How Voltage Drops are Manifested by Lithium Ion Configurations at Interfaces and in Thin Films on Battery Electrodes

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(Dated: July 10, 2015)

Abstract

Battery electrode surfaces are generally coated with electronically insulating solid films of thickness 1-50 nm. Both electrons and Li\textsuperscript{+} can move at the electrode-surface film interface in response to the voltage, which adds complexity to the “electric double layer” (EDL). We apply Density Functional Theory (DFT) to investigate how the applied voltage is manifested as changes in the EDL at atomic lengthscales, including charge separation and interfacial dipole moments. Illustrating examples include Li\textsubscript{3}PO\textsubscript{4}, Li\textsubscript{2}CO\textsubscript{3}, and Li\textsubscript{x}Mn\textsubscript{2}O\textsubscript{4} thin-films on Au(111) surfaces under ultrahigh vacuum conditions. Adsorbed organic solvent molecules can strongly reduce voltages predicted in vacuum. We propose that manipulating surface dipoles, seldom discussed in battery studies, may be a viable strategy to improve electrode passivation. We also distinguish the computed potential governing electrons, which is the actual or instantaneous voltage, and the “lithium cohesive energy”-based voltage governing Li content widely reported in DFT calculations, which is a slower-responding self-consistency criterion at interfaces. This distinction is critical for a comprehensive description of electrochemical activities on electrode surfaces, including Li\textsuperscript{+} insertion dynamics, parasitic electrolyte decomposition, and electrodeposition at overpotentials.

keywords: lithium ion batteries; voltage prediction; density functional theory; computational electrochemistry
I. INTRODUCTION

Unlike pristine noble metal or graphite basal-plane electrodes used in classical electric double layer (EDL) studies, lithium ion battery (LIB) electrodes generally exhibit complex interfaces. Both electron ($e^-$) and Li$^+$ transport can occur inside LIB electrodes. In addition, solid thin films, on the order 1-50 nm thick, are ubiquitous on LIB electrode surfaces and can become part of the EDL. The EDL is critical because key battery processes like Li$^+$ incorporation kinetics (including Li$^+$ desolvation), parasitic reactions, Li-plating, and degradation-inducing phase transformations on electrode surfaces most likely initiate within it. Indeed, “solid electrolyte interphase” (SEI) films covering anodes are relied upon as kinetic barriers that prevent thermodynamic equilibrium in batteries; they are critical for LIB which operate outside the redox stability window of the organic solvent electrolytes used. As discussed below, the EDL is also crucial in computational work because it effectively determines the electrode potential (henceforth “applied voltage” or simply “voltage”) in the simulation cell. Our work examines EDL associated with thin-film coated electrode surfaces, and emphasizes the importance of creating electrode interface models that exhibit consistent electrochemical activities for both Li$^+$ and $e^-$. Examples of solid films on electrode surfaces include Li$_2$CO$_3$ layers formed on pristine cathode oxide surfaces; cathode-coating films made of electrolyte decomposition products; SEI films on anodes arising from reductive decomposition of liquid electrolyte components; artificial protective/passivating coatings including atomic layer deposition (ALD) layers which can undergo phase transformations at low voltages; ALD layers between solid electrolytes and electrodes in all-solid state batteries; and even Li$_2$O$_2$ films deposited on cathodes during fast discharge of Li-air batteries, the re-oxidation of which is accompanied by significant voltage hysteresis and is a root cause of the lack of a suitable liquid electrolyte in Li-air batteries.

Detailed atomic lengthscale understanding of the interfaces and EDL associated with such thin films has remained elusive, partly due to challenges in imaging buried interfaces at sub-nanometer resolution. Even EDLs associated with liquid organic electrolyte in batteries have arguably only recently received systematic experimental studies. Modeling efforts have made much progress in elucidating the structures of solid-solid and solid-vacuum interfaces. However, voltage dependences, particularly in processes involving $e^-$
FIG. 1: Some scenarios for electric double layers (EDL). (a) Voltage drops at electrode/liquid electrolyte interface when the metallic electrode is uncharged. Organic solvent molecules orient themselves to reduce the vacuum voltage (Sec. IV D). (b) Solid films with fixed dipoles, like ferroelectrics, can serve the same purpose as molecules, and represent a novel strategy for electrode passivation (Sec. IV B). (c)-(h) are additions to intrinsic dipole-induced voltage drops of (a) when charges exist on the cathode active material and/or thin films. (c) Pristine, noble metal electrode in contact with liquid electrolyte. (d) Inert thin film intervening between metal and liquid. (e) EDL entirely at metallic electrode/thin film interface (Sec. IV A, IV C). (f) Same as (e), with more charge separation (Sec. IV A). (g) EDL is only partially inside thin film (Sec. IV D). (h) EDL is between redox-active film and liquid electrolyte (Sec. IV E). Yellow and red backgrounds depict Au and liquid electrolyte; light brown textures are solid electrolyte thin films or redox-active cathode materials; green circles are negatively charged counter ions in the liquid electrolyte. For simplicity, cations in the liquid are omitted. Voltage profiles and surface charge densities are caricatures; in the calculations, voltage changes are 1-3 V and film thicknesses (demarcated by vertical dashed lines) are about 1 nm. The plots represent static conditions; ohmic losses add slopes to all flat portions.
transfer like parasitic reactions and undesirable metal plating, have arguably received less theoretical attention. In this work, we apply electronic Density Functional Theory (DFT) calculations to investigate how voltages affect the structures and stoichiometries of thin solid films, their interfaces, and their EDL at atomic lengthscales. In view of the complexities of LIB electrodes, we have adopted simple model systems. The liquid electrolyte is omitted, although a few solvent molecules are included as frozen monolayers in some models to illustrate their huge impact on the voltage. Au(111) surfaces are adopted as model cathodes, instead of transition metal oxides typically found in batteries. Au does not alloy with Li under voltages considered in this work and is a convenient inert electrode. These systems might be realized in ultra-high vacuum (UHV) settings; they dovetail with the use of copper and gold electrodes in recent fundamental battery science experimental studies.

