

Tuning Oxygen Redox Reaction through the Inductive Effect with Proton Insertion in Li-Rich Oxides

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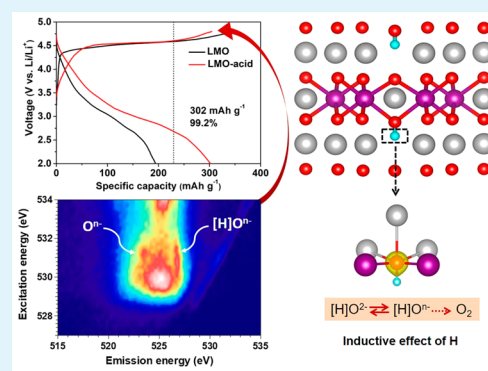
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Supporting Information

ABSTRACT: As a parent compound of Li-rich electrodes, Li_2MnO_3 exhibits high capacity during the initial charge; however, it suffers notoriously low Coulombic efficiency due to oxygen and surface activities. Here, we successfully optimize the oxygen activities toward reversible oxygen redox reactions by intentionally introducing protons into lithium octahedral vacancies in the Li_2MnO_3 system with its original structural integrity maintained. Combining structural probes, theoretical calculations, and resonant inelastic X-ray scattering results, a moderate coupling between the introduced protons and lattice oxygen at the oxidized state is revealed, which stabilizes the oxygen activities during charging. Such a coupling leads to an unprecedented initial Coulombic efficiency (99.2%) with a greatly improved discharge capacity of 302 mAh g^{-1} in the protonated Li_2MnO_3 electrodes. These findings directly demonstrate an effective concept for controlling oxygen activities in Li-rich systems, which is critical for developing high-energy cathodes in batteries.

KEYWORDS: high capacity battery, oxygen redox reaction, proton insertion, Li-rich oxides cathode, resonant inelastic X-ray scattering (RIXS)



The Li-rich transition metal (TM) oxides have received extensive attention in the past years due to their very high specific capacity of more than 280 mAh g^{-1} .^{1–3} In general, the improvement of Li-rich materials is based on one of the parent compounds, Li_2MnO_3 (LMO), which contributes to the excessive Li for the improved capacity. However, the practical employment of the extra capacity of Li-rich compounds has so far been hindered by various detrimental effects triggered by the high-capacity cycling, leading to a notoriously low Coulombic efficiency during the initial cycle of $\text{LMO}^{4–8}$ as well as other practical issues like the voltage decay.^{9–11} Indeed, it has been reported that the practical issue of voltage decay in Li-rich compounds is associated with the oxygen activity.^{12–14} The oxygen release is also associated with a significantly low discharge capacity right after the initial charging due to the irreversible oxygen oxidation reactions at high potentials.^{7,15,16} Other than this initial cycle reversibility issue, it has been accepted now that the critical challenge for improving the cycling capacity of Li-rich compounds is to control the oxygen oxidation process during the high-capacity charging so reversible reactions could be realized. While it seems indeed possible to have highly reversible oxygen redox reactions in low-cost 3d TM oxide materials,¹⁷ such a challenge for Li-rich material remains. The LMO sample provides an excellent model compounds for exploring the methods on controlling

the oxygen activities. Therefore, new strategies and solutions are urgently needed to effectively control the oxygen oxidation process toward a reversible oxygen redox reaction without sacrificing the accessible capacity in 3d TM electrode systems.

As a matter of fact, it has long been known that the oxygen could be stabilized through the so-called “inductive effect” in olivine-structured LiFePO_4 , where phosphor is introduced in the vicinity of oxygen and stabilizes the oxygen involvements in electrochemistry.^{18–20} Therefore, if electrochemically inactive positive ions could be introduced and coupled with oxidized oxygen, an inductive effect could hopefully stabilize the severe oxygen oxidation process. In this work, we successfully demonstrated that the intercalated protons into LMO layered materials could stabilize the oxygen oxidation activities toward reversible oxygen redox, leading to unprecedented Coulombic efficiency with much improved discharge capacity of LMO electrodes. Note that proton is electrochemically inactive with small ionic radii ($r(\text{H}^+) \approx 0.85 \text{ fm}$,²¹ $r(\text{Li}^+) = 0.76 \text{ \AA}$). Previous works indicate that the $\text{Li}^+ - \text{H}^+$ exchange takes place on Li-rich

