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## Tailoring the Surface Properties of $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ by Titanium Substitution for Improved High Voltage Cycling Performance<sup>†</sup>

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The present study aims to provide insights into the behavior of  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  (NMC442) and  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.18}\text{Ti}_{0.02}\text{O}_2$  (NMC442-Ti02) cathode materials under galvanostatic cycling to high potentials, in the context of previous work which predicted that Ti-substituted variants should deliver higher capacities and exhibit better cycling stability than the unsubstituted compounds. It is found that NMC cathodes containing Ti show equivalent capacity fading but greater specific capacity than those without Ti in the same potential range. When repeatedly charged to the same degree of delithiation, NMC cathodes containing Ti showed better capacity retention. Soft x-ray absorption spectroscopy (XAS) spectra for Mn and Co indicated increased reduction in these elements for NMC cathodes without Ti, indicating that the substitution of Ti for Co acts to suppress the formation of a high impedance rock salt phase at the surface of NMC cathode particles. The results of this study validate the adoption of a facile change to existing NMC chemistries to improve cathode capacity retention under high voltage cycling conditions.

### Introduction

Although the performance characteristics of today's lithium-ion batteries are superior to many traditional battery technologies, additional improvement is still needed in order to see advancements in the fields of grid-storage, electric vehicles, and consumer electronics; energy storage is often a bottleneck to progress in these areas. To increase energy density, improvements in cathodes are still needed.  $\text{LiCoO}_2$  was first described as a cathode material by Goodenough *et al.* in 1981 and the majority of Li-ion batteries in commercial use today still employ it as the positive electrode material.<sup>1</sup> In 2001 an alternative chemistry that partially substitutes Ni and Mn for Co was proposed independently by Dahn *et al.*<sup>2</sup> and Ohzuku and Makimura<sup>3</sup> as a replacement for  $\text{LiCoO}_2$ . In these chemistries,  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  are added in equal amounts to maintain charge neutrality of the structure. These  $\text{LiNi}_x\text{Mn}_x\text{Co}_{1-2x}\text{O}_2$  (NMC) cathode materials have been studied

intensively since they were proposed and have been shown to be safer and cheaper than  $\text{LiCoO}_2$ , with higher capacities when charged to 4.2 V in lithium half cells and comparable rate capabilities and specific capacities.<sup>4-6</sup> It is, however, desirable to increase capacity further in NMC materials. One way to do this is to charge them to higher potentials in electrochemical cells, thereby extracting more lithium.

One major road-block to this approach is the capacity fading that occurs at high operating voltages. Lin *et al.* reported contributions to capacity fading and impedance buildup resulting from a combination of structural reconstruction and formation of a surface reaction layer made up of a LiF phase in a complex organic matrix at the surface of NMC particles cycled to high voltages and/or exposed to an  $\text{LiPF}_6/\text{EC-DMC}$  electrolyte. Structural reconstruction to a rock salt (space group  $\text{Fm}\bar{3}\text{m}$ ) or a spinel (space group  $\text{Fd}\bar{3}\text{m}$ ) at the surface of the NMC layered structure (space group  $\text{R}\bar{3}\text{m}$ ) was observed in an annular-dark-field scanning transmission electron microscopy (ADF-STEM) experiment and was confirmed with spatially resolved electron energy loss spectroscopy (EELS) and ensemble averaged x-ray absorption spectroscopy (XAS).<sup>7,8</sup> It is apparent from these results that suppression of rock salt phase formation at the surface of NMC cathode particles would decrease impedance and capacity fading of NMC materials.

The partial substitution of titanium for cobalt on the transition metal (TM) sublattice, yielding a structure with composi-

