First Principles Modeling of Mn(II) Migration above and Dissolution from Li$_x$Mn$_2$O$_4$ (001) Surfaces

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Abstract

Density functional theory and ab initio molecular dynamics simulations are applied to investigate the migration of Mn(II) ions to above-surface sites on spinel Li$_x$Mn$_2$O$_4$ (001) surfaces, the subsequent Mn dissolution into the organic liquid electrolyte, and the detrimental effects on graphite anode solid electrolyte interphase (SEI) passivating films after Mn(II) ions diffuse through the separator. The dissolution mechanism proves complex; the much-quoted Hunter disproportionation of Mn(III) to form Mn(II) is far from sufficient. Key steps that facilitate Mn(II) loss include concerted liquid/solid-state motions; proton-induced weakening of Mn-O bonds forming mobile OH$^-$ surface groups; and chemical reactions of adsorbed decomposed organic fragments. Mn(II) lodged between the inorganic Li$_2$CO$_3$ and organic lithium ethylene dicarbonate (LEDC) anode SEI components facilitates electrochemical reduction and decomposition of LEDC. These findings help inform future design of protective coatings, electrolytes, additives, and interfaces.

keywords: lithium ion batteries; lithium manganese oxide; solid electrolyte interface; ab initio molecule dynamics; computational electrochemistry
I. INTRODUCTION

Lithium ion batteries (LIB) featuring transition metal oxide cathodes and organic solvent-based electrolytes are currently the energy storage devices used to power electric vehicles. Spinel lithium magnesium oxide (Li$_x$Mn$_2$O$_4$ or “LMO”) and nickel-doped high voltage spinel (Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$, “LNMO”) are promising cathode materials. One impediment to their deployment is the dissolution of transition metal ions, which can diffuse to the anode, corrupt the solid electrolyte interphase (SEI) films protecting the graphite anode, and accelerate battery capacity fade. Such degradation is particularly severe at elevated temperature for LNMO and LMO. Cation doping, surface coatings, and other means have been applied to reduce Mn dissolution, but have so far not completely eliminated it. Transition metal loss from other cathode materials is also widely documented. Understanding the detailed Mn dissolution mechanism is crucial for new design principles that can further mitigate this degradation route.

Mn dissolution has often been discussed in connection with Hunter’s disproportionation mechanism,

$$2\text{Mn(III)} \rightarrow \text{Mn(II)} + \text{Mn(IV)},$$

associated with under-coordinated Mn(III) on LMO surfaces. Early computational studies have focused on demonstrating the existence of Mn(II) on LMO surfaces under ultrahigh vacuum (UHV) conditions. A recent study, which includes explicit liquid solvent molecules, reveals that the solvent can coordinate to surface Mn(III) ions, completing their coordination shells, converting them to Mn(IV), and removing the driving force for disproportionation. More in-depth atomic-lengthscale studies of Mn dissolution are clearly needed.

Extensive spectroscopic and imaging studies have been conducted to understand degradation on cathode oxide material surfaces. The existence of liquid electrolyte decomposition products, forming very thin SEI (sometimes called cathode electrolyte interphase or CEI) films on the cathode, has been amply demonstrated. The overall speciation of electrolyte decomposition products have been reported, but elucidation of the atomic structure and chemistry of the active material/SEI interface, expected to be most relevant to Mn dissolution, remains a challenge. The composition of surface films is likely not static but depends on charge/discharge conditions. Scanning transmission electron microscopy (STEM) and other techniques have demonstrated that cycled layered
FIG. 1: (a)-(d) Schematic depictions of key processes studied in this work. (a) A layer of decomposed EC molecular fragments (green) on LMO (001); (b) Mn(II) migration to above-surface sites; (c) Mn(II) dissolution; (d) Mn(II)-assisted reductive decomposition of LEDC to form CO$_2^-$.

Electrolyte electrolyte

nickel/manganese/cobalt (NMC) oxides undergo surface reconstruction to a Mn(II) rock salt phase. Surface reconstruction and phase transformation have also been reported for spinels at elevated temperatures in accelerated aging studies. Under more standard battery operation conditions and at shorter times, Li et al. have applied in-situ soft X-ray Absorption Spectroscopy (XPS) to reveal enhanced Mn(II) content at LNMO/liquid elec-
trollyte interfaces during battery charging, and reduced Mn(II) surface concentration during discharge. This is paradoxical, as more Mn(IV) are expected during the charging process. They interpret the observation as evidence that Mn ions on the electrode surface reacts with the liquid electrolyte.

Other studies have further emphasized the role of specific organic fragments on Mn dissolution. Jarry et al. have applied fluorescence spectroscopy to identify β-diketonate chelating to dissolved Mn, and have proposed a detailed mechanism for the formation of this species from the dimethyl carbonate (DMC) cosolvent used in organic battery electrolytes. Meanwhile computational studies have reported decomposition of ethylene carbonate (EC) on two LMO surface facets. These studies report EC oxidation, ring opening, and proton transfer to LMO surfaces. They omit DMC and do not report β-diketonate formation. However, it can be argued that Mn-chelating organic species other than β-diketonate also facilitate Mn dissolution, even if they lack fluorescence signatures and are not readily detected.

