Aliovalent titanium substitution in layered mixed Li Ni-Mn-Co oxides for lithium battery applications

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Improved electrochemical characteristics are observed for $Li[Ni_{1/3}Co_{1/3-y}M_yMn_{1/3}]O_2$ cathode materials when M=Ti and y<0.07, compared to the baseline material, with up to 15%
10 **increased discharge capacity.**

Layered mixed transition metal oxides $Li[Ni_xCo_{1-2x}Mn_x]O_2$, or NMCs, are attractive candidates for use as cathodes in lithium ion batteries due to their high capacity and the reduced Co content compared to $LiCoO_2$. $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ delivers
15 up to 160 mAh/g after charging to 4.2 V and 200 mAh/g to ~ 4.7 V in a lithium half cell configuration, and has better thermal abuse tolerance than $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$. [1] The electrochemical activity is attributable to redox processes of Ni and Co, whereas Mn remains in the +4 oxidation state during normal charge and
20 discharge. [2] The cobalt in the transition metal layers of the NMCs decreases the number of Li/Ni anti-site defects compared to the parent $LiNi_{0.5}Mn_{0.5}O_2$, resulting in better rate performance. [3] For vehicular applications, it is desirable, however, to reduce the cobalt content further, for reasons of cost, ideally without
25 compromising performance.

Towards this end, we have been investigating full or partial substitution of Co in NMCs with Al, Fe, or Ti. [4] Our results showed that small amounts of Al or Ti are beneficial to electrochemical performance. However, aliovalent substitution of
30 Co (*e.g.* with Ti) is more complex than the corresponding isovalent substitution processes, due to the need for charge compensation. Several mechanisms for this are possible; for example, some Mn^{4+} may be replaced with Mn^{3+}, or a lithium deficiency on *3a* sites may occur. It is also possible to substitute 2
35 Li^+ ions with every Ti^{4+} ion on *3b* (transition metal) sites; this is effectively what occurs with the recently reported $xLiMn_{0.5}Ni_{0.5}O_2 \cdot 1-xLi_2TiO_3$ composites. [5] To gain further insight on Ti substitution processes in NMCs, we have selected the $Li[Ni_{1/3}Co_{1/3-y}Ti_yMn_{1/3}]O_2$ system and describe it in this
40 communication.

Details of the synthesis, electrode preparation, and experimental procedures are given in the electronic supplementary information. Table 1 lists the actual compositions of the materials used in this study, obtained by ICP analysis.
45 Several samples contained a significant excess of lithium and their code names contain the symbol Li to designate this fact.

Table 1 Sample compositions of Ti-substituted NMCs

Composition	Code Name
$Li[Ni_{0.33}Co_{0.33}Mn_{0.34}]O_2$	Ti-00
$Li_{1.03}[Ni_{0.34}Co_{0.29}Ti_{0.02}Mn_{0.35}]O_2$	Ti-02
$Li_{1.03}[Ni_{0.35}Co_{0.25}Ti_{0.03}Mn_{0.36}]O_2$	Ti-03
$Li_{1.10}[Ni_{0.38}Co_{0.21}Ti_{0.03}Mn_{0.38}]O_2$	Ti-03-Li
$Li_{1.12}[Ni_{0.38}Co_{0.16}Ti_{0.07}Mn_{0.39}]O_2$	Ti-07-Li