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tion  $\text{LiNi}_x\text{Mn}_x\text{Co}_{1-2x-y}\text{Ti}_y\text{O}_2$  (NMC-Ti), results in improved cycling performance to high voltages.<sup>9</sup> Kam and Doeff showed that for  $x = 1/3$ , and  $y < 0.04$  the addition of Ti could increase the first cycle specific discharge capacity by up to 15% during cycling to 4.7 V vs.  $\text{Li}/\text{Li}^+$ .<sup>10</sup> Decreased first-cycle inefficiencies and capacity fading for Ti substituted NMCs were also observed and were tentatively attributed to a smaller volume change during lithiation/delithiation in Ti substituted materials.<sup>11</sup> In a computational and experimental investigation of NMC-Ti, Markus *et al.* calculated that the substitution of small amounts of Ti for Co increases the energy of formation at room temperature for the rock salt phase from the NMC layered structure at any given state of charge (SOC).<sup>9</sup> In the same report, the authors also showed that the equilibrium intercalation voltage as a function of lithium content is lower at all but intermediate SOC for Ti-substituted NMC than for the unsubstituted NMC, allowing more Li to be removed during charge to a fixed potential limit.

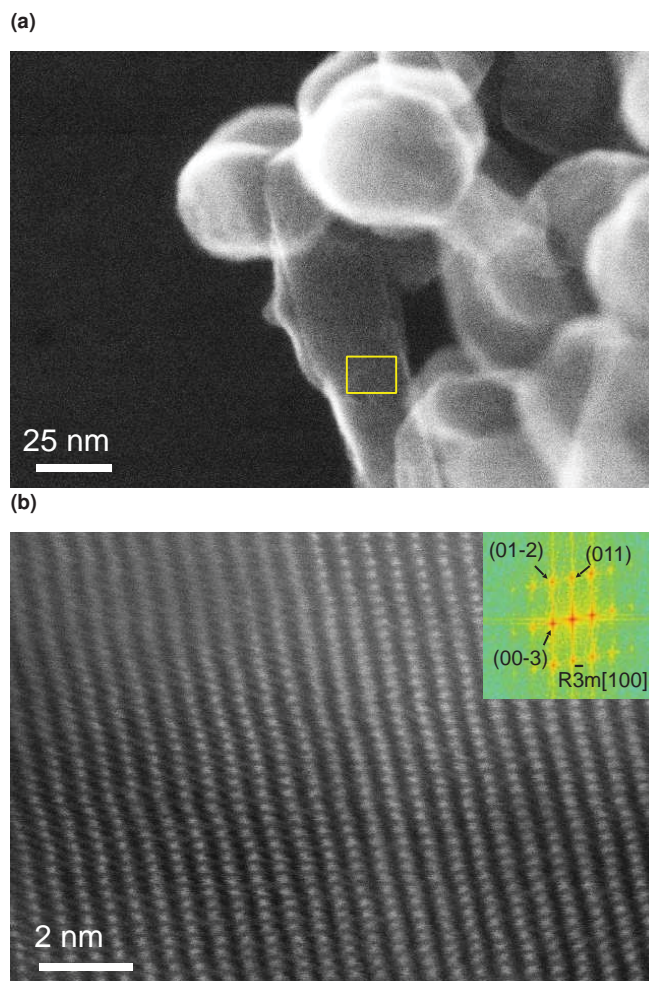
In this report we present galvanostatic coin cell cycling results for cells containing cathodes of compositions  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  (NMC442) and  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.18}\text{Ti}_{0.02}\text{O}_2$  (NMC442-TiO2). We also obtained ensemble averaged soft XAS spectra, and discuss the results of these measurements in the context of cell performance and structural reconstruction at particle surfaces. In particular, we compare capacity versus potential curves of cells containing NMC442 and NMC442-TiO2 cathodes cycled between 2.0-4.7 V. From these measurements, the voltage limits of equivalent Li removal were determined for cells containing the two different cathode materials. Subsequent measurements were then made on cells containing the NMC442-TiO2 cathode material for the same amount of Li removal as for the NMC442 cells cycled to 4.7 V. XAS measurements were made for all cells and correlated to TM oxidation states to estimate the amount of rock salt phase evolved under equivalent Li removal for cells with and without Ti. This allowed the results of Markus *et al.*<sup>9</sup> to be cross-checked using a consistent experimental methodology to form a more complete picture of the effect that Ti substitution has on NMC cathode materials.