These advances make it timely to revisit the mechanism associated with Mn loss from spinel oxides. We distinguish between two processes: Mn(II) migration to non-crystallographic sites above the surface, and subsequent Mn(II) dissolution, as shown schematically in Fig. 1. The (001) surface of stoichiometric LiMn$_2$O$_4$ in vacuum exhibits Li-sites half a lattice plane above surface oxygen ions. Hence it is not surprising that Mn(II) may occupy vacant surface Li-sites as dissolution intermediates. Local minimum states associated with transition metal ion desorption from mineral surfaces immersed in water have also been reported.

We apply ab initio molecular dynamics (AIMD) simulations alongside potential-of-mean-force (PMF) free energy techniques to calculate the barriers associated with these steps. A precedent for this study is Ref. which focuses on LMO dissolution in an aqueous, not organic, electrolyte. That work predicts a dissolution timescale which exceeds battery operation duration for 4-coordinated Mn(III) on the (001) surface. A major difference is that in water, auto-ionization of H$_2$O molecules can release H$^+$ and OH$^-$ along the reaction pathway to help break Mn-O bonds. In organic solvents, that pathway is unavailable, and the dissolution mechanism is expected to be more intricate.

We focus on the LMO (001) surface immersed in an EC liquid. Mn ions are exposed on clean (001) facets. We decorate LMO (001) with partially decomposed EC fragments
and H\(^+\) which are previously predicted,\(^{21}\) and find that these species facilitate transition metal motion. Note that reconstructed (111) is the most stable LMO facet.\(^{40-43}\) However, to model Mn dissolution from (111), it would first be necessary to simulate the loss of surface O\(^2^-\), because all Mn ions reside in subsurface layers.\(^{40-43}\) For similar reasons, we have not considered Li\(_2\)CO\(_3\) films which have been reported on cycled cathode surfaces.\(^{26,29,44,45}\) Since there is no empirical evidence that Mn(II) diffuse through the inorganic SEI components like Li\(_2\)CO\(_3\),\(^{46,47}\) the carbonate layer would have to crack or be oxidatively destroyed during charging for Mn to dissolve.\(^{48,49}\) Along these lines, atomic layer deposition (ALD)\(^{15-17,50-53}\) and other surface protection coatings\(^{54}\) have been applied to reduce Mn loss. One way to further improve ALD-coated electrode is to make them resistant to reactions with the liquid electrolyte. The extent to which organic electrolyte corrodes ALD protective layers can be examined with the computational techniques applied in this work (see Sec. [IV]).

In our modeling work, the exiting Mn(II) is coordinated to a F\(^-\) anion, which originates from decomposition of the standard battery electrolyte counter-ion PF\(_6^-\). In the literature, hydrofluoric acid (HF), which arises from PF\(_6^-\) reaction with trace H\(_2\)O in the liquid electrolyte, has been strongly correlated with increased Mn(II) dissolution.\(^{12,57-59}\) In the supporting information (S.I.) document, we show that HF is not needed to acidify LMO surface to yield surface OH\(^-\) groups that weaken transition metal-binding; trace water already fills that function. Hence it is reasonable to speculate that a main role of HF is to provide F\(^-\) that binds to Mn, at least during the exit from the cathode.\(^{56}\) Some evidence of MnF\(_2\) in the anode SEI has been reported.\(^{55}\) However, MnF\(_2\) XPS signatures are similar to those of LiF, which complicates its detection on cathode surfaces.\(^{45,60}\)

Finally, we address one possible way Mn(II) ions which have diffused through the separator into anode SEI films may disrupt SEI functions.\(^9\) The structure, dispersion, and location of Mn inside the anode is controversial (see Shkrob et al.\(^{46}\) for a critical overview); here we only focus on its catalytic function. Two recent studies\(^{46,47}\) have concluded that Mn exist as isolated Mn(II) complexes situated between inorganic (e.g., Li\(_2\)O, LiF, but especially\(^{46}\) Li\(_2\)CO\(_3\)) and organic (e.g., lithium ethylene dicarbonate, LEDC) SEI components. It is proposed that solvent molecules can diffuse through the porous organic region to coordinate to Mn(II) ions and electrochemically reduce them.\(^{47}\) Mn(II) thus act as conduits for e\(^-\) transfer to solvent molecules. However, this scenario requires pores in the SEI large enough to transmit solvent molecules, which have not been reported in classical force field molec-
ular dynamics simulations. Here we show that Mn(II) plus excess electrons can instead decompose LEDC in redox reactions (Fig. 1d). This mechanism dovetails with recent computational demonstrations that SEI components are not as chemically stable as generally believed. Other experimental studies have suggested the existence of transition metal particles inside the anode SEI. Although this is disputed by electron paramagnetic spectroscopy, we also report simulations of LEDC decomposition on Ni(111) surfaces in the S.I. to address this possibility.

This manuscript is organized as follows. Sec. II describes the methods used and includes a discussion on the challenges of modeling solid-liquid interfaces. Sec. III discusses the results. Sec. IV extrapolates the predictions to design principles or protective coatings. Sec. V concludes the paper with a summary of the main findings.

II. METHODS

A. Computational Challenges and Perspectives

First we briefly discuss the limitations of AIMD modeling of buried liquid-solid interfaces. Imaging and spectroscopic techniques like TEM and XPS have yet to provide atomic lengthscale-resolution structural data that should be the starting points of such calculations. In particular, the precise surface features exposed at the interface, the speciation of decomposed electrolyte fragments (“SEI”) adsorbed on the cathode, the thickness of such SEI layers, and the identity and surface concentration of structural defects that may enhance Mn dissolution, have not been elucidated. In electrochemical settings, there is the additional challenge of determining the surface charge density consistent with the applied voltage.