The model thin films examined in this work, in order of increasing complexity, are Li₃PO₄ (010) (Fig. 2a), Li₂CO₃ basal plane (Fig. 2b), and LiₓMn₂O₄ (111) (Fig. 2c). These are coated on Au(111) on one side and face a vacuum region on the other. Li₃PO₄ is a non-redox-active solid electrolyte. It illustrates the correlation between interfacial dipole densities and voltages. Li₂CO₃ is often found on as-synthesized cathode surfaces. In LIB studies, there is disagreement concerning whether Li₂CO₃ dissolves upon soaking in electrolyte, is formed at high voltages, or is removed at >4 V. In Li-air batteries, Li₂CO₃ is generally accepted to be oxidized and removed above ∼4.5 V. Our goal is not to elucidate the detailed reaction mechanism, but to study the electronic and structural signatures accompanying voltage increase. Redox-active LiMn₂O₄ (spinel LMO) is not used as nanometer-thick films in batteries, but its inclusion here helps illustrate the diversity of interfacial behavior (Fig. 1). Like most LIB cathode materials, LMO is a polaron conductor because Mn can exhibit multiple redox states. It also conducts Li⁺, but is not a band ("metallic") conductor. By classical electrostatics definition, the interior of LMO is not instantaneously at a constant potential. Our LMO/Au interface model provides a well-defined Fermi level (E_F) to demonstrate how voltage control is achieved at atomic lengthscales, and how this affects EC oxidative decomposition on LMO surfaces.

Out of necessity, we critically examine the voltage calibration method used in the theoretical LIB literature (Sec. III). The same experimental voltage governs Li⁺ and e⁻ motion. Indeed, in cyclic voltametry, it is difficult to distinguish currents arising from Faradaic Li-insertion or parasitic processes that involve undesired e⁻ transfer to the liquid. But what
is “voltage” at atomic lengthscales? The absolute electrochemical potential for a charged particle in an atomic configuration is the (free) energy needed to transfer it into a given phase from infinity (see, e.g., Ref. ? ). There can be differences whether the particle is a Li\(^+\) or a e\(^-\). In DFT modeling, the electronic voltage (\(V_e\)) governing electronic motion, and ionic voltage (\(V_i\)) governing Li\(^+\) motion, can and must be distinguished.

First we focus on \(V_e\). Under constant voltage experimental conditions, potentiostats directly control the e\(^-\) (not Li) content. When the phase is a metallic conductor with a well-defined \(E_F\), the voltage associated with transferring e\(^-\) from infinity, multiplied by the electronic charge, is equal to the work function (\(\Phi\)) modulo a constant, just like in photovoltaics (PV)\(^{48}\) and electrocatalytic systems:\(^{49}\) \(\Phi = E_{\text{vac}} - E_F\), where \(E_{\text{vac}}\) is the vacuum level and \(E_F\) is set to zero herein without loss of generality. If the electrode is immersed in liquid electrolyte, \(\Phi\) calculated for the electrode covered by a sufficiently thick liquid layer, divided by the electronic charge, also gives \(V_e\).\(^{50,95}\) \(V_e\) applies even under out-of-equilibrium conditions. It is readily computed in our model systems because vacuum regions exist and qualify as “infinity.” In commercial batteries, there is no vacuum. Nevertheless, our focus on \(\Phi\) is formally correct and emphasizes the synergy between batteries, fuel cells,\(^{68}\) PV,\(^{48,51-53}\) and metal-semiconductor interfaces.\(^{54,55}\) In those research areas, dipoles at interfaces are recognized as properties of paramount importance. At battery liquid-solid interfaces, EDL’s are
FIG. 3: Overview of representative predictions of how EDL affects electronic voltage ($V_e$). The white background is vacuum. Yellow and textured regions are Au and solid thin films, respectively: (a) Li$_3$PO$_4$/Au (Sec. IV A); (b) Li$_2$CO$_3$/Au (Sec. IV C); (c) EC$+$PF$_6^-$/Li$_2$CO$_3$/Au (Sec. IV D); (d) EC/Li$_x$Mn$_2$O$_4$/Au (Sec. IV E). “$V^-_{Li}$” are negatively charged Li$^+$ vacancies. $V_e$ values with and without parentheses are two alternate scenarios. Underlined values are at equilibrium (i.e., $V_e=V_i$).