## Results and discussion

### Electron microscopy and surface area measurements

A combined high resolution scanning electron microscope (SEM) and annular dark-field scanning transmission electron microscope (ADF-STEM) was utilized to study the crystal structure of the synthesized NMC materials. Fig. 1 shows ADF-STEM images taken for pristine NMC442 particles. An atomic resolution image of the region selected in the high resolution image of Fig. 1a is shown in Fig. 1b and demonstrates that the NMC materials exhibit the expected  $R\bar{3}m$  structure, where the transition metal layers (i.e.,  $R\bar{3}m-b$ ) are observed, but the lithium ions on the  $R\bar{3}m-a$  sites were not detected, due to their low atomic mass. The fast Fourier transform (inset) of Fig. 1b shows that the STEM imaging was performed along the  $R\bar{3}m$  [100] zone axis. Atomic resolution ADF-STEM images of Ti-substituted NMC material from previous

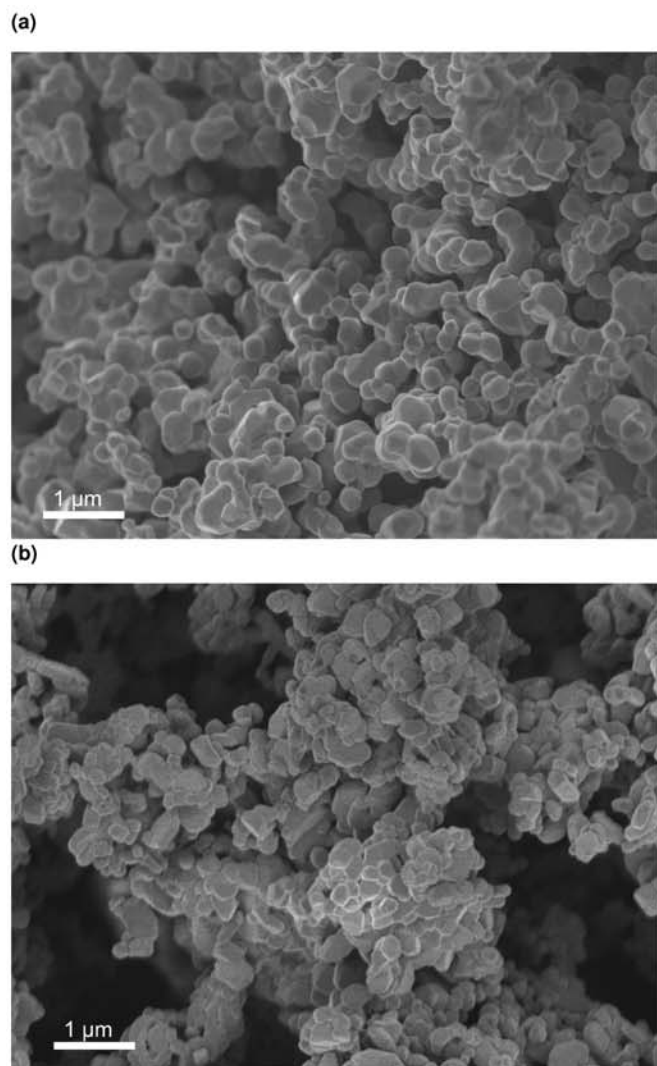
studies show a nearly identical crystal structure to that displayed in Fig. 1b.<sup>7,8</sup>



**Fig. 1** (a) Image of NMC442 particles formed by secondary and back-scattered electrons in a scanning transmission electron microscope (STEM). (b) Atomic resolution annular dark-field STEM image of region selected in image (a), oriented along the [100] direction of the  $R\bar{3}m$  layered structure. These images were collected on a 200 keV aberration-corrected Hitachi STEM instrument with a secondary electron detector.

SEM imaging of as-synthesized NMC cathode powders was carried out for qualitative evaluation of particle morphology using the JEOL JSM-7000F microscope described in the materials characterization section of the supplemental materials. Images obtained for NMC particles with and without Ti substitution are shown in Fig. 2. The average particle size and shape in the two images is very similar. Nitrogen physical adsorption measurements based on Brunauer-Emmett-Teller (BET) theory gave BET specific surface area values of 0.47 and 1.69  $\text{m}^2/\text{g}$  for NMC442-TiO2 and NMC442 powders, respectively. This difference is small enough to conclude that particle morphology and agglomeration will not greatly affect the electrochemical performance of either chemistry relative to the other under low rate cycling conditions. This assumption is supported by the work of Lin *et al.*, where the authors found particle size for NMC materials synthesized by the

same method used here to negligibly affect the surface reduced layer thickness and cycling behavior, within the range of particle sizes tested in their study.<sup>7</sup>

