$LiMn_{0.5}Ni_{0.5}O_2$ cell when charged and discharged between 5.0 and 2.5 V shows spinel-like character with distinct plateaus at approximately 3.6 and 4.6 V (Figure 4) [32]. The 1 V separation of these plateaus during charge is consistent with the extraction of lithium from octahedral sites (at ~3.6 V) and tetrahedral sites (at ~4.6 V) of the structure, as observed for $LiMn_2O_4$ spinel electrodes at ~3 V and ~4 V, respectively [8]; the doublet peak at ~3.6 V is tentatively attributed to lithium extraction from the octahedral sites of the intergrown lithiated-spinel and layered components. The electrochemical reaction

that occurs between 5.0 and 2.5 V is remarkably stable during the early cycles, generating a reversible capacity of 225 mAh/g, which is 80.4% of the theoretical value of the LT-$LiMn_{0.5}Ni_{0.5}O_2$ electrode (280 mAh/g) [32]. The volume change, 2.4%, of the LT-$Li_{1-x}Mn_{0.5}Ni_{0.5}O_2$ structure over such a wide compositional range is surprisingly small, which is a likely contributing factor to the good cycling stability of the electrode.

Preliminary X-ray absorption (XAS) data have indicated that reversible redox reactions occur predominantly on the nickel ions in LT-$LiMn_{0.5}Ni_{0.5}O_2$ electrodes with a minor contribution of manganese redox at ~3 V and the possibility of oxygen redox above 4.5 V [32]. Work is currently in progress to obtain a better understanding of the structural, electrochemical and electronic properties of this complex lithiated-spinel material, which holds promise for aiding the design of a viable Mn-rich cathode system for next-generation Li-ion batteries.

Conclusions

Research at Argonne National Laboratory has revealed several new cathode materials with a lithiated-spinel-type structure that are of potential interest for the Li-ion battery industry. Many of these materials contain high levels of cobalt; they are prepared at 'low-temperature' (e.g., 400 °C) and are designated in lithiated-spinel notation, LT-$Li_2Co_{2-2x}M_{2x}O_4$, or simply LT-$LiCo_{1-x}M_xO_2$ (e.g., M=Al, Ga). Recently, a cobalt-free, lithiated-spinel analogue, LT-Li_2MnNiO_4 (LT-$LiMn_{0.5}Ni_{0.5}O_2$), which is an isomorph of the partially-disordered, 'high-temperature' layered analogue, HT-$LiMn_{0.5}Ni_{0.5}O_2$, has been discovered. LT-$LiCo_{0.85}Al_{0.15}O_2$ is a 'zero-strain' cathode (0% volume expansion) that operates at 3.6 V (vs. lithium), while LT-$LiMn_{0.5}Ni_{0.5}O_2$ operates between 3.6 and 5.0 V (vs. lithium) with 2.4 % volume expansion) lithiated-spinel cathodes. As such, when coupled with a 'zero strain' $Li_4Ti_5O_{12}$ anode (0.2% volume expansion) these materials have exposed a new direction for designing 2 to 3 V, all-solid-state spinel/lithiated-spinel cells, first conjectured by Goodenough and Thackeray 40 years ago [5].

Lithiated-spinel cathodes are of interest for conventional Li-ion batteries in their own right. They are also of interest for stabilizing high-capacity, lithium- and manganese-rich $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (NMC) electrodes compositions to reduce the cost and safety concerns of both cobalt- and nickel-rich Li-ion chemistries.

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Figure Captions

Figure 1. Identical, calculated powder X-ray diffraction patterns of (a) an ideal, lithiated spinel structure LT-$LiCoO_2$ (LT-$Li_2[Co_2]O_4$) with cubic symmetry, Fd-3m, a=8.000 Å and (b) a corresponding, hypothetical layered $LiCoO_2$ structure with trigonal symmetry, R-3m, and an ideal, cubic-close-packed oxygen array, a=2.828 Å, c=13.856 Å, c/a= 4.90.