Our approach is to create model surface structures and study their most relevant properties. In this case, the key metrics are Mn surface migration and dissolution barriers. If the predicted time frames exhibit large discrepancy with measurements, the models are modified. Thus our interfacial model structures should be considered plausible scenarios. Even with this caveat, these calculations are valuable for providing insights into battery degradation at the atom-by-atom lengthscale and bond-breaking sequence-of-event detail not yet available to measurements. These insights will help guide future design of cathode protective coatings and strategies. This work sidesteps the issue of the applied voltage. LMO is a
small-polaron conductor, and the Fermi level of the metallic current-conductor attached to it should be in equilibrium with polaron formation energies at the solid electrode/liquid electrolyte interface.

B. Simulation Details

Finite temperature \textit{ab initio} molecular dynamics (AIMD) simulations are conducted under solvent-immersed conditions. A few static ultrahigh vacuum (UHV) DFT calculations, performed at T=0 K, are also reported. All calculations apply periodical replicated simulation cells, the Vienna Atomic Simulation Package (VASP) version 5.3,\textsuperscript{68–71} and the Perdew-Burke-Ernzerhof (PBE) functional.\textsuperscript{22} Modeling spinel Li\textsubscript{x}Mn\textsubscript{2}O\textsubscript{4} requires spin-polarized DFT+U augmented treatment of Mn 3d orbitals.\textsuperscript{23} The U and J values depend on the orbital projection scheme and DFT+U implementation details; here U − J =4.85 eV is chosen in accordance with the literature.\textsuperscript{74,75} A 400 eV planewave energy cutoff and Γ-point Brillouin zone sampling are imposed. The bulk LiMn\textsubscript{2}O\textsubscript{4} crystal is antiferromagnetic (AFM). We have imposed an AFM ordering on alternate Mn planes along the (011) direction. The electron spin on each Mn ion is examined to determine Mn charge states.

Static geometry optimization simulation cells are of dimensions 34×11.88×11.88Å\textsuperscript{3}. They have a Li\textsubscript{6}Mn\textsubscript{20}O\textsubscript{32}H\textsubscript{8} cathode oxide stoichiometry plus eight EC fragments (C\textsubscript{3}O\textsubscript{4}H\textsubscript{3}). A 10\textsuperscript{−4} eV convergence criterion is imposed.

The AIMD simulation cell is similar to the static cells, but the z-dimension perpendicular to the interface is increased to 46.5 Å\textsuperscript{3}. 32 EC molecules are confined in the space between the organic fragment-decorated oxide surfaces. The cell is pre-equilibrated using simple molecular force field and Monte Carlo (MC) simulations.\textsuperscript{21,76} AIMD simulations start from the final MC-generated configuration. A 10\textsuperscript{−6} eV convergence criterion is imposed at each AIMD Born-Oppenheimer time step. The trajectories are kept at an average temperature of T=450 K using Nose thermostats. Tritium masses on EC are substituted for proton masses to permit a time step of 1 fs. Under these conditions, AIMD trajectories exhibit drifts of less than 2 K/ps. The coordinates and velocities obtained from a 11.5 ps AIMD equilibration trajectory are used in potential-of-mean-force (PMF or \(\Delta W(R)\)) calculations.

All PMF simulations apply two-body reaction coordinates of the form \(R=|\textbf{R}_{\text{Mn}} − \textbf{R}_{\text{O}}|\) or \(R' = z_{\text{Mn}} − z_{\text{Mn'}}\), where \textbf{R} is the position vector of an atom and \(z\) is its position perpendicular
to the interface. The two coordinates are used in Mn surface migration (Sec. III B) and dissolution (Sec. III C) studies, respectively. The specific atoms involved will be described in Sec. III. Harmonic penalties $B_o(R - R_o)^2/2$ or $B_o(R' - R_o)^2/2$ are added to DFT+U energies in a series of windows with a progression of $R_o$ values, separated by 0.3 Å, spanning the reaction paths. $B_o$ is set at 4 eV/Å². $\Delta W(R) = -k_B T \log P(R)$ where $P(R)$ is the probability that a $R$ value is observed, after adjustment to remove the effect of the umbrella sampling constraint. A similar procedure is used for the coordinate $R'$. The elevated temperature is only adopted to accelerate the molecular dynamics. The final $\Delta W(R)$ and $\Delta W(R')$ expressions assume a temperature of $T=300$ K.

Along the $R'$-coordinate, each window is initiated by taking a configuration 1 ps into the trajectory from the previous window. For the $R$-coordinate, a new window is generated a few ps into the trajectory from three windows away ($\Delta R_o=-0.9$ Å). These tentpole windows are then used to create starting configurations in adjacent windows with $\Delta R_o=\pm 0.3$ Å. This scheme is adopted to pre-estimate the size of the barrier before computing the entire $\Delta W(R)$. The first 1 ps in each window is used for equilibration and discarded. Statistics are collected for the next 10 ps. Statistical uncertainties in $W(R)$ are estimated by splitting the trajectory in each window into five, calculating the standard deviation, and propagating the noise across windows assuming gaussian statistics.

