

# Identification of dopant site and its effect on electrochemical activity in Mn-doped lithium titanate

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Doped metal oxide materials are commonly used for applications in energy storage and conversion, such as batteries and solid oxide fuel cells. The knowledge of the electronic properties of dopants and their local environment is essential for understanding the effects of doping on the electrochemical properties. Using a combination of X-ray absorption near-edge structure spectroscopy (XANES) experiment and theoretical modeling we demonstrate that in the dilute (1 at. %) Mn-doped lithium titanate ( $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ , or LTO) the dopant  $\text{Mn}^{2+}$  ions reside on tetrahedral (8a) sites. First-principles Mn K-edge XANES calculations revealed the spectral signature of the tetrahedrally coordinated Mn as a sharp peak in the middle of the absorption edge rise, caused by the  $1s \rightarrow 4p$  transition, and it is important to include the effective electron-core hole Coulomb interaction in order to calculate the intensity of this peak accurately. This dopant location explains the impedance of Li migration through the LTO lattice during the charge-discharge process, and, as a result - the observed remarkable 20% decrease in electrochemical rate performance of the 1% Mn-doped LTO compared to the pristine LTO.

## I. INTRODUCTION

Understanding working mechanisms in functional nanomaterials (e.g. catalysts, electrocatalysts, battery and energy materials, actuators, etc.) at the atomistic level opens up new

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opportunities for their rational design [1-4]. In many materials with advanced optical, magnetic, electronic, mechanical, and catalytic properties, new functionalities arise due to changes in local environment and electronic structure with doping or substitution [5-10]. The AB<sub>2</sub>O<sub>4</sub> type spinel lithium titanate (Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub>, or LTO) is a promising anode material for Li-ion batteries (LIBs). Owing to various attributes such as zero-strain, long cycle life, and relatively high potential range (1.5 V vs Li<sup>+</sup>/Li) in the charge/discharge process, LTO has demonstrated outstanding cyclability and safety in high power LIBs over conventional graphitic anode materials [11-13]. Among several factors limiting the commercial use of LTO as anode material in LIBs is its poor electronic conductivity, restricting its rate capability[13]. Doping with various metals (such as Mg, V, Cr, Mn, Co, Ni, Cu, Zn, Y, etc.) has been broadly adopted by several groups as an efficient and effective way to increase electronic conductivity and therefore improve the rate capability of LTO[14-24]. However, enhanced electronic conductivity does not guarantee enhanced rate performance [14,24], and, indeed, dramatic variations in electrochemical properties on doping have been observed [11,25,26]. As an example of the ongoing debates in the case of Mn doped LTO (referred to as Mn-LTO in this article), Doretta *et al.*[18] have reported reduced conductivity while Hulya *et al.*[19] have reported increased conductivity compared to the pristine LTO. Among other possible scenarios, these variations in the conductivity and related rate performances have been attributed to the different locations of dopants in LTO lattice and the impact on the Li ion diffusivity [15,16,18-22].

In pristine LTO, tetrahedral 8a sites are believed to be occupied by Li<sup>+</sup> ions, while the octahedral 16d sites are randomly occupied by Li<sup>+</sup> and Ti<sup>4+</sup> ions with a 1:5 ratio [26]. Since Li<sup>+</sup> ions migrate through the LTO lattice via tetrahedral/octahedral sites, the occupancy of these sites by dopants should have an important effect on Li ion transport and thus electrochemical properties of LTO electrodes [8,9,11,27]. For example, the doping on the tetrahedral (8a) site is expected to be detrimental for Li ion conductivity due to the blocking of Li ion diffusion pathways [13]. However, the dopant location in LTO is a subject of debate. Earlier investigations suggest octahedral location for dopants [15-17,19-24]. Others have reported mixed (tetrahedral and octahedral) or tetrahedral coordination of dopants in LTO [18-21]. One important example is (1-30)% Mn doped LTO, which has been a focus of several investigations [17-19]. In their experiments with 10% Mn doped LTO, Doretta *et al.*[18] proposed tetrahedral Mn, while Hulya *et al.*[19] proposed octahedral Mn for the same concentration. In order to resolve the controversy on the dopant site in the doped LTO and its impact on electrochemical performance, it is

important to establish a general and reliable methodology to provide local structural information around the dopant atom.

X-ray absorption near edge structure (XANES) spectroscopy is a premier technique for the purpose of dopant site identification, because it contains information about the local coordination geometry and electronic properties of a particular atomic species [28]. While XANES modelling is still a challenging problem in general, the progress achieved during the last decades in developing theoretical XANES codes enables the use of XANES for quantitative analysis of molecular and bulk compounds [29,30]. In this work we used theoretical modeling of XANES spectra of the Mn K edge to identify the location of Mn dopants in the spinel LTO lattice. We correlate the Mn doping site with the substantial reduction of rate performance of Mn-doped LTO compared to the pristine LTO anode.

## **II. METHODS**

### **A. Material Synthesis**

The samples of pristine and 1 at. % Mn doped LTO were prepared by solid state reactions as described previously [31]. The pristine and Mn doped LTO samples were made in the same conditions and thus have similar granularity (Figure SM 1). The details of their characterization by multiple complementary techniques and the results can be found elsewhere [31,32].

### **B. X-Ray Absorption Spectroscopy Measurements**

Mn K-edge (6540 eV) XANES measurements were performed at the ISS beamline of the National Synchrotron Light Source – II (NSLS-II) at Brookhaven National Laboratory. The sample powder was pressed into a pellet for the measurements at the Mn K edge. The X-ray absorption coefficient data were measured in the fluorescence mode, using a multi-element silicon drift detector (SDD). 20 scans were averaged to improve the signal to noise ratio. For the purpose of comparison with the parent LTO, we collected Ti K-edge XANES data of Mn doped LTO in the transmission mode (for this the powder was mixed with boron nitride to prepare a pellet) at the beamline BL2-2 at Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory.