Figure 2. A comparison of the electrochemical profile of a Ni-substituted Li/LT-$LiCo_{0.9}Ni_{0.1}O_2$ cell that operates by a two-phase lithiated spinel-to-spinel reaction at constant voltage (~3.6 V) with the profile of an Al-substituted Li/LT-$LiCo_{0.9}Al_{0.1}O_2$ cell that operates by an apparent single-phase process between 3.5 and 4.2 V.

Figure 3. Essentially identical synchrotron X-ray diffraction patterns of LT-$LiMn_{0.5}Ni_{0.5}O_2$ with two partially-disordered structural models (a) lithiated spinel and (b) layered.

Figure 4. Electrochemical profile of a Li/LT-$LiMn_{0.5}Ni_{0.5}O_2$ cell 5.0 and 2.5 V showing spinel-like character with distinct plateaus at ~3.6 and 4.6 V.

FIGURES

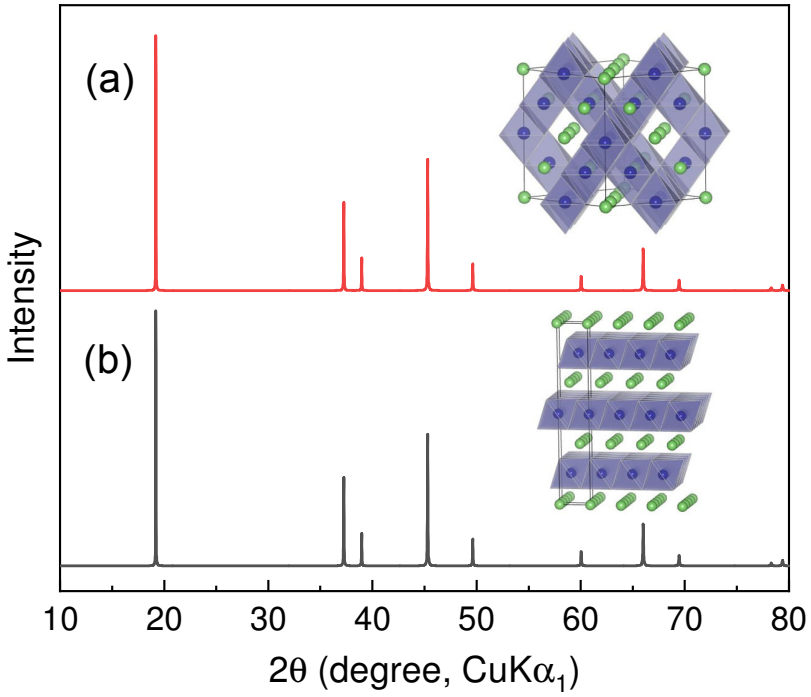

FIGURE 1

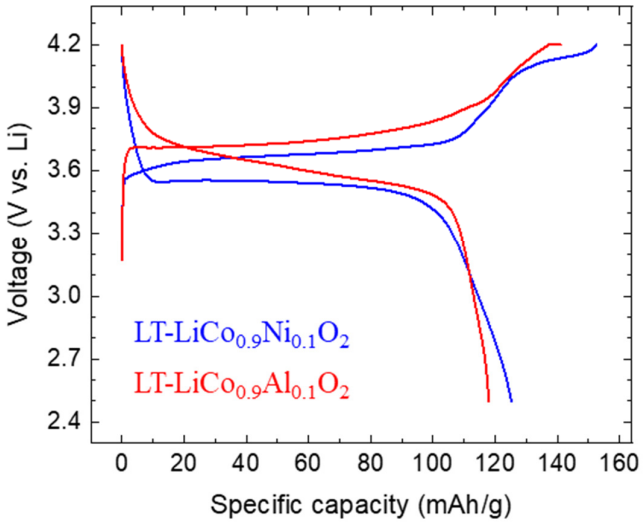
Voltage (V vs. Li)
4.2
3.9
3.6
3.3
3.0
2.7
2.4
0
20
40
60
80
100
120
140
160
Specific capacity (mAh/g)
LT-LiCo0.9Ni0.1O2
LT-LiCo0.9Al0.1O2