We do not apply the popular metadyamics method, based on non-equilibrium trajectories, to compute the PMF. The main reason is that Mn migration involves many moving parts, and diffusive molecular motions are critical. The umbrella sampling approach used herein permits us to run trajectories of variable lengths that are not determined ahead of time. This allows a more systematic treatment of diffusive motion.

In the absence of $F^-$ ions, our PMF calculation yields a barrier that is too high compared to experimental timescales. See the S.I. To obtain a lower barrier, we have manually added a $F^-$ anion coordinated to the migrating or “tagged” Mn. A further 1.4 ps AIMD simulation is conducted for equilibration purpose, and a PMF calculation is restarted with this added $F^-$. 

A different set of AIMD simulations involve the interface between LEDC and Li$_2$CO$_3$ (Fig. III). The cell size is 16.59×19.79×30 Å$^3$. The lateral cell dimensions are those of the Li$_2$CO$_3$ (001) surface cell. A bilayer of LEDC, which exhibits molecular “crystal structure” with slightly smaller lattice constants, is placed on the lithium carbonate surface,
and the atomic coordinates are optimized. Unlike cathode simulations, modeling of the LEDC/Li$_2$CO$_3$ interface includes a vacuum region in the simulation cell.

Finally, some limited thermodynamics calculations are conducted using the DFT/PBE0 functional.$^{28}$

III. RESULTS

A. Ultrahigh Vacuum Condition Calculations

Figs. 2a-b depict two perspectives of the dry LMO (001) surface optimized at T=0 K. Each of the four adsorbed, partially decomposed EC fragments coordinates to two surface Mn ions via two of its three CO$_3^-$ oxygens. Thus initially, each surface Mn ion is coordinated to four LMO framework O$^{2-}$ and/or OH$^-$ plus a O atom of the EC fragment. It would have been 6-coordinated except for the surface O-vacancies, created when each EC fragment abstracts one O$^{2-}$ from the (001) surface and donates a H$^+$ to form Mn-OH-Mn bridges.$^{21,33}$ The multi-proton configuration depicted in Fig. 2a-b optimizes the energy. This is the starting point of liquid-state Monte Carlo pre-equilibration of liquid EC configuration, during which the LMO and decomposed EC fragment atoms are frozen.

Fig. 2c examines the possibility that two Mn-OH groups may disproportionate into Mn-O-Mn and H$_2$O. The reaction is endothermic by 1.21 eV. While the removal of a surface O$^{2-}$ by two H$^+$ would have yielded Mn ions which are even more under-coordinated, and facilitated their dissolution, no justification for H$_2$O formation is found. This behavior is in contrast to the clean LMO (001) surface saturated with OH$^-$ groups.$^{21}$

B. Migration of Mn to an Above-Surface Position

During AIMD equilibration (before any PMF harmonic constraint is imposed), a few of the decomposed EC fragments have one of their O atoms collapse on to LMO surface oxygen vacancy sites, leaving some Mn uncovered. This allows those Mn to be coordinated to the electrolytes and actually facilitates Mn removal. Mn must ultimately bind to electrolyte molecules (EC and/or anions) to dissolve. During Mn departure from the surface, the EC fragment O atoms weakly-bound to LMO can be readily pulled off the surface again. As
FIG. 2: (a)-(b) Two perspectives of the 4 decomposed EC molecules covering each surface of the periodically replicated, dry LMO (001) simulation cell; (c) attempt to create a H$_2$O molecule. The color key is the same as in Fig. 1.

discussed in Sec. II, we tag one such exposed Mn as the dissolving species, add a F$^-$ to it, and use the harmonic constraints inherent to $\Delta W(R)$ simulations to progressively pull it off its initial lattice site. See Fig. 3a, which also depicts the reaction coordinate $R$.

The $\Delta W(R)$ associated with the above-surface migration of this Mn is shown in Fig. 4. Fig. 3b depicts the tagged Mn ion near the onset of the $\Delta W(R)$ plateau. It is now 4-coordinated: to the F$^-$, a decomposed EC fragment, and a O$^{2-}$ and a OH$^-$ on the LMO surface. The carbonyl oxygen of an intact EC molecule that has diffused to the vicinity of the Mn is only slightly further away, not shown in this snapshot; it binds to Mn in part of the trajectory. Fig. 3c depicts a configuration taken from the plateau window. The Mn ion has “rolled over” to the other side of the axis formed by the surface O$^{2-}$ and OH$^-$ (see Fig. 1b for illustration).

A harmonic constraint is not needed or used in the plateau sampling window (Fig. 3d-
FIG. 3: (a)-(f) Snapshots along the reaction profile of Fig. 4. Panel (a) depicts the same configuration as (b) with a 90° rotation. The color scheme is as in Fig. 2. O and H atoms are depicted as stick figures; only Mn, Li, and F ions are spheres, and intact solvent molecules are removed for clarity. The tagged Mn ion is in black. The two blue dashed lines represent Mn(II)-O (“R”) and Li⁺-O distances (see text).