the manifestations of complex surface dipole distributions associated with applied voltages; it is in effect our computational potentiostat. Based on our calculations, we propose the manipulation of surface dipoles as a novel electrode passivating strategy (Fig. 1b).

Li$^+$ ions are only indirectly controlled by potentiostats; they slowly redistribute in response to changes in electronic configurations. We define the Li “voltage” ($V_i$) as the (free) energy difference between Li chemical potential in a system and the lithium metal cohesive energy per Li divided by $|e|$. This definition is widely used as the sole voltage estimate in the LIB theory literature.$^{56-59}$ At equilibrium, when the voltage is pinned at the redox potential of Li-insertion reactions, $V_e$ must be equal to $V_i$. Thus $V_i$ should be considered a self-consistent criterion at interfaces. By itself, $V_i$ can give incorrect voltages when modeling parasitic processes induced by $e^-$ transfer, and it may not govern the dynamics of Li$^+$ insertion processes adequately.

PF$_6^-$ anions on Li$_x$Mn$_2$O$_4$ surfaces are found to accelerate EC decomposition in their vicinity (not shown; Sec. IV F).
Fig. 3a-d offers a preview of our results, pertinent to issues discussed above. The rest of the paper is organized as follows. Sec. 2 discusses and reconciles different definitions of voltage in DFT calculations in more detail. Sec. 3 describes the methods used. The results are given in Sec. 4 and Sec. 5 summarizes the paper. A supporting information (S.I.) document provides further details about our three model systems, compares the modeling of battery interfaces with geochemical and other liquid-oxide interfaces, and discusses Li$_2$CO$_3$ oxidation thermodynamics. Experimentalist readers are encouraged to skip to Sec. IV.

II. VOLTAGE CALIBRATION IN DFT CALCULATIONS

DFT calculations are conducted at constant number of electrons, not constant electrochemical potential. Estimating and maintaining voltages in periodically replicated, condensed phase DFT simulation cells have long been recognized as a challenge. Recently we have applied an *ab initio* molecular dynamics (AIMD)-based Li$^+$ transfer free energy method to predict voltage dependences of redox processes at interfaces between liquid electrolytes and lithium-intercalated graphite. AIMD has also been coupled with continuum approximations of liquid electrolytes to model constant voltage conditions on pristine electrodes. But present-day AIMD simulation time scales are too short to extend to Li$^+$ motion *inside* LIB electrodes or the surface films coating them except at significantly elevated temperatures. This work focuses on how applied voltages affect solid films.

Thus we model solid interfaces at zero temperature. With sufficient equilibration time and in the presence of Li$^+$ and e$^-$ reservoirs, the total number of electrons ($n_e$) and Li$^+$ content ($n_{Li^+}$) in an electrode in a LIB are governed by the chemical potentials for electrons ($\mu_e$) and Li$^+$ ions ($\mu_{Li^+}$), respectively. $E_F$ of a metallic electrode is $\mu_e$ modulo a constant. Here we have not used $\bar{\mu}_e$ or $\bar{\mu}_{Li^+}$, the notations for total electrochemical potentials of e$^-$ and Li$^+$ precisely because constant-charge DFT calculations and terminologies are being applied to infer constant-potential electrochemical properties. Surface potential contributions to $\bar{\mu}$’s should naturally be present in our simulation cells, which feature explicit interfaces.
A. Electronic Voltage ($\mathcal{V}_e$) from Work Function

The electronic voltage of an atomic configuration which is band conductor, imposed by a potentiostat, not necessarily at equilibrium with respect to $n_{Li}$ or the Li$^+$ occupation sites, is defined as

$$\mathcal{V}_e = \Phi/|e| - 1.37 \text{ V},$$  \hspace{1cm} (1)

if the Li$^+/Li(s)$ reference is used. In the literature, values of 1.39 V and 1.44 V have been adopted; the small discrepancy is a measure of possible systematic error. In the DFT formulation, the $e^-$ configuration finds its ground state instantaneously. $\mathcal{V}_e$ pertains to infinitesimal changes in $n_{e}$, which leaves the system uncharged. Note that Refs. 72 and 73 deal with $\mathcal{V}_e$ despite the fact that Li$^+$ is transferred, because the excess $e^-$ is left on the metallic electrode at its Fermi level. As stated in Ref. 73, the free energy of that graphite edge-plane system has yet to be optimized with respect to the surface Li-content. In the present work, $\mathcal{V}_e$ are always reported for locally optimized atomic configurations so that all forces are zero.