The Athena<sup>†</sup> software from the Demeter data analysis package [33] was used for the data alignment, merging, and normalization.

### C. Electrochemical Measurements

For electrochemical measurements, electrodes were prepared by mixing 80 wt % active material (pristine and doped LTO powder, individually) with 10 wt % acetylene black and 10 wt % polyvinylidene fluoride (PVDF). A glass fiber GF/F (Whatman) filter was used as the separator and ethylene carbonate (EC)/dimethyl carbonate (DMC)/ LiPF<sub>6</sub> (1:1:1) was used as the electrolyte. The 2032 type coin cells were assembled in an Ar glovebox, with metallic lithium foil (MIT Crop.) as the counter electrode. The discharge/charge measurements were carried out on an Arbin Instrument (BT-2400) test system at several different rates (0.2C, 0.5 C, and 1 C) at ambient temperature (The C-rate is a measure of current normalized by the battery's capacity, e.g., for a 1 Ah battery capacity 1 C = 1 A).

### D. Computational Details

Ab initio simulations presented in this study consist of two steps. In the first step, structural relaxation of Mn doped LTO was carried out within spin-polarized density functional theory (DFT) using projected augmented wave (PAW) potentials [34] as implemented in Vienna Ab Initio Simulation Package (VASP) package [35,36]. The exchange-correlation potential was evaluated under the generalized gradient approximation using the Perdew, Burke, and Ernzerhof (PBE) [37] functional. The kinetic energy cutoff of the plane-wave basis was chosen as 550 eV, and the Brillouin zone was sampled with a 4×4×2  $\Gamma$ -centered grid. In order to improve the treatment of the strongly correlated 3d orbitals of Mn and Ti, the DFT+U method [38] was employed. The value of the effective Hubbard U parameter was chosen as 3 eV for both Mn and Ti ions as suggested by M. Capdevila-Cortada *et al.*[39]. A Gaussian broadening of 0.5 eV was chosen to plot the projected density of states (PDOS) using VASP.

In the second step, Mn K-edge XANES spectra were simulated for the optimized structures using the OCEAN package [40,41]. Ground state wave functions and orbital energies, which are input for OCEAN calculations, were obtained from plane-wave norm-conserving pseudopotential calculations using Quantum ESPRESSO package [42] with a kinetic energy

cutoff of 100 Rydberg. The same Brillouin zone sampling and DFT+U treatment as in the previous step were used. The final state effects were included through the effective electron – core-hole interaction, treated by the Bethe-Salpeter equation [43]. A total of 1280 bands were included (up to 100 eV above the Fermi level) to compute the screened core-hole potential in OCEAN calculations. Core-hole lifetime broadening was included using a fixed energy Lorentzian broadening applied on the computed spectra with a full width at half maximum (FWHM) of 1.1 eV [44]. In order to account for broadening by the excited state lifetimes, an additional variable energy Lorentzian broadening was applied [45-47]. The FWHM of Lorentzian broadening was chosen as  $(E-E_{\text{onset}})/10$  with  $E_{\text{onset}}$  being the onset energy of the main edge of the calculated spectra.

### III. RESULTS AND DISCUSSION

Figure SM 2 shows that the Mn doped LTO electrode exhibits reasonable cycling stability at a low rate (0.2C). Discharge/charge at different rates were also performed both on pristine LTO and Mn doped LTO electrodes and the voltage profiles are presented in Figures 1 (a-c). All the curves show that the insertion/extraction of Li ions into/out of the LTO framework occurs at stable potential plateaus of 1.54 V (discharge) and 1.58 V (charge) vs.  $\text{Li}^+/\text{Li}^0$ . Despite that specific capacity decreases with increasing C-rate in the both types of LTO electrodes, the capacity of pristine LTO is significantly higher than that of doped LTO at the same C-rates (Fig. 1 a-c). Our electrochemical measurements demonstrate the maximum capacity of  $150 \text{ mAhg}^{-1}$  for pristine LTO (Fig. 1 c), which is reasonably high considering the large size of the particles (in the micron range- see Fig. SM 1 for more details) and comparable to other reports, generally ranging from  $140 \text{ mAhg}^{-1}$  to  $160 \text{ mAhg}^{-1}$  at similar rate of 0.2C as compared to a theoretical specific capacity of  $175 \text{ mA h g}^{-1}$  [13]. In Mn-LTO, the specific capacity at 0.2C is reduced to  $\sim 122 \text{ mAhg}^{-1}$ , which is nearly a 20% decrease compared to the pristine LTO (Fig. 1 c). Such a large capacity drop in the 1% Mn-doped sample is intriguing, because it cannot be attributed to the difference in grain size or morphology, as both samples were synthesized by the same method and thus have the similar granularity (Fig. SM 1). In search of a possible explanation for this puzzling behavior, in the following sections we investigate the dopant sites of Mn atoms in LTO by a combination of XANES spectroscopy and theoretical modeling.

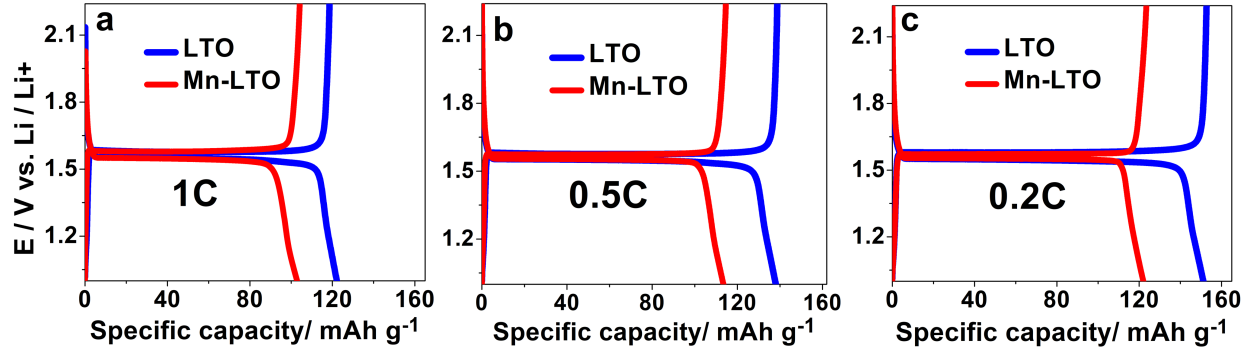


FIG. 1. Voltage profiles during discharge/charge for pristine LTO and Mn-doped LTO. The electrochemical measurements were performed at 3 different rates, 1C (a), 0.5C (b), and 0.2C (c), in the voltage range between 1.0 and 2.2 V (vs. Li/Li+); see also cycling performance in the supplementary material (Figure SM 2).