e); the system is metastable in this region for at least 10 ps, showing that it is a reaction intermediate. The onset of the plateau coincides with the activation of concerted solid- and liquid-state motions. At this point, the tagged Mn has become sufficiently far from the LMO surface that a subsurface Li⁺ ion can reversibly occupy the site vacated by this Mn (Fig. 3e). The time-dependence of this motion is illustrated by the red line in the inset of Fig. 4. The distance between this Li⁺ and a subsurface O²⁻ to which it is initially coordinated fluctuates between 2 and 4.5 Å within picosecond time scales as the Li⁺ moves back and forth. For a comparison, the black line corresponds to the pre-plateau sampling window “C” (Fig. 3c), where the tagged Mn ion still repels Li⁺ intrusion. The corresponding Li⁺/O²⁻ distance
FIG. 4: Free energy profile of Mn migration to above the surface. “A”-“F” correspond to the panels in Fig. 3a-f. Inset: distance between a subsurface Li$^{+}$ and a subsurface O$^{2-}$ ion initially coordinated to it. The black and red lines are for sampling windows C and D/E, respectively.

fluctuates around $\sim$2 Å, the typical length of a stable Li$^{+}$/O$^{2-}$ ionic bond.

Before PMF constraints are applied, all Mn on the surface exhibit +3 charge states in every snapshot we have examined. Thus no stable Mn(II) is found on the liquid-immersed, EC fragment-decorated LMO (001) surface. In the absence of the F$^{-}$ (S.I.), when the Mn-O$^{2-}$ distance $R$ is 2.5 Å or beyond, the tagged cation is found to have gained an $e^{-}$ from other Mn(III) to become a Mn(II) in all AIMD snapshots examined. Fig. S1 shows that such a displacement costs less than 0.25 eV. At this point in the reaction profile, the system is at least $\sim$1.2 eV from reaching the end-of-reaction point (S.I.). This emphasizes that, in terms of dissolution kinetics on this surface, Hunter disproportionation is far from sufficient.

When F$^{-}$ is present in the simulation cell (Figs. 3-4), the tagged Mn can fluctuate between
+2 and +3 charge states in AIMD snapshots taken about 0.7 ps apart. In the $R \sim 3$ Å and plateau windows in Fig. 4, this Mn is a Mn(II) in 53% and 72% of the snapshots, respectively.

Comparing $\Delta W(R)$ at $R = 2.0$ Å and 5.5 Å, the free energy barrier $\Delta G^*$ is determined to be 1.25±0.09 eV. The uncertainty corresponds to twice the standard deviation. The predicted $\Delta G^*$ is consistent with a reaction rate of one every 27000 years at room temperature if a canonical kinetic prefactor of $10^{12}$/s is assumed. Experimentally, Mn dissolution is observed within a much shorter time frame. Therefore $\Delta G^*$ is overestimated. A 1.05 eV barrier would correspond to a more reasonable 117-hour rate at room temperature. For a comparison, the dissolution barrier of 4-coordinated Mn(III) at the LMO (001)/water interface has been predicted to be either 1.8 or 1.4 eV, depending on whether a rescaling factor is used. These values correspond to Mn ejection into liquid water without going through an intermediate. In principle, the “coordination number” reaction coordinate used in Ref. 39 can support a two-step mechanism where Mn settles into an above-surface, non-crystallographic intermediate, but the free energy valley associated with this may be too small to detect.

Imposing harmonic biases with larger $R_o$ does not lift the tagged Mn ion into the liquid electrolyte because the reaction coordinate $R$ allows the Mn to slide along the surface instead. Imposing a constraint on the Li$^+$-subsurface O$^{2-}$ distance (inset of Fig. 4), only, leads to larger $R$ values, but the F$^-$ anion now falls onto the oxide surface (Fig. 3f). Since F$^-$ is not part of any reaction coordinate, this event is irreversible and prevents further free energy calculations.

The existence of Mn(II) above the surface oxygen plane, coordinated to decomposed organic fragments, appears consistent with the interpretation of Ref. 31. This experimental work emphasizes enhancement of Mn(II) concentration at the liquid/solid interface during battery charging, where the cathode voltage is high and more electrolyte decomposition should occur. One caveat is that Fig. 4 seems to suggest that the free energy change ($\Delta G$) of Mn surface migration is identical to the barrier value ($\Delta G^*$). If so, $\Delta G = 1.25$ eV would imply an extremely small population of Mn(II) on the surface. This argument ignores further steps, beyond the scope of our calculations, that can stabilize surface Mn(II). One is the continuous diffusion of Li$^+$ ions from the bulk oxide region to the surface, occupying the original Mn surface site, blocking Mn return, and yielding a favorable entropy change. This is especially likely during charging when Li$^+$ are being de-intercalated. The concerted diffusion of a
chain of Li\(^+\), reminiscent of the “knock-on” effect in Li\(_2\)CO\(_3\),\(^{77}\) is at present beyond AIMD studies. This is because Li\(^+\) bulk diffusion exhibits barriers of 0.2-0.6 eV inside LMO.\(^{79-81}\) Such barriers, although not excessive, correspond to Li\(^+\) motion time-scales that exceed AIMD trajectory lengths, unless the non-equilibrium metadynamics technique is used to deal with all possible Li\(^+\) diffusion degrees of freedom. Another Mn stabilization scenario is the diffusion of EC molecules or surface organic fragments to complete the octahedral Mn(II) solvation shell. The tagged Mn is undercoordinated in Fig. 3c. Steric hindrance and slow EC diffusion have likely prevented it from reaching 6-coordination so far in the trajectory. Note that Ref. 31 involves LNMO while our model is Ni-free; therefore quantitative agreement should not be expected.