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The powder diffraction patterns of the Ti-substituted NMCs are shown in Fig. 1, along with that of the parent compound. With the exception of sample Ti-07-Li, all peaks in all the patterns could be indexed to the R $\bar{3}$m space group. For
55 Ti-07-Li, an additional shoulder is observed at $2\theta \approx 43.8º$ suggesting the presence of a secondary phase. This is tentatively assigned to a spinel of unknown composition and suggests that the solubility limit for Ti is below about 7 atom percent. The substitution causes systematic shifts in peak positions and peak
60 broadening, indicating that Ti is incorporated in the transition metal layers. Preliminary Rietveld refinements (not shown) indicate that the unit cell volumes increase as Ti content goes up, as would be expected for substitution of the Co^{3+} ion with the larger Ti^{4+} ion. Scanning electron micrographs (SEMs) of these
65 samples show that they consist of primary particles ~ 75-100 nm in diameter and are highly agglomerated into larger secondary particles with micron-sized pores. Substitution does not affect the particle morphologies. Fig. 2 shows a typical SEM image of one of the samples.
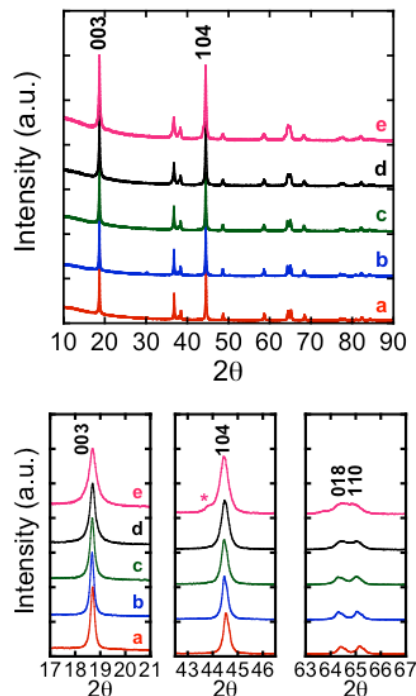

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Fig. 1 Top: XRD powder patterns of (a) Ti-00, (b) Ti-02, (c) Ti-03, (d) Ti-03-Li, and (e) Ti-07-Li. **Bottom:** Expansions of selected regions of the patterns. An asterisk marks an impurity peak at about $2\theta \approx 44°$ (middle).
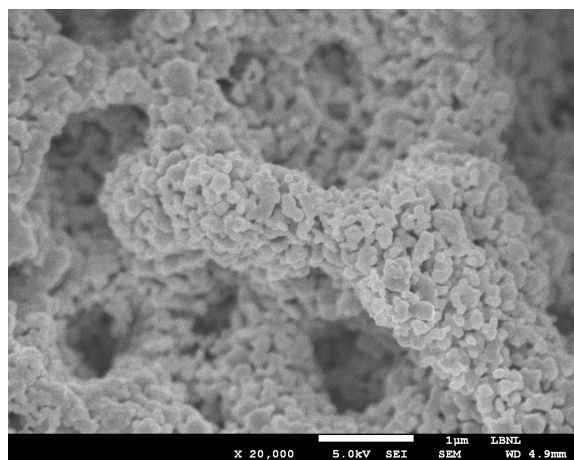
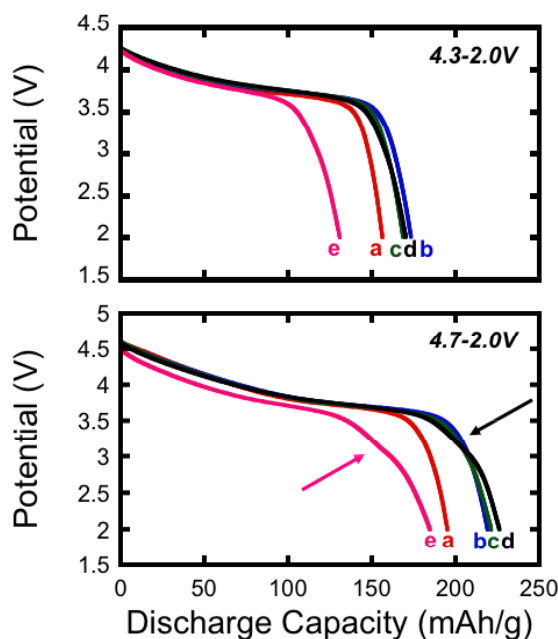**Fig. 2** SEM image of the Ti-00 powder. The morphology is typical of the NMCs used in this study.