FIGURE 2

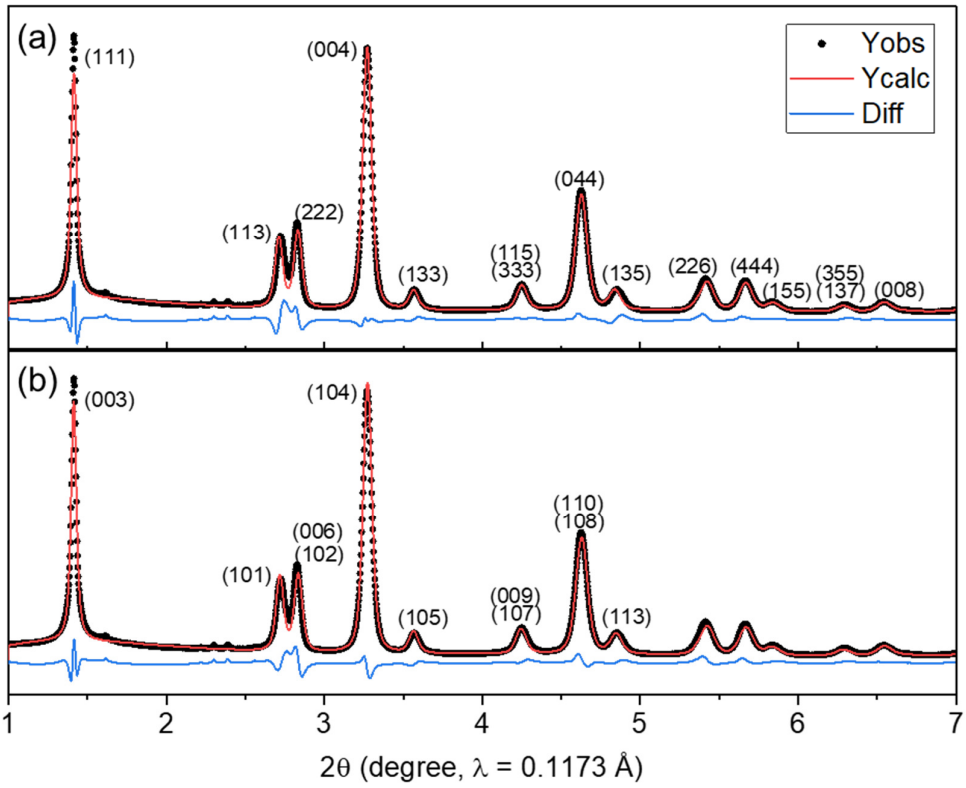
(a)
(111)
(004)
(113)
(222)
(133)
(115)
(333)
(044)
(135)
(226)
(444)
(155)
(355)
(137)
(008)
Yobs
Ycalc
Diff
(b)
(003)
(104)
(101)
(006)
(102)
(105)
(009)
(107)
(110)
(108)
(113)
1
2
3
4
5
6
7
2θ (degree, λ = 0.1173 Å)

FIGURE 3

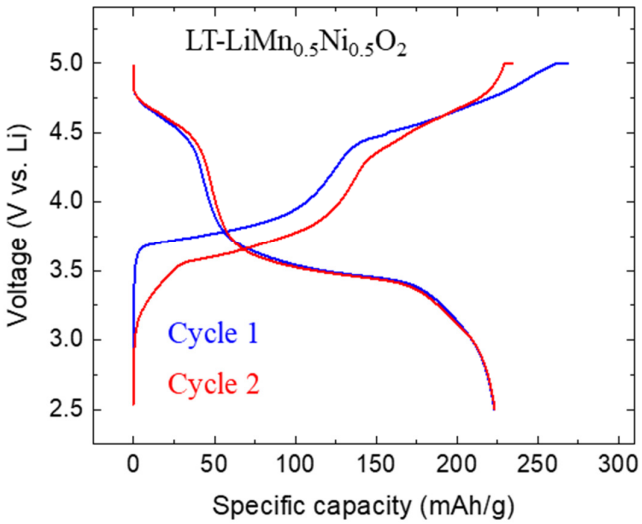
LT-LiMn0.5Ni0.5O2
Voltage (V vs. Li)
5.0
4.5
4.0
3.5
3.0
2.5
0
50
100
150
200
250
300
Specific capacity (mAh/g)
Cycle 1
Cycle 2

FIGURE 4