C. Mn(II) Dissolution from the LMO Surface

This subsection describes the dissolution of the above-surface Mn ion into the liquid electrolyte. For this purpose, we assume this configuration is at zero free energy, due to stabilization events not included in Sec. III B, and ignore the work done to arrive at it.

We start with the unconstrained configuration shown in Fig. 3e, and switch to a different reaction coordinate, \(R' = |z_{\text{Mn}} - z_{\text{Mn}'}|\), where (Mn’) is another Mn on the (001) surface layer (Fig. 5a). In most of the sampling windows in this PMF calculation, the tagged Mn is in the Mn(II) charge state. This Mn ion is initially coordinated to a surface O\(^2-\) and a surface OH\(^-\) in Fig. 5a, in addition to a F\(^-\) and a decomposed EC fragment. To accelerate dissolution, we manually move a H\(^+\) from another OH\(^-\) group on the same surface to the O\(^2-\) coordinated to that Mn. The exiting Mn is now coordinated to two surface OH\(^-\) groups (Fig. 5b). This mimics the effect of either proton migration or further solvent degradation-induced donation of H\(^+\) to the surface. Electrostatically, it is reasonable that H\(^+\) preferentially binds to an O\(^2-\) bridging a Mn(II) and a Mn(III) ion rather than an O\(^2-\) bridging two Mn(III) on the surface.

Figs. 5c-d are taken from a trajectory in a sampling window with an umbrella constraint centered around \(R_o = 4.4\) Å. The average free energy of this window is \(~0.88\) eV (Fig. 6). These panels depict the before-and-after snapshots of an unexpected reaction that accompanies Mn(II) release into the liquid electrolyte. In Fig. 5e, taken at the beginning of the trajectory, one of the two Mn(II)-OH\(^-\) bonds is already broken. At this stage, AIMD simu-
FIG. 5: (a)-(d) Snapshots along the Mn(II) dissolution reaction coordinate $R'$. Panel (a) depicts the configuration in Fig. 3e rotated by 90 degrees. In (b), a proton is manually moved to the O$^{2-}$ bonded to the surface Mn(II), and the configuration is re-equilibrated. The O atoms of the two relevant OH$^-$ groups, only, are depicted as spheres. The H-atom of one of the these OH$^-$ groups is obscured in panel (c). The color scheme is as in Fig. 3. In addition, both the tagged Mn and the surface Mn used to define the new coordinate $R'$ are in black.

Simulations have led to substantial OH$^-$ re-arrangement. Comparison with Fig. 5b reveals that the OH$^-$ detached from the Mn(II) has moved more than 2 Å along the surface. In fact, the $R' < 3$ Å part of (Fig. 5) is recomputed by starting from such a OH$^-$ displaced configuration and reducing the constraint distance $R_o$ progressively in new sampling windows.

The remaining OH$^-$ tethering the Mn(II) to a surface Mn(III) is in the vicinity of an EC fragment adsorbed to the surface (Fig. 5c). 3.6 ps into the trajectory associated with this window, the Mn(II) dissociates from this OH$^-$. At 4.9 ps, the Mn(II)-OH distance shrinks back to 2.9 Å. At that point, instead of reforming the Mn(II)-OH$^-$ ionic bond, the OH$^-$ attacks the -CHO group of the EC fragment nearby to form a -CH(OH)(O$^-$) motif. The final configuration is depicted in Fig. 5d, taken 11 ps into the trajectory. The unusual species, like a -COOH group attacked by a H$^-$, is not expected to be extremely stable. Indeed the C-OH covalent bond has a tenuous $\sim 1.55$ Å bond length. Its formation reflects the strong nucleophilic nature of OH$^-$ weakly solvated by an aprotic liquid electrolyte.
Once the OH$^-$ attacks the organic fragment, it is released from both the LMO surface and the tagged Mn(II) (Fig. 5d). The Mn(II)-OH$^-$-Mn(III) bridge is permanently broken. The inset to Fig. 6 indeed shows that, after the OH$^-$ attack, \( R' \) fluctuates around 4.4 Å which is the precisely the umbrella constraint distance \( R_o \) in this window. Therefore the Mn(II) is undergoing free diffusion, constrained only by the PMF harmonic potential. The C-OH bond formation is not reversible within our AIMD trajectory timescales. Not even the metadynamics technique\(^{38}\) could have accelerated the C-OH bond formation because no bond is broken, and the reaction relies on diffusion of the EC fragment. Thus Fig. 6 does not truly represent a reversible work. We regard the predictions of this subsection as semi-quantitative. However, the mechanistic steps described herein may be generally applicable to transition metal ion dissolution in organic solvents.

**D. Mn(II)-assisted decomposition of LEDC**

Finally, we explore possible capacity-fade mechanisms caused by Mn(II) corruption of the anode SEI. This section originates from our attempt to compare the binding energy of Mn(I) with the \( \beta \)-diketonate of Ref. 32, and the cohesive energy between Mn(I) and the EC decomposition fragment used to decorate LMO (001) in this work. When taken out of the LMO surface and an \( e^- \) is added, the Mn(II)/EC-fragment complex spontaneously decomposes. This suggests that similar redox decomposition reaction may also occur in anode SEI organic components, like EDC.