B. Lithium Metal Cohesive Energy ($\mathcal{V}_i$) for Voltage

In the “lithium cohesive energy” ($\mathcal{V}_i$) approach, discrete and matched numbers of $e^-$ and Li$^+$ are added/subtracted simultaneously:

$$\mu_{Li} = E(n_{Li}+, n_e) - E(n_{Li}+, 1, n_e - 1)$$
$$= E(n_{Li}+, n_e) - E(n_{Li}+, 1, n_e) + E(n_{Li}+, n_e) - E(n_{Li}+, n_e - 1)$$
$$\approx \mu_{Li}^+ + \mu_e.$$  \hspace{1cm} (2)

The last equality holds when the system approaches infinite size. Here $E(n_{Li}+, n_e)$ is the zero temperature total energy after optimization of all interior degrees of freedom. The $T = 0$ K voltage is then given by

$$\mathcal{V}_i = (\mu_{Li} - E_{Li(s)})/|e|,$$  \hspace{1cm} (3)

where $E_{Li(s)}$ is the cohesive energy of lithium metal, predicted to be 1.57 eV using the DFT/PBE functional. No net charge is introduced. There is an ambiguity concerning whether $\mu_{Li}(n_{Li})$ should be $E(n_{Li} + 1) - E(n_{Li})$ or $E(n_{Li}1) - E(n_{Li} - 1)$. We have chosen
the latter definition (Eq. 2). $\mu_{Li}$ is used instead of $\mu_{Li^+}$ to control $n_{Li}$ because the former is the widely used convention, and because it is harder to control charged particles due to the periodic boundary condition adopted. In the literature, $\mathcal{V}_i$ is generally averaged over a wider range of Li content than in the present work.\textsuperscript{56,57}

$\mathcal{V}_e$ and $\mathcal{V}_i$ are not necessarily equal. A transparent example is a pristine Li metal slab in vacuum. $\mathcal{V}_i=0$ by definition. Yet the work function of Li(100) is reported to be 2.93 eV.\textsuperscript{75} This translates into an electronic voltage of $\mathcal{V}_e=1.51$ V (Eq. 1)! Indeed, if the Li surface is covered with a poor SEI that allows $e^-$ transfer but Li$^+$ transfer is slowed to beyond experimental timescales – the opposite of what a good SEI does – the lithium slab acts as an $e^-$ emitter, the voltage of which must be governed by its $E_F$. For Li(s) to truly exhibit 0 V vs. the LIB Li$^+$/Li(s) reference in $e^-$ transfer processes, net surface charge densities and electrode-electrolyte interface contributions must be accounted for. Organic solvent decomposition can occur on uncharged Li (100) surface under UHV conditions despite the relatively high (1.51 V) potential, but in these reactions the metal surface is a reactant and Li$^+$ are produced.

C. Relation between $\mathcal{V}_e$ and $\mathcal{V}_i$

(1) $\mathcal{V}_e=\mathcal{V}_i$ at equilibrium. Under this condition, $\mathcal{V}_i$ controls the Li content. Thus Eq. 3 should be interpreted as a self-consistency criterion. $\mu_{Li}=(\Phi-1.37$ eV$+1.57$ eV) from Eqs. 1, 3, and the PBE estimate of $E_{Li}(s)$. Identifying $\Phi$ as $\mu_e$, Eq. 2 implies that $\mu_{Li^+}$ becomes a voltage-independent 0.20 eV. This reflects that Li$^+$ is in excess in an infinite reservoir. A related point has been made in the fuel cell literature.\textsuperscript{68} In that case H$^+$ concentration at the interface, governed by the pH, is also strongly coupled to the predicted voltage.

(2) When $\mathcal{V}_i<\mathcal{V}_e$, and the voltage is held fixed by the potentiostat, and Li$^+$ and $e^-$ sources are present, the Li content should spontaneously decrease (as permitted by kinetics) so that $\mathcal{V}_i$ rises towards $\mathcal{V}_e$. But $\mathcal{V}_i$ does not always increase with decreasing $n_{Li}$. Going back to the lithium solid example: if the potentiostat is set at 1.51 V in solution, the entire Li slab dissolves. If instead an electrically disconnected Li solid is dipped into an electrolyte, some Li$^+$ ionizes, leaving a negatively charge, possibly SEI-covered, Li surface. Now it is the electronic voltage $\mathcal{V}_e$ which decreases to 0 V vs. Li$^+$/Li(s) to coincide with $\mathcal{V}_i$. 