Due to the complexity in the Li/Ti site occupation (e.g. multiple sites with different local symmetries and the randomness in the occupancy of the  $16d$  site), identifying the site of the dopant atom in LTO is a difficult task. In our previous study [48], following Ziebarth *et al.*[49], we modeled the atomic structure of LTO using a hexagonal supercell containing two chemical formula equivalents of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as presented in Figure 2. This model was chosen to construct a minimum super cell for computational efficiency that satisfies the correct stoichiometry at the  $16d$  sites with a 1:5 Li to Ti molar ratio. The most stable configuration was found to correspond to the largest distance between Li ions at  $16d$  sites such that the electrostatic repulsion is minimized [49]. Because of translational and rotational symmetry, some Li and Ti sites are equivalent in the structural model. Inequivalent Li and Ti sites are presented in Figure 2 with different colors. Li ions at  $16d$  sites are six-fold coordinated in the octahedral environment, while Li ions at  $8a$  sites are four-fold coordinated in the tetrahedral environment. Li sites can be classified into 5 types labelled as Li- $16d_1$ , Li- $16d_2$ , Li- $8a_1$ , Li- $8a_2$ , and Li- $8a_3$ . All Ti sites in LTO are octahedrally coordinated. Four inequivalent Ti sites are labelled as Ti- $16d_1$ , Ti- $16d_2$ , Ti- $16d_3$ , and Ti- $16d_4$ . In addition to  $16d$  and  $8a$  sites, there are empty  $16c$  sites in LTO (not shown in Fig. 2) that are six coordinated and located in between two Li- $8a$  sites. Li ions at  $8a$  sites migrate to the  $16c$  sites during Li intercalation [48], while the locations of Ti- $16d$  ions remain unaffected. When pristine LTO is doped with Mn atoms, it is expected that Mn ions will replace one of Li or Ti ions at  $16d$  and  $8a$  sites (as shown in Fig. 2) or fill an empty  $16c$  site. The identification of the Mn dopant site from the experiment is extremely challenging due to the difficulty in extracting atomic scale information and the multiple possible doping sites for Mn,

some or all of which can be occupied. XANES spectroscopy is a premier method for locating the dopant site, due to its chemically specific sensitivity to local coordination environment and charge state of dopants [50-52]. In previous work by us and others, XANES studies of many types of dopants were used to identify their location in the host structure [53-55]. Determination of the local atomic environment from given sets of XANES data is an inverse problem of modelling and cannot be solved easily. Hence, we present our analysis in detail, starting from the analysis of the raw data, followed by the computational modelling of possible Mn dopants sites in LTO, to identify the site showing the best agreement between theory and our experiment.

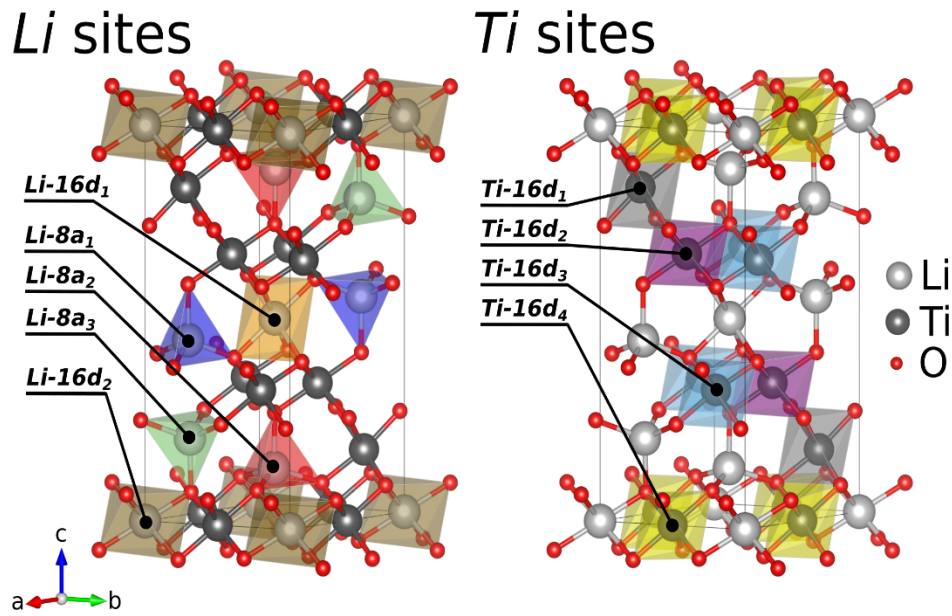


FIG. 2. Atomic structure of spinel lithium titanate (LTO) in the hexagonal unit cell. Inequivalent Li (left) and Ti (right) sites are denoted by different colours.

A typical transition metal K-edge XANES spectrum provides the information on the oxidation state, electronic charge state and local coordination of the absorber [52]. In the literature, energy position of the main absorption edge is defined either as the energy corresponding to the half of the absorption edge step height, the energy of the maximum of the absorption peak, or the first inflection point. The energy position may shift because of many factors such as the change in the oxidation state, bond covalency, the nature of the ligands, coordination numbers, and electronegativity of the anion [56-58]. Figure 3 shows the edge step

normalized K- edge XANES spectra of pristine and Mn-doped LTO sample at the Ti and Mn-edges. The Ti K-edge XANES spectrum of Mn doped LTO does not show any visible change compared to the pristine LTO (Fig. 3 a), consistent with Ti remaining in the  $Ti^{4+}$  state [48].