We create a periodically replicated interface model where two layers of LEDC are placed on a 4-layer Li$_2$CO$_3$ (001) surface slab. In view of Refs. 46 and 47, a Mn(II) is placed between these two components; it replaces a Li$^+$ ion on the Li$_2$CO$_3$ surface in contact with LEDC. An excess \( e^- \) is also added, making the simulation cell charge-neutral. A high-spin spin-state appropriate to Mn(I) is imposed, and a combination of AIMD simulations and geometry optimization calculations are conducted. Instead of a Mn(I) ion, the procedure generates a locally stable structure in which Mn(II) persists and is 5-coordinated. The excess \( e^- \) is localized on the CO$_3$ end of an EDC coordinated to the Mn(II), which adopts a characteristic \( sp^3 \) hybridization. See the S.I. for details.

In an attempt to create a 6-coordinated Mn(II), two LiF dimers are inserted near the Mn(II) ion, and geometry optimization is re-initiated. Even after this addition, the Mn(II)
FIG. 6: Potential-of-mean-force for Mn(II) dissociation from the above-surface LMO site as a function of the new reaction coordinate $R'$. Inset: Reaction coordinate ($R'$) as a function of time in the rightmost sampling window where Mn(II) is released into the liquid electrolyte. The arrow indicates the approximate time of OH$^-$ attack on an organic fragment (see text). A-D refer to panels in Fig. 5.

remains 5-coordinated, moving 2.55 Å away from one of the O-atoms initially coordinated to it before LiF are introduced (Fig. 7a-b). The reason may be the large concentration of negative charges surrounding Mn(II) in an interfacial site that is not well-stabilized by long-range Madelung forces. The excess electron is now delocalized over the simulation cell.

Starting from the Fig. 7b configuration, AIMD simulations are conducted at $T=350$ K for 5 ps. Within 0.5 ps, a CO$_2^-$ radical anion is released from the R-CO$_3^-$ end of a EDC bonded to Mn(II). Both this species and the RCHO$^-$ remnant are coordinated to the Mn(II) for a time (Fig. 7c), but diffuse away within another 4.5 ps (Fig. 7d). The rapid diffusion of
negatively charged species from Mn(II) is somewhat surprising, even considering the elevated temperature used in the simulations. This may again reflect the large local concentration of negative charge surrounding the Mn(II). While the existence of MnF$_2$ motifs in the SEI has been suggested, F$^-$ is not necessary for CO$_2$ release. The simulation cell obtained prior to adding the two Li$^+$F$^-$ pairs reacts in an analogous way (S.I.).

Due to the divalent cation induction effect, the Mn(II)(EDC)$_n$ complex should more readily accept an e$^-$ from the anode at low voltages than the rest of the SEI components. Ref. 47 proposes that solvent molecules like EC can diffuse through the porous organic SEI component (e.g., LEDC), coordinate to Mn(II), and be reductively decomposed. Our calculations suggest an alternate scenario: further reductive decomposition of organic SEI components like EDC coordinated to Mn(II) (Fig. 1d). The CO$_2^-$ radical anion released can readily diffuse through the organic SEI layer without the need of large pores. It can
subsequently attack the liquid electrolyte outside the SEI layer, causing more capacity fade. The EDC molecule that loses a CO$_2$ becomes detached from the Mn(II). We have not conducted a sufficiently long AIMD trajectory to discover its ultimate fate, or to see whether other EDC can diffuse to and replenish the Mn(II) coordination shell, causing continuous CO$_2^-$ release as long as $e^-$ are available.

From these calculations, our picture of anode SEI-embedded Mn(II) coordination structure, function, and mode of transport from cathode is more dynamic than that of Shkrob et al.\textsuperscript{46} Two-electron reduction of Mn(II) at the interface has not been examined in this modeling work. Other researchers have reported possible Mn metal clusters inside the anode SEI.\textsuperscript{18,55,63} For completeness, the S.I. shows that EDC also decomposes on transition metal surfaces.

IV. DISCUSSIONS – RELEVANCE TO COMPUTATIONAL DESIGN

A key finding of this work is the sheer complexity of Mn migration and dissolution mechanisms. Many moving parts are involved. This section focuses on two issues that may help design of novel interfaces and protective strategies which are more resistant to transition metal dissolution. They are unexpected chemical reactions with the organic fragments, and the role of OH$^-$.

Regarding chemical reactions, we first stress that the widely-quoted statement, that organic carbonate solvents are “stable” until the cathode potential exceeds $\sim$4.5 V, is somewhat misleading. It refers only to oxidative or electrochemical stability, not intrinsic thermodynamics. If one use a solid-state battery component definition of stability,\textsuperscript{82,83} EC, DMC, and organic fragments derived therefrom, whether they are on the anode or cathode, are typically thermodynamically unstable.\textsuperscript{64} Ref.\textsuperscript{21} has pointed out that, by itself (without removing $e^-$),

$$\text{EC} \rightarrow \text{CO}_2 + \text{CH}_3\text{CHO},$$

is exothermic by 0.317 eV at T=0 K, not counting zero-point energy which further favors the reaction. It is evidently hindered by slow kinetics at room temperature. In contrast, all-solid-state battery components are generally annealed at elevated temperatures, which facilitates the attainment of thermodynamic equilibrium. When EC is allowed to react with even fully lithiated (i.e., discharged) spinel oxide, the reaction is also exothermic.\textsuperscript{21,33,84}
Decomposed EC fragments on LMO surfaces create surface oxygen vacancies and protonates the cathode surface. These fragments themselves are thermodynamically metastable. In the vicinity of transition metal ions, excess $e^-$/holes, and/or OH$^-$, these comparatively high-energy-content fragments may undergo further unexpected reactions unless the reaction barrier is high. Therefore one attribute of an ideal cathode surface is either a kinetic stability towards organic electrolyte decomposition altogether, or sacrificial inactivation of electrocatalytic centers on cathode surfaces in order to prevent organic radical attack of the cathode oxide.