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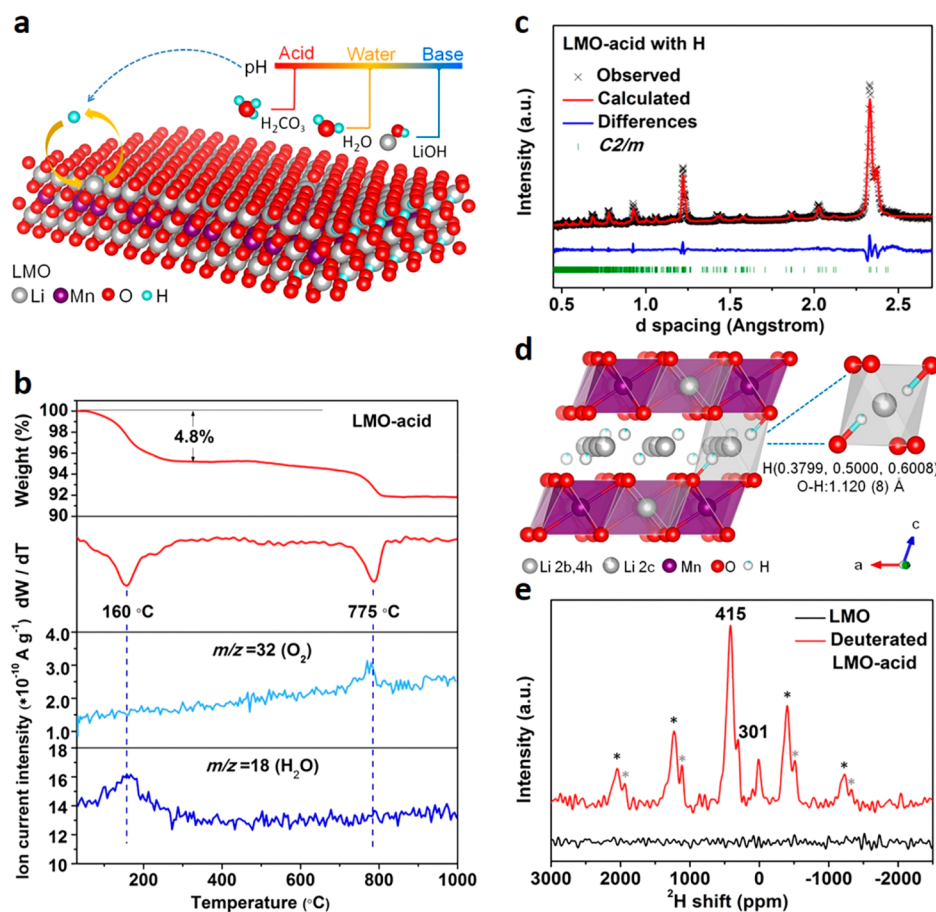


Figure 1. Characterization of protons for pristine and solution-treated LMO. (a) Schematic of solution-treating process for pristine LMO and solutions with different pH values. (b) TGA-MS data for LMO-acid sample. (c) Rietveld refinement of the normalized ND patterns with protons for the LMO-acid sample. (d) Schematic representation of protons sites from the refinement of ND patterns. (e) ²H NMR spectra for LMO and deuterated LMO-acid samples. The primary peak at ~415 ppm for the deuterated LMO-acid sample is due to ²H insertion into the structure. Asterisks indicate sidebands.

cathodes;^{22–25} however, the intrinsic mechanism of the protonation effect on the electrochemical properties and especially on the oxygen redox activities has not been explored before. Here, we have employed the structural verifications through X-ray and neutron diffraction experiments to probe the location of proton in LMO prepared by mild solution treatments. More importantly, mapping of resonant inelastic X-ray scattering (mRIXS) experiments and calculation data reveal directly that the oxidized oxygen interacts with the introduced protons, providing an effective inductive effect to maintain the oxygen redox activities toward high discharge capacity in protonated LMO.