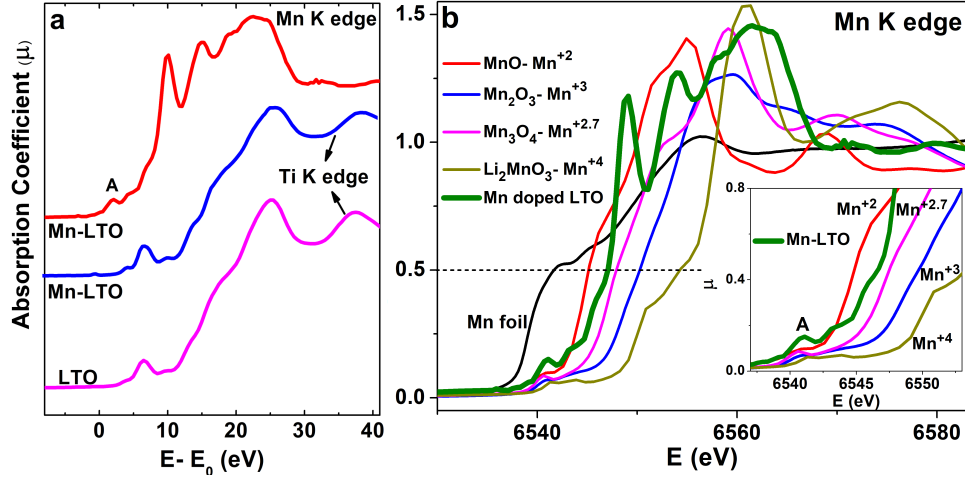


FIG. 3. (a) Normalized K-edge XANES spectra of Mn and Ti edges in the pristine and Mn doped LTO samples plotted versus photoelectron energy  $E-E_0$ , where  $E_0$  is the ionization energy of the 1s electron for Ti (4965 eV) and Mn (6540 eV). (b) Edge step normalized Mn K-edge XANES spectra of doped LTO sample along with Mn standards such as MnO,  $Mn_2O_3$ ,  $Mn_3O_4$  and  $Li_2MnO_3$  are also shown. Mn foil spectrum is used for photon energy calibration. The inset shows enlarged pre-edge.

We will now focus on the Mn K-edge XANES data (Fig. 3b). Together with the Mn doped LTO sample, we have plotted spectra of Mn standards such as MnO ( $Mn^{2+}$ ),  $Mn_2O_3$  ( $Mn^{3+}$ ),  $Mn_3O_4$  ( $Mn^{2+/3+}$ ) and  $Li_2MnO_3$  ( $Mn^{4+}$ ). To characterize the oxidation state of Mn in LTO, we compare the position of its XANES spectrum at the 0.5 edge step level with those in the standard compounds. That comparison places the oxidation state of Mn in LTO between, approximately, 2+ and 2.7+, consistent with independent electron paramagnetic resonance (EPR) results showing Mn to be in the 2+ state in the same material [32].

As shown in Figure 3b (inset) the pre-edge feature A for Mn doped LTO is the highest with respect to the standards. This effect is an indication of the less symmetric environment, on average, of Mn in LTO compared to those in standard compounds. As shown in Figure 2, the Mn dopant can occupy either octahedral (Ti/Li-16d and 16c) or tetrahedral (Li-8a) sites in LTO. Also, based on previous reports on the standards used, Mn atoms exist either in (regular or distorted) octahedral geometry (in MnO,  $Mn_2O_3$ ,  $Li_2MnO_3$ ) or mixed (tetrahedral as well as



octahedral) coordination geometry (in  $\text{Mn}_3\text{O}_4$ ) which result in different peak heights in their pre-edge region (see the inset of Fig. 3b) [57,58]. There are other compounds such as  $\text{YMnO}_3$ ,  $\text{YMn}_2\text{O}_5$  and  $\text{Li}_4\text{Mn}_2\text{O}_5$  where Mn has also been reported to be in trigonal bipyramidal, square pyramidal and spherically distorted octahedral coordination [59-61]. The variations in the height of the peak A, corresponding to the dipole-forbidden  $1s \rightarrow 3d$  transition, are due to the different sub-mixtures of  $p$  states at that energy range. The variation in the  $p$ - $d$  hybridization character depends on the Mn-O bond lengths and the displacement of the Mn atom from the center of mass of the local polyhedron [50,62,63]. Therefore, based on the pre-edge features, we conclude that the Mn environment is distorted from the ideal octahedral one. However, from this observation alone, we cannot discriminate between the two possible scenarios: a) the strongly distorted octahedral environment of the Ti/Li-16*d* and 16*c* site or b) the tetrahedrally coordinated Li-8*a* site. A mixed site placement may also explain the data. Because of the limitations of such a qualitative approach to XANES interpretation, we also performed theoretical XANES calculations.

Based on the structural model of LTO shown in Figure 2, we investigated the energetics of Mn doping in various possible sites with DFT total energy calculations. The pristine LTO structure contains 8 Li, 10 Ti, and 24 O atoms in the unit cell. We first looked at Li substitution and compared ground state total energies of fully relaxed Mn-LTO structures for all possible Mn-doping configurations as shown in Figure 2. The Li-8*a*<sub>3</sub> site (Fig. 2a) turned out to be the most stable Li site for Mn substitution. The Li-8*a*<sub>2</sub>, Li-8*a*<sub>1</sub>, Li-16*d*<sub>1</sub>, and Li-16*d*<sub>2</sub> sites are 132, 205, 270, and 421 meV higher in energy for Mn substitution. This analysis was also performed for Ti sites (Fig. 2b). When one of the Ti ions is replaced with Mn, it corresponds to 10% Mn substitution. Based on total energy calculations, the Ti-16*d*<sub>2</sub> site is the energetically most favourable Ti site for Mn substitution. Total energies of Mn substitution at Ti-16*d*<sub>1</sub>, Ti-16*d*<sub>3</sub>, and Ti-16*d*<sub>4</sub> with respect to Ti-16*d*<sub>2</sub> site are 19, 30, and 56 meV higher. Because of the large number of possible 16*c* interstitial sites for Mn, we performed the calculation on a representative configuration.