Here we focus on the ALD protection strategy instead of new electrolytes or additives. Experimental investigations have shown that Mn dissolution is already much reduced, but is not completely eliminated, by existing ALD coatings. It is likely that the ALD layers will have to crack, develop pores, or otherwise partially decompose to allow Mn dissolution through them. More diagnostic studies to pinpoint ALD film breakdown and SEI formation on cathode ALD films will be extremely useful. Computationally, an important goal is to elucidate ALD-film breakdown mechanisms. For each ALD coating material, one can model electrolyte decomposition under ultrahigh vacuum conditions, with a judiciously chosen electron sink in the simulation cell to mimic cathode charging conditions. Such calculations should provide insights about the most susceptible degradation pathways that need to be mitigated.

Regarding restricting OH$^-$ activation of metal dissolution: cathode oxides or protective coating materials based on oxide tend to form OH$^-$ in the presence of H$^+$. Reducing the H$_2$O content in the electrolyte and using solvent molecules that do not donate H$^+$ to cathode surfaces are clearly ideal. In addition, some material surfaces, like TiO$_2$, are more resistant to reacting with H$_2$O to form OH$^-$ groups than others. We also propose that metal ions with 3+ and 4+ formal charges in the protective coating layers will raise OH$^-$ migration barriers. This is significant because, in this work, OH$^-$ migration is shown to facilitate metal dissolution on LMO not coated by ALD layers. This observation appears consistent with anecdotal rankings of successful ALD oxide coatings in the literature. One exception is the divalent-metal ion-based magnesium fluoride coating. It has proved promising in passivating LNMO, although capacity fade still occurs in less than 100 cycles at 45°C. Note that there are competing desirable attributes for protective coatings, like high Li$^+$ mobility, resistance towards cracking, and others.
V. CONCLUSIONS

We have applied *ab initio* molecular dynamics (AIMD) simulations to investigate Mn loss from spinel Li$_x$Mn$_2$O$_4$ (001) (“LMO”) surfaces. We distinguish between Mn migration to above-surface, non-crystallographic sites to form Mn-decomposed EC fragment complexes, and Mn(II) dissolution from these surface sites. We also explore the consequence of Mn(II) lodged between the organic and inorganic layers of the solid electrolyte interphase (SEI) after it has diffused through the separator.

When the exiting Mn is bonded to a F$^-$, which can come from PF$_6^-$ decomposition, we predict the formation of an above-the-surface Mn intermediate which is in the Mn(II) charge states a majority of the time. This is in qualitative agreement with the enhancement of Mn(II) content on the surface of Ni-doped LMO during battery charging.$^{31}$ A $\Delta G=1.25\pm0.09$ eV free energy barrier ($\Delta G^*$) is predicted for this process. This $\Delta G^*$, consistent with years of reaction time, is slightly overestimated, perhaps due to DFT inaccuracies. Mechanistically, it is found that concerted solid-state Li$^+$ and liquid electrolyte motions at the interface facilitate Mn(II) migration to the above the surface.

The next step – Mn(II) dissolution from the surface – must be discussed semi-quantitatively. We assume that the Mn which has migrated above the LMO surface is stabilized by external means and restart AIMD free energy calculations. Dissolution is aided by the existence of sufficient H$^+$ so that the exiting Mn(II) only exhibits OH$^-$ bridges to the oxide surface. OH$^-$ attack on an organic fragment is also observed in our simulations. Future work will examine whether such an attack is a general phenomenon. The frequently quoted Hunter mechanism of surface Mn(III) disproportionation to form Mn(II) is only one early step in a complex process.

Finally, Mn(II) lodged between the organic (LED) and inorganic (Li$_2$CO$_3$) regions of the SEI covering the graphite anode surface can readily decompose EDC molecules coordinated to it to give CO$_2^-$ radical anions if excess electrons arrive from the anode. CO$_2^-$ can diffuse through the organic SEI region, without requiring large pores to exist, and then attack the liquid electrolyte outside the SEI, leading to capacity fade. Our finding that the organic SEI on the anode surface can undergo chemical reactions dovetails with recent computational work focused on SEI instability.$^{64}$ It is also related to the “redox shuttle” route of e$^-$ transport through the anode SEI.$^{91}$
In terms of computation, AIMD simulations of the free energy barrier associated with Mn loss prove to be challenging. Concerted solid- and liquid-state motion usually requires different simulation time scales, and many moving parts and unexpected chemical reactions can occur while the transition metal ion moves through the interface. Given the dearth of atomic-length-scale experimental interfacial structures as starting points of simulations, our models should be considered plausible scenarios that can yield useful insights.

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Supporting Information Available

Further information are provided on simulations of Mn(II) surface migration in the absence of F\(^{-}\); EDC decomposition in the absence of F\(^{-}\); EDC decomposition on the Ni(111) surface; and H\(_2\)O attack on the LMO (111) surface. This information is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).

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