In experiments, the pristine LMO was prepared by a conventional solid-state method (see the Methods section in the Supporting Information). The solution-treating process is schematically shown in Figure 1a, where pristine LMO material was treated by solutions with different pH values under mild conditions (Table S1). The layered structure with space group of *C2/m* and general morphology are well remained in the treated samples (Figures S1 and S2). Because the pH value of the solution is the only variable in the solution-treating process, it is suspected that the content of protons in different samples may vary. The stoichiometry of Li and Mn was examined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and shows a strong dependence on the pH values of the solutions (Table 1). The proton content

Table 1. Chemical Analysis Data for the Solution-Treated Li_{2-x}H_xMnO₃ Samples

sample	pH ^a	x ^b	x ^c	Li/Mn ^d
LMO				2.04
LMO-acid	~4.0	0.48	0.47	1.50
LMO-water	~7.0	0.23	0.24	1.80
LMO-base	~12.0	0.21	0.20	1.83

^aFor the treating solution. ^bFrom elemental analysis data. ^cFrom TGA-MS data. ^dFrom ICP-AES data; the *x* value has been corrected with pristine LMO sample to remove the effect of surface water.

was then determined by thermal gravity analysis mass spectrometry (TGA-MS) measurement (Figures S3–S5). For the solution-treated sample, a 18 *m/z* peak is detected at around 160 °C (Figure 1b), corresponding to the removal of water molecules from the combination of lattice protons and oxygen in the sample.^{24,26–28}

The occupancy and location of protons in the crystal structure were investigated by neutron diffraction (ND), which possesses high sensitivity for detecting low-atomic-weight elements, such as Li, H,^{29–31} and D.²³ The refinement was performed with the starting model of LMO³² with proton (Figure 1c). By combination of the results from density functional theory (DFT) calculation (Figure S6 and Table S2) and bond valence sum (BVS) maps (Figure S7 and Note S1),

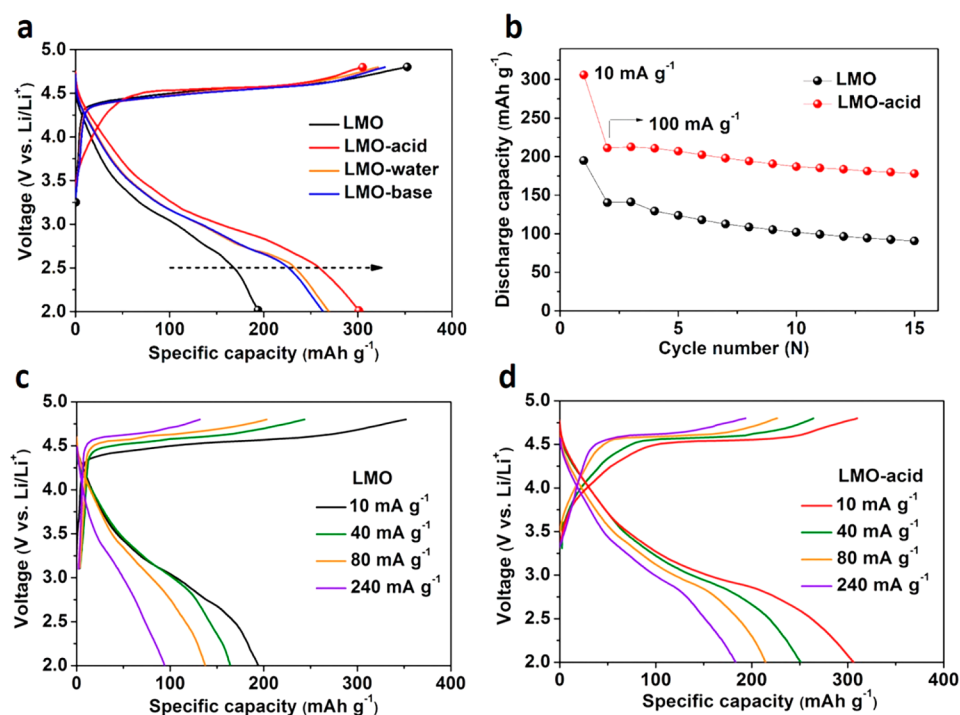


Figure 2. Electrochemical properties of pristine and solution-treated LMO. (a) Initial charge–discharge voltage profiles of pristine and solution-treated LMO samples obtained from Li half-cells at a current density of 10 mA g^{-1} . (b) Cycling performance of the pristine and LMO–acid samples when cycled at 10 mA g^{-1} in the initial cycle and 100 mA g^{-1} in extended cycles. (c, d) Initial charge–discharge voltage profiles of LMO and LMO–acid samples at different current densities.