For Li-8*a*<sub>3</sub> site, which is the energetically most favourable configuration among Li sites, our calculation yields a high total magnetization of 6.0 Bohr magneton ( $\mu_B$ ) per unit cell. This high-spin state can be interpreted as Mn ion in the 2+ charge state with all 3*d* orbitals half occupied (five spin-up) according to Hund's rule. We considered several scenarios for distributing the

extra electron density (caused by the substitution of  $\text{Li}^+$  by  $\text{Mn}^{2+}$ ). The results for the Mn XANES spectrum were indistinguishable for the two spin configurations we considered: 1) one  $\text{Ti}^{4+}$  ion was reduced to  $\text{Ti}^{3+}$  and 2) the electron density was delocalized among all Ti ions in the unit cell. On the other hand, replacing Ti-16 $d_2$  with Mn simply leads to the formation of  $\text{Mn}^{4+}$  with remaining three  $3d$  electrons half occupying  $t_{2g}$  orbitals. As a result, the system has an intermediate magnetization of  $3.0 \mu_B$  per unit cell.

Next, we performed Mn K-edge XANES simulations for Mn doped at Li-8 $a_3$ , Li-16 $d_1$ , Ti-16 $d_2$  and 16 $c$  sites and compared them with the experimental XANES spectrum. XANES spectra were calculated using the OCEAN package, which treats the electron-core hole interactions explicitly by solving the Bethe-Salpeter equation (BSE) [40,41]. OCEAN spectra calculated for Mn ion placed at 16 $c$ , Ti-16 $d_2$  and Li-16 $d_1$  octahedral sites apparently lacks XANES pre-edge feature “A” as highlighted in rectangular area in Figure 4. The calculated main edge features are also clearly different from experimental Mn-LTO spectrum. On the other hand, excellent agreement between computational XANES of Mn ion placed at Li-8 $a_3$  site and experimental Mn-LTO XANES is observed as shown in Figure 4. In addition, the  $\text{Mn}^{2+}$  state at the Li-8 $a_3$  site is consistent with the EPR results. Based on total energy calculations and XANES simulations, we conclude that Mn doping in LTO happens through the substitution of the Li at the 8 $a$  site.

Finally, we analysed the XANES spectrum of Mn-LTO in more detail. Distinct peaks are visible in the spectrum, and we label them by letters (A through J) as shown in Figure 4. To identify effects of core-hole interactions, the spectrum of Li-8 $a_3$  calculated without BSE is also shown in Figure 4 for comparison. In order to reveal origins of main edge peaks labelled by D-J, we further calculated projected-density of states (PDOS) of Mn-doped LTO at Li-8 $a_3$  site as shown at the bottom of Figure 4. Except for some variations in the intensities, features labelled by D-J are all present in the spectrum without BSE. From the correlation between Mn- $p$  PDOS and the calculated XANES, we can clearly see that features labelled by D through J originate from mostly  $1s \rightarrow 4p$  transitions. On the other hand, features labelled by A, B, C disappear in the absence of core-hole interactions (without BSE), as the electron—core-hole interaction modifies the oscillator strength significantly in the pre-edge region. A closer look at the PDOS of Mn  $3d$ -states in the conduction region (Fig. 4) reveals hybridization of the Mn  $3d$  states with  $4p$  states. We assign feature A to  $1s \rightarrow 3d$  transition which is dipole-forbidden but is activated because

of contributions from Mn 3d and 4p hybridization. O 2p states have substantial contribution to the low energy side of the spectrum below 6560 eV.

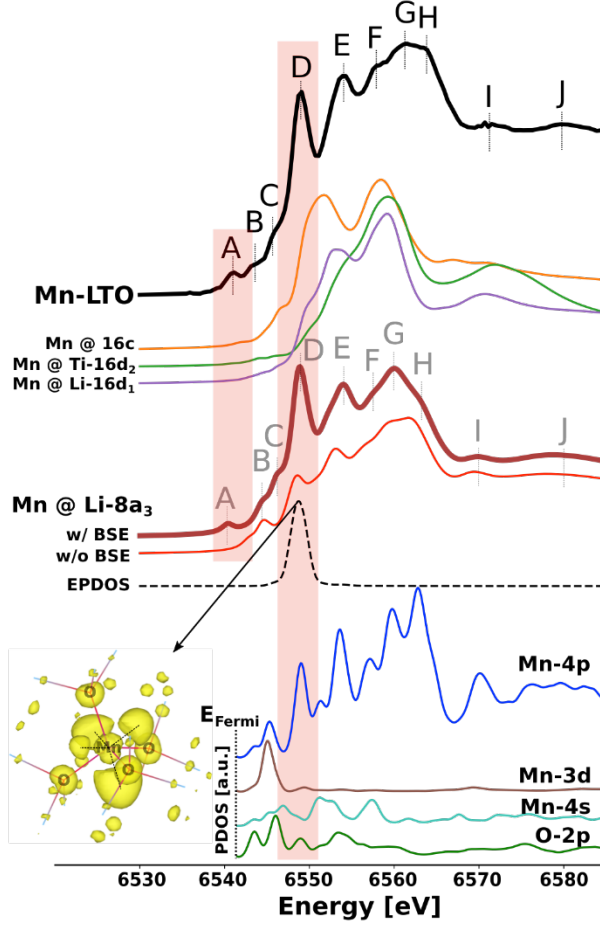


FIG. 4. Comparison of calculated XANES spectra of Mn K-edge for several Mn absorption sites with experimental spectrum. Major features in the spectra are labelled by letters A-J. Electron-hole wavefunction corresponding to peak D is shown in the isosurface plot. Projected density of states (PDOS) of the Mn at Li-8a<sub>3</sub> site and four oxygen atoms surrounding Mn are aligned with corresponding XANES. Fermi level was set to the minimum of conduction bands.