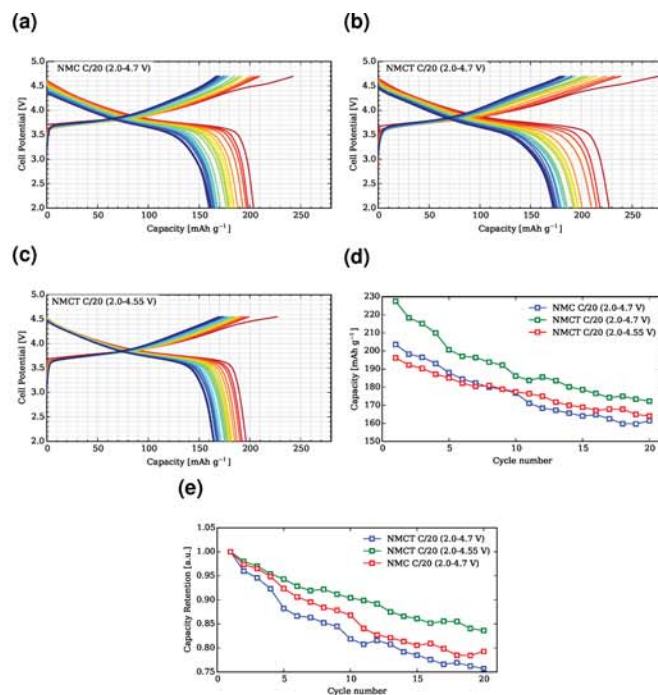


**Fig. 2** SEM micrographs of (a) NMC442 particles and (b) NMC442-TiO<sub>2</sub> particles.

### Electrochemical cycling

The capacity-voltage curves of cells containing NMC442 and NMC442-TiO<sub>2</sub> are shown in Figs. 3a and 3b, respectively. From these figures, and from Fig. 3d, it is apparent that the presence of Ti in the cathode material results in greater specific capacity with comparable capacity retention. This finding is well in line with that predicted by Markus *et al.* and consistent with the cycling performance reported in the previous study by Lin *et al.*<sup>7,9</sup>

In order to investigate the relative cycling stability of the Ti-substituted NMC cathode, it was necessary to determine the potential for the Ti-containing material at which Li removal was equivalent to that for the Ti-free material at 4.7 V. Comparing Figs. 3a and 3b, it is observed that the voltage for which the charge capacity of the Ti-containing material is equivalent to the



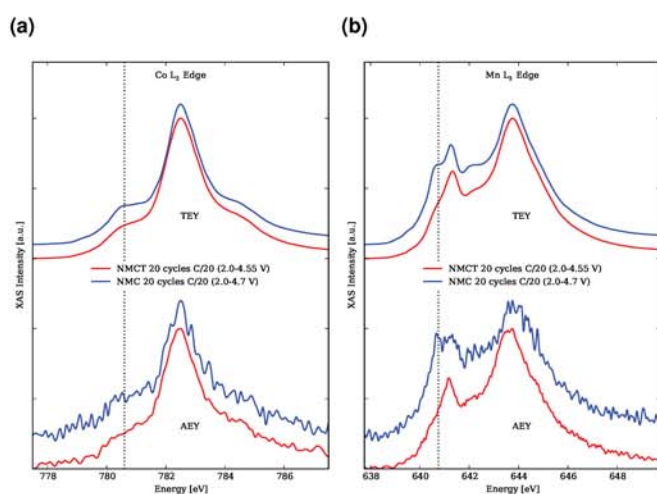
**Fig. 3** Galvanostatic cycling data for cells cycled from 2.0-4.7 V at C/20 with cathodes containing (a) NMC442 and (b) NMC442-TiO<sub>2</sub>, and (c) for a cell cycled from 2.0-4.55 V with a cathode containing NMC442-TiO<sub>2</sub>. (d) shows the variation of discharge capacities with cycle number and (e) shows the fraction of discharge capacity retained as a function of cycle number, normalized to the first cycle value. (NMC indicates NMC442 and NMCT indicates NMC442-TiO<sub>2</sub>).