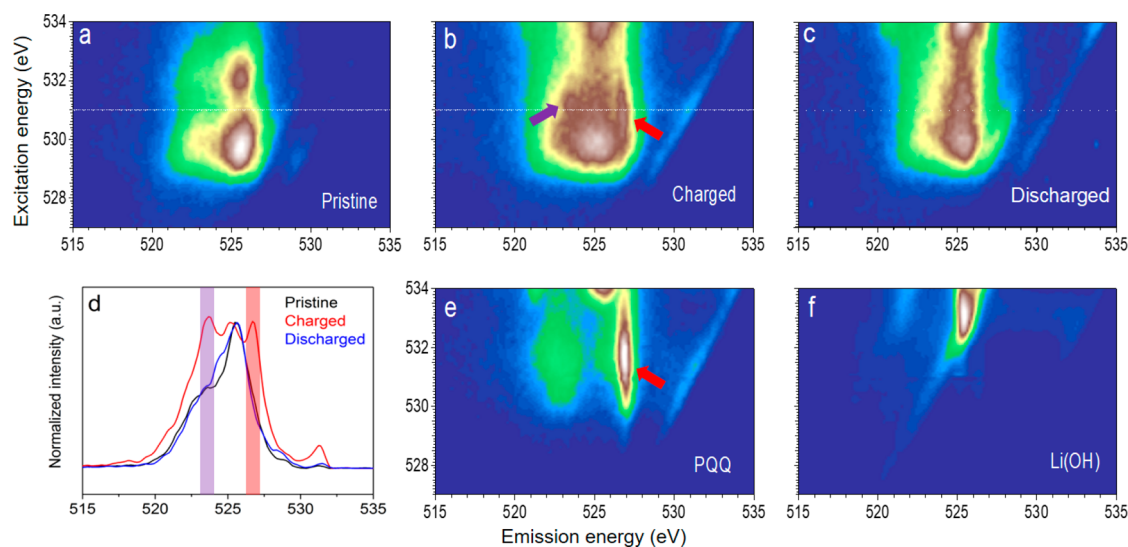


Figure 3. Electronic structures of O probed by mRIXS. (a–c) Mapping and (d) single energy (excitation energy of 531 eV) of O K-edge mRIXS spectra for LMO–acid with different electrochemical states: the pristine, 4.8 V charged, and 2.0 V discharged, respectively. The intensities in (d) are normalized after subtracting the background intensity. The striking oxidized oxygen (purple arrow) and O–H bonding (red arrow) signals are observed in 4.8 V charged LMO–acid. (e, f) Mapping of O K-edge mRIXS spectra for PQQ and Li(OH) references.

the protons are located in Li octahedral vacancies of the Li layers, moving off center toward the oxygen atoms with an O–H distance of $1.120(8) \text{ \AA}$ (as illustrated in Figure 1d). The refinement is improved with the decrease of the R_{wp} value (Tables S3 and S4) for the LMO–acid sample, which supports the existence of protons in the interstitial sites. The content of protons yielded from ND refinement is in the same trend as that of TGA-MS and elemental analysis. The discrepancy of the proton amount from different methods may come from the differences in sensitivities and probe area for protons.

The insertion of protons can be further observed by using solid-state nuclear magnetic resonance (ssNMR) spectroscopy (Figure 1e). Compared with the pristine LMO which shows no ^2H signals, the acid-treated sample displays a dominant isotropic resonance at 415 ppm . According to previous reports,^{23,33,34} a large shift of resonance can be a result of the hyperfine interaction between protons and its adjacent Mn ions, through the intervening oxygen anions. Thus, the peak at 415 ppm is assigned to protons inserted inside the bulk lattice. A minor peak at 301 ppm may come from protons in different

locations (Figure S8), which is consistent with ND results. The peak at around 7 ppm may come from surface absorption.^{33,34}

Therefore, the combined experiments based on TGA-MS, ssNMR, and ND consistently confirm that protons are inserted into the LMO layered structure via the $\text{Li}^+ - \text{H}^+$ exchange process to form LMO-acid through the solution treatment (Table 1). It is also important to note that the O–H distance in the treated sample (1.12 Å) is longer than the typical bond length in OH^- systems (<1 Å). This indicates that the intercalated H^+ does not really bond to O and form an OH^- group.