Lithium half-cells containing the subject materials were cycled at 0.1 mA/cm^2 or about C/10 rate (Fig. 3). The discharge profiles after charge to 4.3 V are typical of stoichiometric NMCs, but samples Ti-02, Ti-03 and Ti-03-Li deliver somewhat higher specific capacities than Ti-00. In contrast, Ti-07-Li is markedly inferior, most likely due to the presence of the impurity phase. When the charge limit is extended to 4.7 V, the differences between the Ti-substituted compounds and the baseline material are even more apparent. The specific capacity is increased by as much as 15% (up to 235 mAh/g) for several of the Ti-substituted samples. Furthermore, the two compounds with the greatest lithium excess, Ti-03-Li and Ti-07-Li, show an additional feature in the discharge profile at about 3.0 V, which is not evident in profiles after charging to 4.3 V. This is suggestive of an activation process whereby electro-active Mn is generated, similar to that which occurs in Li-excess NMCs and composite materials (*e.g.*, those containing a Li_2MnO_3 component) after charge to high potentials; *i.e.* concomitant loss of lithium and oxygen and structural rearrangement. [6] If so, this indicates that some of the excess lithium is indeed present in the transition metal layers (*3b* sites), rather than in an impurity phase on particle surfaces (*e.g.*, Li_2CO_3). Ti-02 and Ti-03, in contrast, do not show this feature, do not contain a large excess of lithium, and deliver nearly the same very high capacity as Ti-03-Li. Thus, neither the presence of excess lithium on *3b* sites nor an activation process is essential for delivering the higher capacities observed for some of the Ti-substituted NMCs. Furthermore, these observations suggest that charge compensation can occur either by co-substitution of Li on *3b* sites or by one of the other mechanisms suggested above.

The origins of the increased capacities for several of the Ti-substituted samples during 0.1 mA/cm^2 discharges, are, as yet, not completely understood. The rate capabilities are not substantially different than that of the baseline NMC, but higher capacities are obtained at every current density tested between 0.1 and 2.0 mA/cm^2 (not shown) for samples not containing excess lithium. To minimize kinetic effects, lithium half-cells containing the subject cathodes were potentiostatically stepped between 4.3 and 2.0 V in 10 mV increments at a rate equivalent to about C/50. Somewhat higher specific capacities were obtained in all cases, compared to the galvanostatic discharges at 0.1 mA/cm^2. Table 2 includes the results of these experiments, including the observed first cycle irreversible capacities expressed as a percentage of the initial charge capacity.

Fig. 3 Discharges at 0.1 mA/cm^2 from 4.3-2.0V (top) or 4.7-2.0V (bottom) of lithium cells containing (a) Ti-00, (b) Ti-02, (c) Ti-03, (d) Ti-03-Li, and (e) Ti-07-Li. Arrows point to the additional feature at 3.0V in the discharge profiles from 4.7-2.0V of cells containing Ti-03-Li and Ti-07-Li.

Table 2 Results of slow potentiostatic experiments on lithium half cells containing Ti-substituted NMCs

Sample	Disch. Cap., mAh/g	% Irrev. Cap.
Ti-00	184	7.3
Ti-02	196	5.8
Ti-03	190	5.4
Ti-03-Li	182	8.7
Ti-07-Li	182	12

Relatively high first cycle coulombic inefficiencies are characteristic of cells containing NMC materials and are observed even after partial charging. [7] It has been suggested that lithium diffusion becomes increasingly sluggish as the *3a* sites become nearly fully occupied, making it difficult to recover all of the charge capacity under normal conditions. The observation that the so-called irreversible capacity can be completely recovered after discharge to low voltages supports the hypothesis that kinetic limitations are responsible for the phenomenon. The results in Table 2 show that first cycle irreversible capacities are somewhat lower in cells containing Ti-02 and Ti-03 than in the one with Ti-00. Cells with Ti-03-Li and Ti-07-Li, however, have comparatively high irreversible capacities, perhaps due to the onset of the activation processes discussed above. It is possible to explain the lower irreversible capacities in the Ti-02 and Ti-03 electrodes if lithium deficiencies in the *3a* sites compensate for the aliovalent substitution. This would lower the apparent coulombic inefficiencies, by reducing the initial charge capacities. However, the discharge capacities should remain the same as in the parent compound (or decrease as a consequence of a higher degree of ion-mixing, as often happens with materials synthesized with lithium deficiencies). The increased discharge capacities suggest that charge compensation in the substituted