charge capacity for the Ti-free material at 4.7 V (243 mAh g<sup>-1</sup>) occurs between 4.5 and 4.6 V. The first cycle charge capacity of a cell containing the NMC442 cathode material is ~243 mAh g<sup>-1</sup>; in Fig. 3b it is apparent that the potential corresponding to this first cycle charge capacity is ~4.55 V for the NMC442-TiO<sub>2</sub> cathode material. Electrochemical cycling of cells containing the NMC442-TiO<sub>2</sub> cathode material was then carried out between 2.0-4.55 V to isolate the effect of Ti substitution at an equivalent degree of Li removal (Fig. 3c). The Ti-containing material cycled between 2.0-4.55 V demonstrates less capacity fading over 20 cycles than both the Ti-containing and Ti-free materials cycled between 2.0-4.7 V at C/20 (Fig. 3e) and has comparable specific capacity to the Ti-free material charged repeatedly to 4.7 V (Fig. 3d).

### Soft XAS

In Fig. 4, soft XAS measurements for Mn and Co are shown for the cathodes (stopped in the discharged state) whose electrochemical performance is given in Figs. 3a and 3c. In the pristine NMC material, Mn and Co have been shown to have formal oxidation states of +4 and +3, respectively.<sup>7,12-14</sup> The two measurement types shown are total electron yield (TEY) and Auger electron yield (AEY) and probe the surface with depth sensitivities of ~2-5 nm and ~1-2 nm, respectively.<sup>7</sup> For both measurement types, a visible low energy shoulder (indicated by a dotted line in Fig. 4)

is far more apparent near the  $L_3$  edges of both Mn and Co spectra of the Ti-free material than for the cathode material containing Ti. This effect is more pronounced for the Mn spectra and in AEY mode for both elements. The low energy shoulders arise mainly from the evolution of transition metal  $3d$  bands to higher occupancies (reduced oxidation states),<sup>7,12,13,15</sup> suggestive of rock salt phase formation at the surfaces of the NMC particles or reduced metal complexes in the cathode electrolyte interfacial region.<sup>16</sup> The fact that the AEY spectra show greater contributions from reduced species than the TEY spectra suggests that the surface reduced layer thickness is less than the depth sensitivity of the TEY measurement type. These results are consistent with the model of Markus *et al.* which predicts that the addition of ~2-3 at% Ti to the NMC layered structure delays formation of rock salt.<sup>9</sup>



**Fig. 4** Normalized AEY and TEY spectra for (a) Co and (b) Mn  $L_3$  edges for both NMC442 and NMC442-Ti02 after cycling galvanostatically to potential limits corresponding to equivalent Li removal during charge. Dotted line indicates the position of the +2 oxidation state peak. Electrodes were measured in the discharged state. The spectra were plotted as received, without further signal processing (e.g., smoothing).

## Conclusions

Stoichiometric NMC cathodes with compositions  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  and  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.18}\text{Ti}_{0.02}\text{O}_2$  were cycled in Li-ion half-cells under two distinct experimental conditions: to the same voltage limits and to the same degree of Li removal. Cells cycled between 2.0-4.7 V at a current of C/20 for 20 cycles showed greater capacity for the  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.18}\text{Ti}_{0.02}\text{O}_2$  material than for the  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  material, with similar capacity fading. Cells cycled to the same degree of lithium removal at a rate of C/20 for 20 cycles showed equivalent capacities, as expected, but there was decreased fading for the Ti-substituted material. Soft XAS analysis of those cells cycled to the same degree of lithium removal showed a greater degree of TM reduction at the surfaces of NMC particles without Ti substitution, in accordance with the findings of Markus *et al.*, indicating that there should be less formation of rock

salt on particle surfaces for the Ti-substituted variant at any given state-of-charge.<sup>9</sup> Substitution of ~2-3 at% Ti for Co in  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  results in higher specific capacities when cells are cycled between 2.0-4.7 V or improved capacity retention for similar degrees of lithium extraction during high voltage cycling.

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