The initial cycle voltage profiles of the pristine LMO and solution-treated samples are compared in Figure 2a, Figure S9, and Table S5. All samples exhibit a long plateau region at ~4.5 V vs Li/Li^+ , which is mainly ascribed to the removal of Li^+ and oxidation of oxygen anion.^{35,16,36} Compared with LMO, the initial discharge capacity of LMO-acid is as high as 302 mAh g^{-1} with a Coulombic efficiency of 99.2%, which is superior compared to various optimizations of LMO systems in previous reports. In the first 15 cycles, the LMO-acid sample exhibits a higher discharge capacity (Figure 2b). The conventional LMO exists extremely poor cycling,³³ which is associated with many aspects, such as $\text{Mn}^{3+/4+}$ redox participation, Mn dissolution, surface interactions, structural evolutions, and so on.^{7,37,38} As elaborated below, since protonation improves only the oxygen activity, capacity decay remains obvious upon extensive cycles in the LMO-acid system. Further improvements could be gained through other modifications such as surface coating and/or doping, which is outside the scope of this work. Besides, LMO-acid delivers greatly improved rate capability (Figure 2c,d). Meanwhile, the LMO material was also synthesized at a higher temperature (750 °C) with no impure phase, which shows similar electrochemical performance in the initial cycle after acid treatment (Figure S9).

As introduced above, one of the electrochemical issues in LMO is the large initial irreversibility associated with the irreversible oxygen oxidation. The unprecedented improvement of the discharge capacity in LMO-acid indicates an important effect of proton that could stabilize the oxygen activities. Therefore, we provide a comprehensive study of the mechanism of protonation effect on oxygen redox through mRIXS, which has become a tool of choice for studying the bulk oxygen redox reactions.^{39–43} Figure 3 displays the O K-edge mRIXS results on oxygen activities in LMO-acid series samples. Strikingly, two features emerge in the 4.8 V charged LMO-acid electrode (Figure 3b). One is the known feature at 523.7 eV emission energy (purple arrow), which indicates lattice oxygen is oxidized into reversible oxidized oxygen during charging.^{39–41} The evolution could be clearly seen in the RIXS cuts shown in Figure 3d. In contrast, the pristine LMO series without proton insertion does not display the same oxygen features (Figure S10), whose specific meaning and analysis are not a topic of this work. Upon discharge, this oxygen feature fades out, indicating a reversible oxygen reduction reaction. The significantly improved Coulombic efficiency and the reversible evolution of the oxidized oxygen mRIXS feature in our protonated LMO-acid directly confirm that the lattice oxygen redox is largely reversible in LMO-acid.

Another strong feature (red arrow in Figure 3b) has not been reported previously, which is thus critical for understanding the protonation effect. We investigated the origin of this new feature through comparison with several reference

compounds. It is worth noting that, as elaborated below, such a feature is associated with specific chemical bonding state that may exist in some organic species such as glue or binder; we therefore have tested the results of the electrodes at different electrochemical states more than once by different experimentalists to make sure that the systematic evolution of this feature is intrinsic and consistently shows up in our LMO-acid samples only at the charged state. Figures 3e and 3f display the mRIXS results collected from pyrroloquinoline quinone (PQQ) and $\text{Li}(\text{OH})$ reference samples. The selection of these two sets of references is inspired by their very different O–H bonding: PQQ is a known redox cofactor in biological systems with H^+ only moderately bonded to the oxygen. Actually quinone-based materials have recently been reported to be good battery electrodes with H^+ and other alkali ions reversibly bound and unbound from oxygen, again indicating a moderate bonding of H^+ to the oxygen.^{44,45} On the contrary, the O–H in $\text{Li}(\text{OH})$ is a well-formed $(\text{OH})^-$ group with strong bonding that is hard to break. The mRIXS result of PQQ (Figure 3e) displays the clear signature of the moderate O–H bonding configuration at exactly the same emission energy of 527 eV as that of the feature in our protonated LMO electrode (red arrows in Figure 3b,e). In sharp contrast, such a feature is completely missing in the $\text{Li}(\text{OH})$ sample (Figure 3f) with all signals at relatively much higher excitation energies (vertical axis). Therefore, the comparison between the LMO-acid electrode and the PQQ/ $\text{Li}(\text{OH})$ references provides a direct evidence that the protons introduced into LMO-acid is only moderately coupled to the oxygen, which is consistent with the calculation and ND results. The observation that such a feature is strong in charged electrodes indicates that (i) the intercalated protons are not extracted in the charged state and (ii) more importantly the interaction between protons and oxygen gets enhanced in the oxidized states, which is exactly the state that needs the stabilization of the oxidized oxygen. Such a spontaneous enhancement of O–H bonding in the charged state naturally stabilizes the oxidized oxygen through the inductive effect that has long been known in other battery electrodes like LiFePO_4 .^{18–20}