Peak D is a distinct feature of Mn-LTO as shown in Figure 3b, which is absent in Mn-K edge of other standards. In order to gain further insights into this peak, we investigated its charge density distribution in both spatial and energy domain. For a given core electron excitation ( $S$ ), the two-body electron-hole wavefunction can be expressed as

$$\chi^S(\mathbf{r}_e, \mathbf{r}_h) = \sum_k \sum_c A_{ck}^S \psi_{ck}(\mathbf{r}_e) \psi_{1s,k}^*(\mathbf{r}_h), \quad (1)$$

where  $\psi_{1s,k}^*$ ,  $\psi_{ck}$ , and  $A_{ck}^S$  are the Mn 1s core hole wavefunction, electron wavefunction of wave vector  $\mathbf{k}$  in the conduction bands, and the eigenvectors of the excitation  $S$ , respectively. For a localized core hole at the Mn atom, the real space charge density is given by  $|\chi^S(\mathbf{r}_e, \mathbf{r}_h = \mathbf{r}_{Mn})|^2 = |\sum_k \sum_c A_{ck}^S \psi_{ck}(\mathbf{r}_e)|^2$ , where  $\mathbf{r}_{Mn}$  is the ionic position of the excited Mn atom, and averaged over the polarization directions. We further introduce the excitation-projected density of states (EPDOS) to capture the charge density distribution in the energy domain, which is defined as

$$\text{EPDOS}(S, E) = \sum_k \sum_c |A_{ck}^S|^2 \delta(E - E_{ck}), \quad (2)$$

where  $E_{ck}$  is the orbital energy of the empty state  $\psi_{ck}$ . The charge density isosurface of peak D is shown in Figure 4.

Locally the shape and orientation of the charge density on the Mn exhibit  $sp^3$  hybrid orbitals in a tetrahedral arrangement, which is indicated by dashed black lines connecting four blobs with the one centred on the Mn. These unoccupied orbitals avoid the tetrahedral Mn-O bonds, pointing into the interstitial. Polarization-averaged EPDOS of peak D is shown in Figure 4 in the dashed line with a Gaussian broadening of  $\sigma=0.5$  eV. As highlighted by the rectangular area, it is well localized within the energy range of approximately 5 eV and contains pronounced Mn 4p contributions and significant Mn 4s and O 2p contributions. Although peak D is already present in the site-specific Li-8a<sub>3</sub> spectrum without BES, the peak intensity is significantly underestimated, which highlights the importance of including the electron-core hole screened Coulomb interaction in the simulated Mn XANES spectra. Another important feature of peak D is that the wavefunction of the excited electron is extended beyond O 2p orbitals in the nearest-neighbour shell, as one can clearly see even longer range contributions from Ti 3d orbitals and 2p orbitals of non-bonded oxygen atoms in Figure SM 3 at a lower isovalue than that in Fig. 4.

The charge density analysis indicates that peak D is characteristic of the tetrahedral Mn, which is absent in the Mn K-edge standards with pure six-coordinated Mn in Figure 3b, except for Mn<sub>3</sub>O<sub>4</sub> with mixed Mn tetrahedral (1/3) and octahedral (2/3) occupancies. We further investigated XANES spectrum of Mn<sub>3</sub>O<sub>4</sub>. As shown in Figure 3 (b), Mn<sub>3</sub>O<sub>4</sub> lacks spectral feature D although it has tetrahedral sites. Comparison of the experimental XANES spectrum at the Mn-K edge of Mn<sub>3</sub>O<sub>4</sub> with those for site-specific and site-averaged spectra is presented in Figure SM 4. Although peak D is missing in Mn<sub>3</sub>O<sub>4</sub> XANES, the theoretically calculated site-specific

XANES spectrum of tetrahedral site of  $\text{Mn}_3\text{O}_4$  closely resembles Mn-K edge of Mn-LTO with well-defined peak D. The absence of the peak D in the site-averaged spectrum is a consequence of the predominance of the octahedral sites of  $\text{Mn}_3\text{O}_4$  in the averaged spectrum. This analysis strengthens our claim that peak D is a characteristic spectral fingerprint of tetrahedrally coordinated Mn.

Based on the combination of experimental and theoretical XANES spectroscopy results we pinpointed the tetrahedral Mn site location in the LTO lattice, which can have a big impact on Li ion diffusivity. Li ion diffusion in LTO is an intriguing topic that has attracted extensive research efforts in recent years. Schmidt *et al.* [64] reported steep Li diffusivity increase during lithiation at the low charging stage in the NMR measurement. This remarkable behavior was attributed to the role of Li-16*d* in stabilizing the subnanometer phase boundary featuring Li-8*a*/Li-16*c* face-sharing local motifs [65]. The significance of the Li-8*a*/Li-16*c* face-sharing local motif in the rate performance of LTO was further supported by in situ Ti K-edge XANES analysis [48]. Furthermore, Reuter *et al.* observed Ti anti-site-like defects stabilized by the configurational disorder in molecular dynamic simulations, which are characterized by a displacement of a Ti ion from a 16*d* to a 16*c* site and a shift of the Li ion on an adjacent 8*a* to the original 16*d* site [66]. A fast, local, and correlated Li ion diffusion was believed to be a key element in the sudden rise of the Li conductivity at the early stage of charging [66].