(3) When $V_i > V_e$ and the voltage is held fixed, the Li content should in general increase to lower $V_i$. This may not occur in all cases. For example, when all available Li$^+$ insertion sites are filled in fully lithiated LiC$_6$, the electrode becomes supercapacitor-like. $V_e$ now controls the net surface electronic charge$^{72}$ and $V_i$ ceases to matter. Conducting simulations under such non-equilibrium conditions are crucial to understanding many phenomena in batteries. An example is the kinetics of metal plating$^{4,76,77}$ at overpotentials – an explicitly non-equilibrium phenomenon, a major safety issue in LIB, but also a critical process for batteries featuring rechargeable metal anodes. This discussion highlights the primacy of $V_e$ when computing voltages.

Eq. 3 was originally applied to bulk crystalline electrode simulation cells, and $V_i$ has been identified as the redox potential$^{56,57,80}$ Li should remain in the solid when the applied potential is lower than $V_i$. In these special cases of simulation cells without interfaces, the Li(s) cohesive energy approach ($V_i$) is *neither consistent nor inconsistent* with $V_e$. This is because the electrostatic potential at any point in space is only defined to within a constant in the interior of a crystal$^{78}$, therefore neither $V_e$ nor $E_F$ is well-defined without specifying interfaces. Thus metals terminated in different crystal facets exhibit different $\Phi$’s$^{79}$ Much more significant changes in $\Phi$ can be induced using adsorbed molecules.$^{48}$ Using DFT+U or hybrid DFT functional methods, $V_i$ has generally been predicted to be in good agreement with measured open circuit voltages in bulk transition metal oxide simulation cells. The errors are at most a few hundred meVs.$^{80}$ This suggests that interfacial contributions may be small on most battery cathode surfaces. Our work suggests that artificial interfaces can be potentially be engineered to give larger, beneficial effects. Molecular adsorption effects will be emphasized in Sec. IV D.

DFT calculations of interfaces are usually performed in finite-sized, periodically-replicated simulation cells kept at overall charge neutrality. In the literature, in DFT calculations without ions in the electrolyte (or without any electrolyte at all), the $V_i$ approach has therefore assigned a wide range of voltages to LIB interfaces at charge neutrality. In other words, a continuous range of potentials-of-zero-charge (PZC) have been assigned by DFT. Yet simple “classical” electrodes such as pristine noble metals usually permit one PZC at voltages away from PZC, the surface is charged. If liquid electrolyte is present, the electrode surface can exhibit non-zero charges, compensated by counterions in the electrolyte. In this work, we illustrate this effect by adding PF$_6^-$ anions under UHV conditions.
III. METHODS

DFT calculations are conducted using the Vienna Atomic Simulation Package (VASP) version 5.3 and the PBE functional. Modeling spinel \( \text{Li}_x\text{Mn}_2\text{O}_4 \) requires spin-polarized DFT and the DFT+U augmented treatment of Mn 3d orbitals. The \( U \) and \( J \) values depend on the orbital projection scheme and DFT+U implementation details; here \( U-J=4.85 \text{ eV} \) is chosen to taken from the literature. The charge state on Mn ions are determined from the approximate local spin polarization \( s_z \) reported by the VASP code; \(|s_z|=3/2, 4/2, \text{ and } 5/2 \) are assigned to Mn(IV), Mn(III), and Mn(II), respectively. For \( \text{Li}_3\text{PO}_4 \) and \( \text{Li}_2\text{CO}_3 \), most calculations exclude spin-polarization. A few spin-polarized calculations are performed to confirm that this is adequate. A 400 eV planewave energy cutoff and a \( 3\times3\times1 \) Monkhorst-Pack grid are applied in all cases. Increasing the cutoff or the \( k \)-grid changes the predicted absolute energies by at most 0.1 eV; energy differences, which are the relevant quantities, are much smaller.

Our model systems are asymmetric slabs: \( \text{Li}_2\text{CO}_3 \) basal plane, \( \text{Li}_3\text{PO}_4 \) (010), and \( \text{LiMn}_2\text{O}_4 \) (111) slabs on one side of 4-layer thick Au(111) (Fig. 2). The standard dipole correction is applied to negate image interactions in the periodically replicated, charge-neutral simulation cells. Au is a metallic conductor and its \( E_F \) is well defined. Work functions (\( \Phi \)) are the differences between \( E_F \) and vacuum levels. Two vacuum-surface interfaces exist per asymmetric slab, and two vacuum levels, for bare and coated Au(111) respectively, are obtained. Four layers of Au atoms do not give a completely converged \( \Phi \) for uncoated Au(111). Therefore we have shifted the two computed \( \Phi \) of each system by the difference between the predicted Au(111) \( \Phi \), and the fully converged Au(111) \( \Phi=5.15 \text{ eV} \). The shift is at most 0.1 eV. We also report the net surface dipole density \( \delta \), which is the total dipole moment of the simulation cell in the direction perpendicular to the surface divided by the lateral surface area. The dipole moment is computed as the sum of all charges (including electron density defined on a grid) multiplied by their displacement from a user-specified center of the cell, and is reported by the VASP code. \( \delta \) should be independent of the cell-center in a charge-neutral simulation cell as long as the choice locates the artificial dipole layer inside the vacuum region. More details on the thin film models, and rationale for crystal facets chosen, are provided in the S.I.
### TABLE 1: Electronic ($V_e$) and ionic ($V_i$) voltages of a Li$_3$PO$_4$ (010)/Au(111) interface cell as the number of Li vacancies at the inner surface of the Li$_3$PO$_4$ slab varies. Exceptions: cases $a$ and $b$ involve removing a Li from a middle layer or from the outer surface of Li$_3$PO$_4$. $V_i$ is defined for incremental Li subtraction, e.g., the “-1” value refers to the difference between the total energies of “-1” and “-2.”