To further understand the effect of protons on oxygen redox reaction, the DFT calculations were performed with the model of LMO and $\text{Li}_{1.75}\text{H}_{0.25}\text{MnO}_3$ (LHMO) (Figure 4a,b and Figure S6), in which the proton is at the site of (0.3799, 0.5000, 0.6008). From the calculated density of states (DOS) results, the band gap of DOS in LHMO decreases compared to that in pristine LMO, consistent with the lower beginning potential in LHMO based on both experimental and theoretical results (Figure S11). Unlike pristine LMO, which is well ordered and has only two environments for the oxygen atoms (i.e., O 4i and O 8j sites), a variety of local oxygen environments exist in LHMO. The oxygen atoms are thus labeled from O1 to O12 according to the different distances between O and H atoms. The proton with high polarization nature forms O–H bonding with O10, which places the DOS for O10 relatively down in energy (Figure S11). The possibility of O_2 release at various delithiation stages was calculated by the Gibbs free energy (Figure 4a, Figure S12, and Note S2). The value of ΔG is below zero at highly charged states, which means the lattice oxygen tends to release; this is consistent with the observation of oxygen gas at high level of delithiation.^{15,46,47} However, after $\text{Li}^+ - \text{H}^+$ exchange, even at high charged states ($x = 1.25$ and 1.5), the value of ΔG increases, which suggests it is more difficult for the oxygen to