Our Mn K-edge XANES modeling identified Li-8*a* site as the Mn doping site. This atomic level structural information can be qualitatively correlated with the significant (~20%) rate performance drop in several ways that we outline here (more detailed, quantitative modeling is beyond the scope of this work). First, the large  $\text{Mn}^{2+}$  ion at the tetrahedral 8*a* site can block the Li interstitial diffusion pathway. Mn doping decreases available Li sites for Li diffusion. Similar effects have been observed in Mg doped LTO, where the occupation of the 8*a* sites by Mg retards Li ion diffusion, lowers the gravimetric capacity, and reduces the electrochemical reversibility of the reaction [14]. More importantly, a Mn-dopant at the 8*a* site can quench the Ti anti-site defects, effectively disabling the fast local Li diffusion around the empty 8*a* sites in the Ti anti-site defects. In addition, Mn may create local strain defects that can strongly affect Li transport, in analogy with the significant V-V bond stretching found in ~1% Cr doped  $\text{V}_2\text{O}_3$  [67].

#### IV. CONCLUSIONS

Using a combination of X-ray absorption near-edge structure experiment and theoretical spectroscopy modeling we demonstrated that  $\text{Mn}^{2+}$  ions in 1% Mn doped LTO occupy tetrahedral (*8a*) sites. As a result, Mn ions are expected to block the Li diffusion pathway, adversely affecting the rate performance of LTO. The latter was found experimentally to be 20% lower than in pristine LTO prepared under the same conditions. Our results explain the observation of decreased electrochemical activity in Mn-doped LTO qualitatively and provide directions for further modeling of Li ion transport and electrochemical activity. This same method can be used in the future for systematic analyses of other dopants and different battery materials in a broad concentration range. We also revealed a spectroscopic fingerprint of tetrahedrally coordinated Mn which may be useful for characterization and to guide design of Mn-based LTO battery materials.

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‡Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Science and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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# Identification of dopant site and its effect on electrochemical activity in Mn-doped lithium titanate

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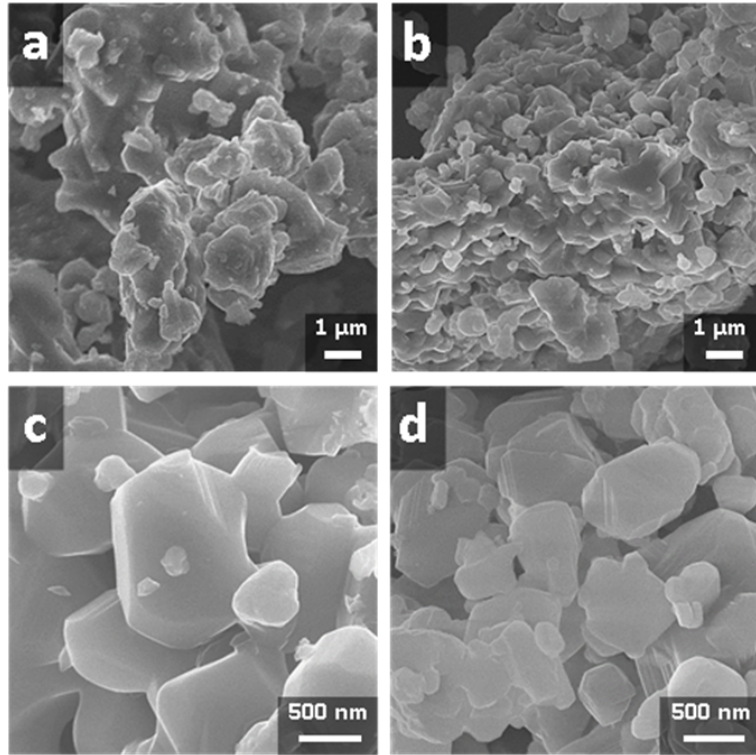
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In this Electronic Supplementary Material (ESM), we present additional information on the cyclic performance (Mn doped  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ ) and SEM images for micron sized pristine and doped samples. Electron-hole wavefunction isosurface and comparison of the experimental and theoretical XANES spectra in Mn-LTO and  $\text{Mn}_3\text{O}_4$  samples are shown as well