NMCs occurs via replacement of a small amount of Mn^{4+} with Mn^{3+} instead. The mixed oxidation states for Mn may result in higher electronic conductivities for the fully lithiated Ti-substituted compounds. If electronic rather than ionic conductivity limitations cause the observed kinetic sluggishness near the end of discharge in cells containing NMCs, this may explain the positive effects of Ti substitution that are observed. This decreases the apparent irreversibility, resulting in the higher discharge capacities that are seen. This, however, requires further study.

Better capacity retention upon cycling is observed for cells containing several of the Ti-substituted materials, regardless of the voltage window used (Fig. 4). Although some NMCs can deliver high capacities after charging to high potentials, fading is often severe (as is seen for Ti-00 in this example). Composite (Li_2MnO_3 stabilized) materials with high capacities usually exhibit better cycling behavior, but require the activation process discussed earlier. The loss of oxygen damages particle surfaces, resulting in poor rate capability. This initial result for the Ti-substituted materials suggest that it may be possible to obtain a stable higher capacity upon cycling than is usual for the stoichiometric NMCs, without needing activation or sacrificing rate capability.
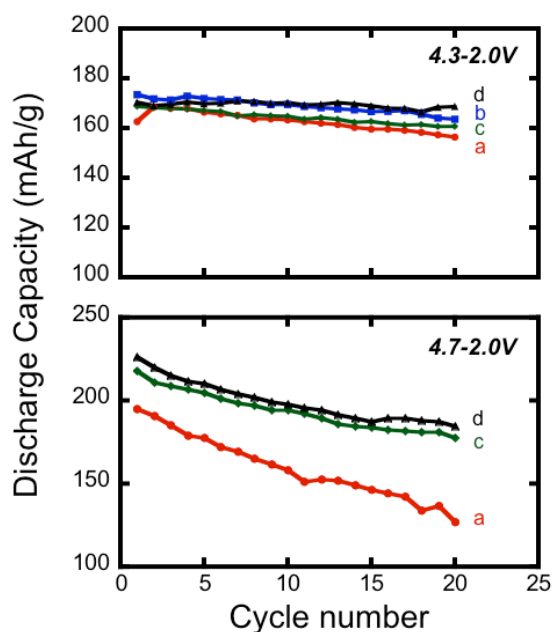

Fig. 4 Discharge capacity as a function of cycle number for lithium cells containing (a) Ti-00, (b) Ti-02, (c) Ti-03, and (d) Ti-03-Li. Cells were discharged at 0.1 mA/cm^2 between 4.3 or 4.7 and 2.0V.

In summary, partial substitution of Ti for Co in $Li[Ni_{1/3}Co_{1/3-y}M_yMn_{1/3}]O_2$ cathodes results in higher discharge capacities and better cycling characteristics in cells containing them. The mechanism of the aliovalent substitution is of interest and influences the observed electrochemical properties. In some cases, Li co-substitutes with Ti on transition metal sites to compensate for charge, resulting in a lithium-excess material. The higher discharge capacity after charge to 4.7 V is probably attributable to an activation process similar to that seen in composite NMC materials containing a Li_2MnO_3 component, in which both Li and oxygen are removed at high potentials. In other cases, the charge compensation occurs, most likely, by replacement of some Mn^{4+} with Mn^{3+}, and the higher capacity that is observed is not contingent upon an activation process. The reasons for the improvement are not completely understood, but may be the result of higher conductivities in the as-made materials that arise as a result of mixed valence states for Mn. The higher capacities do not come at the expense of poorer rate or cycling behavior, suggesting that low levels of aliovalent Ti substitution may be a route to preparing NMC materials with superior electrochemical properties, without the disadvantages of composite materials. Further work on this system is planned in order to investigate the origins of the improvement and will be reported in a subsequent publication.

Notes and references

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