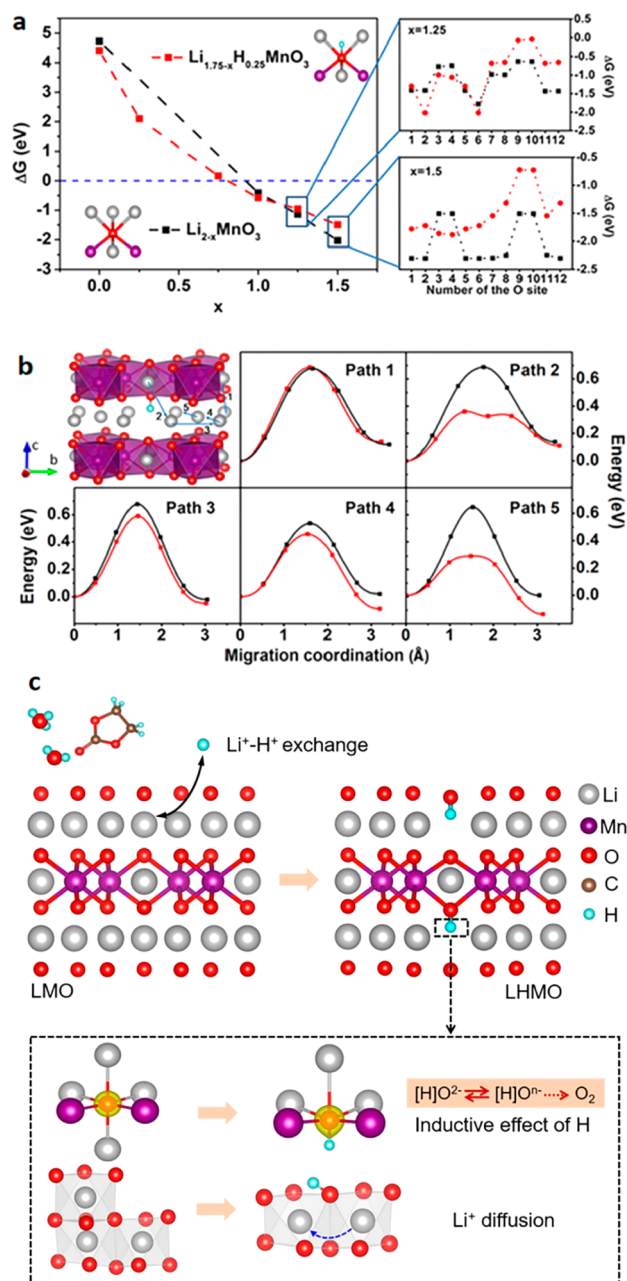


Figure 4. Intrinsic mechanism of proton insertion. (a) Gibbs free energy for oxygen release reaction during delithiation process for $\text{Li}_{2-x}\text{MnO}_3$ and $\text{Li}_{1.75-x}\text{H}_{0.25}\text{MnO}_3$ ($x = 0, 0.25, 0.75, 1.0, 1.25,$ and 1.5). (b) Schematic illustration of the possible Li^+ diffusion paths. The paths are shown by blue lines connecting two Li sites and labeled from 1 to 5. The migration barriers are compared in LMO (black) and LHMO (red). (c) Schematic illustration for reaction mechanism. The protons insert into the layered structure via chemical/electrochemical treatment. During cycling, the oxygen activity could be modified with the inductive effect from the proton and effective Li^+ diffusion, leading to a controlled oxidation of the oxygen and reversible oxygen redox reactions.

release from LHMO, especially for the oxygen atoms close to protons. This protonation effect is in perfect agreement with our mRIXS observations, which show a reversible evolution of the oxidized lattice oxygen feature with high discharge capacity.

Considering that the electrochemical process is dependent on both the charge compensation and Li^+ diffusion process, the

behavior of Li^+ diffusion is exploited here. The results (Figure 4b and Table S6) show proton insertion facilitates the Li^+ diffusion via reducing the energy barrier for Li^+ hopping. Noticeably, the promoted Li^+ diffusion may also accelerate the reduction kinetics of peroxy-like species.⁴⁸ This additional benefit explains the experimental findings of the improved rate performance of LMO–acid (Figure 2c) and increased Li^+ diffusion coefficient (Figure S13).

In summary, a series experimental and theoretical studies are performed toward the protonation effect on electrochemical performance of the representative LMO system. The special role that protons play on the electrochemical performance of LMO is schematically summarized in Figure 4c. Partial substitution with protons alters the oxygen activities through an effective inductive effect. Such a modified oxygen activity leads to outstanding initial cycle performance with greatly improved discharge capacity of 302 mAh g^{-1} and an unprecedented Coulombic efficiency of 99.2%. The demonstrations and characterizations in this work not only reveal and explain the critical effect of protonation on electrochemistry involving oxygen redox reactions; more importantly, it paves a new way for the fundamental understanding on stabilizing oxygen redox reactions, which is critical for optimizing high-capacity cathode materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.9b21738>.

Methods; figures for XRD patterns of the pristine and solution-treated LMO; SEM images; TGA data and TGA-MS data; MS data and XRD patterns of the pristine and solution-treated LMO samples after TGA-MS test; schematic representation of the optimized model; schematic of LMO with protons insertion from BVS maps; fitted ^2H MAS NMR spectra obtained at 50 kHz for deuterated LMO–acid sample; electrochemical performance; mapping of O K-edge mRIXS spectra for LMO; DFT studies on the intrinsic mechanism of protons insertion; convex hull of at different Li concentrations; Nyquist plots of cells after initially discharged to 2.0 V; tables for the pH values of solutions during the solution-treating process; comparison of energy for LHMO with protons in different sites; refinement results for the solution-treated and deuterated LMO; refined crystallographic parameters; electrochemical data in initial cycle; calculated activation barriers for different Li^+ diffusion paths; notes for the calculation of BVS maps; calculation on Gibbs free energy for the oxygen evolution (PDF)

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Notes

The authors declare no competing financial interest.

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