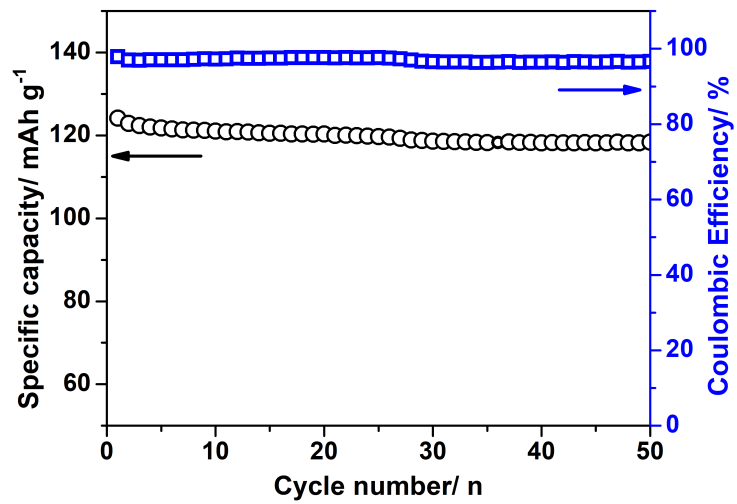
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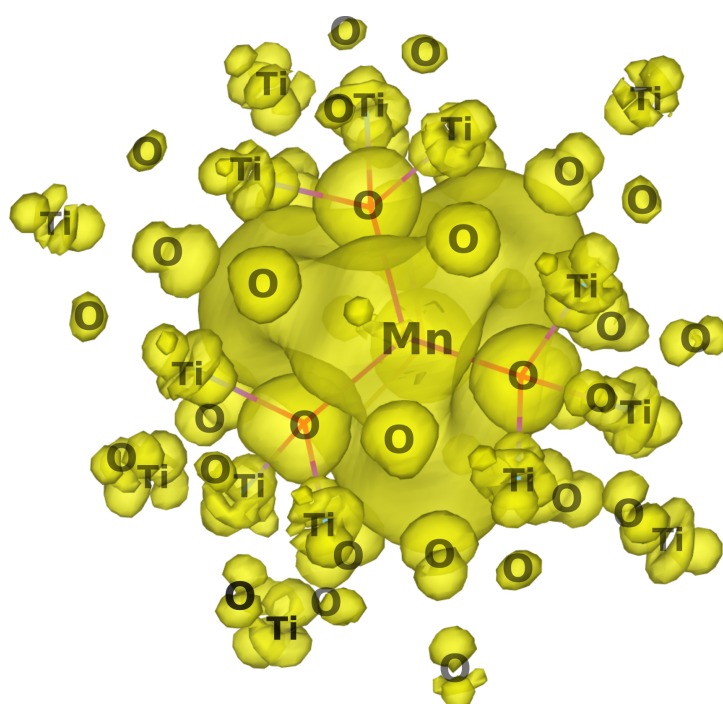
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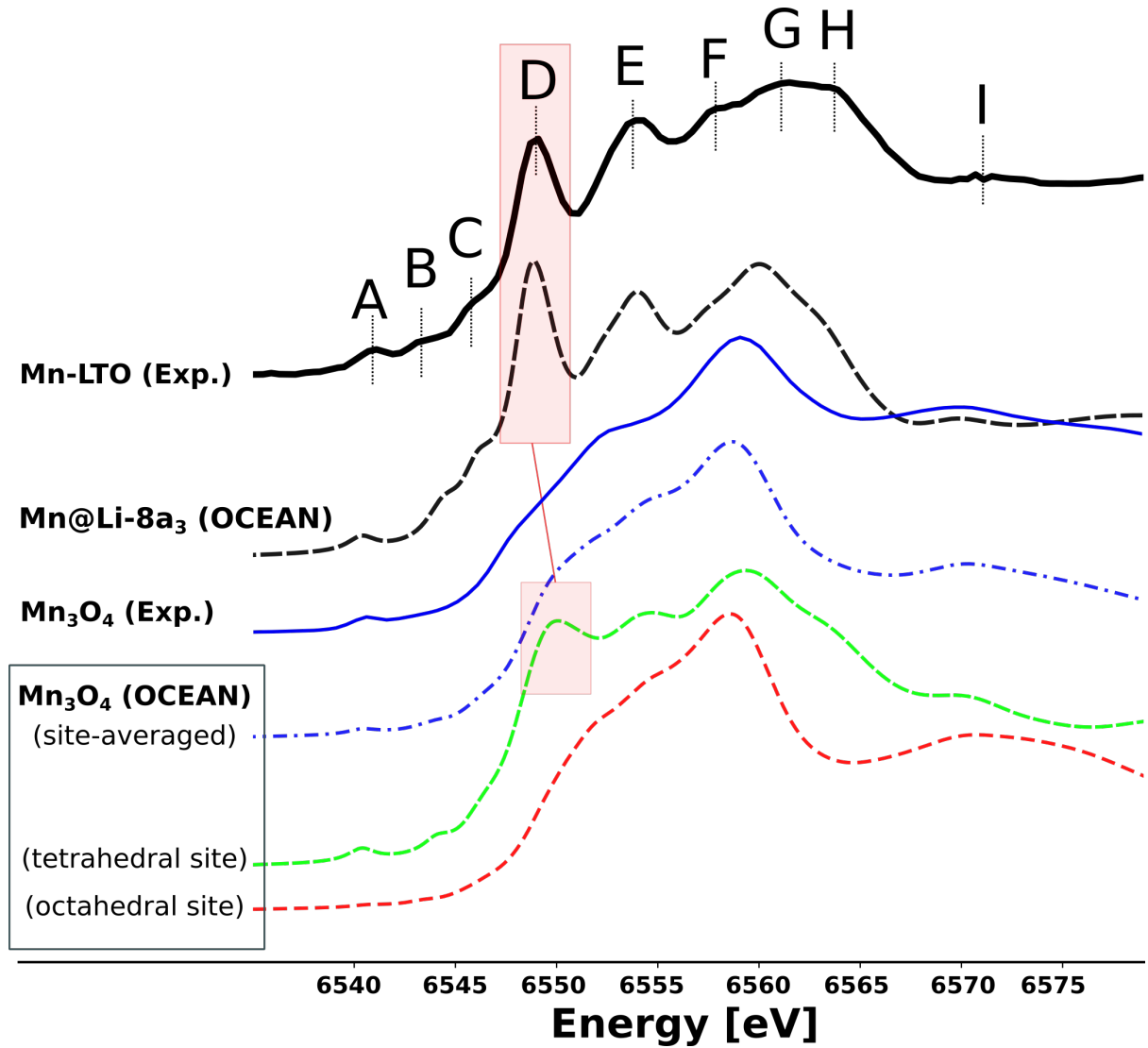
**FIG. SM 1.** SEM images of pristine LTO (a,c) and Mn-doped LTO (b,d), shown on different scales.



**FIG. SM 2.** The cycling performance at 0.2C between 1.0 and 2.5 V (vs. Li/Li<sup>+</sup>) for Mn doped LTO.



**FIG. SM 3.** Electron-hole wavefunction isosurface corresponding to peak D of Mn-LTO. A small isovalue (13% of that used in Fig. 4 of the manuscript) was used in order to show the electron density of O 2p and Ti 3d orbitals beyond the 1<sup>st</sup> shell O 2p orbitals.



**FIG. SM 4.** Comparison of the Mn K-edge XANES spectra of Mn-LTO and Mn<sub>3</sub>O<sub>4</sub>. Both spectra are very well reproduced by simulated spectra using OCEAN, where Mn in Mn-LTO is located at the tetrahedral Li-8a<sub>3</sub> site of LTO and Mn in Mn<sub>3</sub>O<sub>4</sub> occupies both tetrahedral and octahedral sites in the 1:2 ratio. The OCEAN simulation in both cases showed that peak D originates from the tetrahedrally coordinated Mn.