| $\Delta N$(Li) | 0   | -1  | -2  | -3  | -4  | -1$^a$ | -1$^b$ |
|----------------|-----|-----|-----|-----|-----|--------|--------|
| $V_e$          | 2.86| 3.26| 3.59| 3.92| 4.19| 3.76   | 4.59   |
| $V_i$          | 3.07| 3.23| 3.58| 3.65| NA  | (3.69) | (4.10) |

IV. RESULTS

#### A. Au(111)/Li$_3$PO$_4$/Vacuum (Fig. 3a for Summary)

First we examine the $V_e$ of a non-redox active system: a thin $\beta$-Li$_3$PO$_4$ (010) solid electrolyte film on Au(111). We start with the stochiometric Li$_3$PO$_4$ slab with all Li$^+$ sites occupied ($\Delta N$(Li)=0, Fig. 2b). The work function is $\Phi=4.23$ eV. This translates into $V_e=2.86$ V vs. Li$^+$/Li(s), which is reduced from the bare, charge-neutral Au(111) surface value $V_e=3.78$ V ($\Phi=5.15$ V) by 0.88 eV. In the absence of Au, the Li$_3$PO$_4$ slab is symmetric and does not exhibit a net dipole moment. The fact that it modifies the Au $\Phi$ is not due to charge transfer between Au and Li$_3$PO$_4$. The spatially decomposed electronic density of state (DOS) (Fig. 4a) shows that the phosphate Kohn-Sham valence band edge, located at about $-1.5$ eV of the phosphate, is far from the Fermi level residing on Au orbitals. The Li$_3$PO$_4$ conduction band edge is higher than 5 eV and the vacuum level is at 4.23 eV (not shown in the panel).

Thus the stoichiometric slab must have induced image charges which set up surface dipoles. Indeed, the net surface dipole density ($\delta$) of the entire simulation cell is predicted to be finite; $\delta = -0.0048 |e|/\AA$, or $-0.023$ Debye/Å$^2$. The negative sign means that the dipole points into Li$_3$PO$_4$ from Au (111). Using

$$\Delta V_e = 4\pi \delta/(|e|),$$

where all quantities are in atomic units, this “small” $\delta$ should yield a large $-0.86$ V shift between bare and phosphate-coated Au(111). This explains the $-0.88$ V difference deduced...
FIG. 4: Kohn-Sham orbitals of Li$_{3-x}$PO$_4$/Au decomposed on to atoms at their coordinates perpendicular to the interface. $\Delta N$(Li) is (a) 0; (b) $-1$; (c) $-3$; (d) $-1^a$; (e) $-1^b$. The vacancies are in the phosphate layer closest to Au$(111)$ (Fig. 5a-b) except for panel (d) (case $a$, middle of slab, Fig. 5c) and (e) (case $b$, vacancy in outermost layer, not depicted in Fig. 5). $E_F$ is shifted to zero in each case; vacuum levels are not aligned, and are at 4.23, 4.63, 5.29, 5.16, and 6.19 eV in the five panels. Au and thin-film-based orbitals are depicted in black and red, respectively. $\rho_c=0.007$ is used for determining orbital locations.$^{88}$

from work function differences discussed above. DFT calculations give an aggregate $\delta$, that includes screening, induced-dipoles, and depolarization effects, not individual contributions. Hence no effective dielectric constant is present in Eq. 4.$^{55}$

Under strictly UHV conditions, no net charge can be introduced. Net bulk or surface charges lead to infinite repulsive energies due to long-ranged coulombic repulsion. Instead, we raise the voltage by removing matched Li$^+/e^-$ pairs, as is normally done in DFT calculations.$^{33,80}$ The configuration space associated with removing multiple Li is large. We assume that Li vacancies are weakly interacting, and their formation energetics only depend on their positions in the $z$ direction, perpendicular to the surface. Vacancies on the same layer of Li$_3$PO$_4$ are placed as far apart from each other as possible. With $\Delta N$(Li)$=-4$, two
different configurations with all Li-vacancies right at the interface are indeed found to yield total energies within 30 meV of each other.

Removing one Li (i.e., $\Delta N(\text{Li})=-1$) from the $\text{Li}_3\text{PO}_4$ layer in contact with Au is most energetically favorable (Fig. 5a). It also gives the lowest $V_e$ at this $n_{\text{Li}}$ content. The DOS there reveals no charge transfer between Au and $\text{Li}_3\text{PO}_4$ (Fig. 4b). Some spurious $\text{Li}_3\text{PO}_4$ "orbitals" in contact with Au(111) are above $-1.0$ eV, but they likely arise from the arbitrary spatial decomposition scheme; the valence band edge should be taken as $-1$ eV where at least two layers of $\text{Li}_3\text{PO}_4$ atoms exhibit the same orbital level. A net negative charge must remain at the Li-vacancy site, compensated by a positive charge on Au(111) (Fig. 1e). This charge separation modifies $\delta$ to $-0.0029$ $|e|$/Å which should yield a voltage shift of $-0.53$ V from the bare Au(111) value. Using explicit $\Phi$ calculations, $V_e$ is found to rise to 3.28 V, shifted from the Au(111) $V_e$ by $-0.52$ V (Table I), which is quantitatively explained by the change in $\delta$. The phosphate valence band edge is raised by about 0.45 eV relative with $E_F$ on the Au surface (Fig. 4b). Removing more Li at the phosphate-gold interface augments $\delta$ in the positive direction, increases $V_e$ (Table I), and raises the valence band edge proportionately (Fig. 4c). Finally, removing a single Li inside the phosphate slab (Fig. 4d) or at the phosphate-vacuum interface (Fig. 4e) yields a larger $V_e$ than if the vacancy is right at the Au(111) surface (Table I). In the latter case, the phosphate valence band edge now coincides with $E_F$.

So far we have not discussed the ionic voltage ($V_i$) governing the Li content. Table I
shows that $V_e$ exhibits a significantly larger slope as a function of $\Delta N(Li)$ than $V_i$ as long as Li are removed from the interior interface. The two voltage definitions should intersect at only one point. $V_e$ approaches $V_i$ between $\Delta N(Li)=-1$ to $-2$. Away from that solid-state PZC, equilibrium ($V_e=V_i$) can be achieved with a net surface charge compensated by liquid electrolytes (Fig. 1g, Sec. IV D), just like on noble metal electrodes. Models with non-equilibrium interfacial Li content are “wrong” in the sense that they only have transient existence.

Removing a Li sitting deeper inside the phosphate layer (Fig. 1f, 5b) shows signs of yielding self-consistency: $V_e=3.78$ V, $V_i=3.69$ V (Table 1). However, the relative free energy ($\Delta G$) of this alternative $\Delta N(Li)=-1$ configuration, evaluated using

$$\Delta G = G(\Delta N(Li)) - G(0) - \Delta N(Li)\mu_{Li},$$

is less favorable than $\Delta N(Li)=-3$ where all Li vacancies are at the interface (Table 1 fifth column), at a similar Li chemical potential ($\mu_{Li}=V_i$). In general, if $V_i$ increases upon successive Li removal right at the interface, Eq. 5 favors removing multiple Li there, rather than removing a single Li further inside the slab – even if the latter yields the same $V_i$. Thus Fig. 1f should not be a candidate for equilibrium interfaces, at least under these UHV conditions. If a liquid electrolyte is present, it cannot be ruled out that Li$^+$ vacancy near the outer surface may be stabilized; we speculate that this could even yield a multitude of equilibrium Li$^+$ configurations in Li-containing films, and therefore more than one PZC at different voltages.

### B. Electrostatics-based Passivation Strategy

These results emphasize that the interfacial dipole density ($\delta$) is one atomic lengthscale determinant of applied voltages. From Eq. 4 a thin dipole sheet is expected to give rise to a step-like voltage drop at the interior interface of Li$_3$PO$_4$ (Fig. 1f), which is therefore not an inert, passive coating (Fig. 1d). At long enough times such that Li$^+$ can insert and relax their configurations, this solid electrolyte should absorb much of the voltage drop/rise at the sharp metal/electrolyte interface. If a liquid electrolyte exists in the vacuum region of Fig. 5, it should experience a reduction in the extreme potential exerted by the cathode (Fig. 1f), in effect widening the liquid stability window. Solid films coated on anodes should
TABLE 2: Electronic ($V_e$) and ionic ($V_i$) voltages for a Li$_2$CO$_3$ basal plane/Au(111) interface as the number of Li vacancies at the inner surface of the Li$_2$CO$_3$ slab varies. No adsorbed molecule exists.

Work analogously; in that case, the film, or at least its interface with the anode, must be able to incorporate extra Li. The above discussions suggest a new design principle for “smart” artificial SEI passivating lithium ion battery anodes and high-voltage cathodes. Traditional SEI relies on Li$^+$-conducting but e$^-$ insulating films to slow down e$^-$ tunneling from electrodes to organic-solvent based electrolytes. They are not designed to affect the voltage experienced by the liquid electrolyte, which thermodynamically speaking should still decompose at battery operating conditions. Our proposed scheme focuses on local thermodynamics, not e$^-$ tunneling kinetics.

A fast Li$^+$ transport rate is crucial for successful implementation of passivation based on Li$^+$-motion induced interfacial dipoles. Another route, not involving Li motion, is to incorporate permanent dipoles that can re-orient, such as ferroelectric films (Fig. 1b). Ferroelectric surfaces have already been used to manipulate photochemical reactivities. Most ferroelectrics are not Li$^+$ conductors. However, electrostatic effects are long-ranged, and it is likely that non-continuous ferroelectric films, lined with gaps that Li$^+$ can pass through, can serve to reduce extreme voltages experienced by liquid electrolytes.

C. Au/Li$_2$CO$_3$/vacuum (Fig. 3b) for Summary

The band alignment between Au(111) and the stoichiometric Li$_2$CO$_3$ basal plane (Fig. 2) is similar to that predicted for Au/Li$_3$PO$_4$. In the S.I., the Au(111)/Li$_2$CO$_3$(001) interface is also shown to be qualitatively similar. The broad correspondence suggests that the predicted behavior is universal for non-redox-active films.

The valance and conduction band edges of the $\Delta N$(Li)=0 basal Li$_2$CO$_3$ slab bracket the Au Fermi level (Fig. 4a), indicating no e$^-$ transfer. $V_i$ associated with this Li$_2$CO$_3$ slab is
predicted to be 3.53 V, very close to $V_e=3.58$ V there. Thus the PZC somewhat fortuitously occurs at stoichiometry. Next, we raise the voltage and try to oxidize Li$_2$CO$_3$ by removing successive Li$^+/e^-$ pairs. The most favorable Li vacancies are at the Au/carbonate interface (Fig. 7a-b). As Li are further removed (Fig. 7c, Fig. 6b-c), $V_e$ increases (Table 2). The valence band also rises until the occupied states at the Au/carbonate interface reaches $E_F$ (Fig. 6d). At this point, $e^-$ transfers from Li$_2$CO$_3$ to Au(111). Oxidation under UHV conditions thus initiate from the Au/Li$_2$CO$_3$ interface. The redox reaction pins $V_e$, which ceases to increase with another Li removal (Table 2). This is reminiscent of “Fermi level pinning” at metal-semiconductor interfaces by surface/defect states, except that in LIB the “defects” are mobile Li$^+$ vacancies, not static impurities, and their density can be much higher. When 6 Li vacancies are created at the interface, $V_e$ increases again. This may due to the complete removal of $e^-$ from some surface states. Unlike Li$_3$PO$_4$, the interfacial layer of Li$_2$CO$_3$ starts to lose structural integrity with removal of multiple Li$^+$ (Fig. 7c).

Removing one Li from the middle of the Li$_2$CO$_3$ slab (the hole remains on the Au surface) is less favorable by 0.25 eV compared to removing Li$^+$ at the Au/carbonate interface. Removing a Li$^+$ on the vacuum surface (Fig. 7d) is less favorable by another 0.22 eV, and $V_e$=4.50 V, much higher than the most energetically favorable Li$^+$ vacancy at the interior Au(111) interface. These configurations reveal an inhomogeneity in the energy landscape perpendicular to the interface that may strongly affect Li$^+$ transport—especially if Li$^+$ has to escape from the interior interface to the outer carbonate surface to the liquid electrolyte.

**D. Au/Li$_2$CO$_3$/EC/vacuum** (Fig. 8c) for summary

Next we use this Li$_2$CO$_3$ example to illustrate the impact of including explicit molecules in the theoretical models. A monolayer of adsorbed ethylene carbonate (EC) molecules is shown to exhibit profound effect on predicted voltages. Such molecular adsorption might be realized under UHV settings. We stress that frozen EC layers at $T = 0$ K cannot be considered adequate approximations of liquids at finite temperature.

Fig. 7e corresponds to Fig. 7a except for the adsorbed EC monolayer. The solid film atomic structure, energetics of successive Li removal ($V_i$, Tables 2 and 3), and DOS (Fig. 6a and Fig. 8a, after shifting $E_F$ to zero), are almost identical with or without EC. This is unsurprising because the EC layer neither transfers $e^-$ to nor form a chemical bond with
FIG. 6: Kohn-Sham orbitals of Li$_{2-x}$CO$_3$/Au decomposed on to atoms at their coordinates perpendicular to the interface. (a): stoichiometric; (b): 2 Li$^+$ vacancies inside; (c): 3 Li$^+$ vacancies inside; (d): 4 Li$^+$ vacancies inside. $E_F=0.0$ eV. The vacuum levels are at 4.93, 5.40, 5.40, and 5.40 eV in the four panels. Au and thin-film-based orbitals are depicted in black and red, respectively. $ho_r=0.005$.

FIG. 7: Li$_{2-x}$CO$_3$/Au: (a): 1 Li$^+$ vacancy inside; (b): 2 Li$^+$ vacancies inside; (c): 4 Li$^+$ vacancies inside; (d): 1 Li$^+$ vacancy outside. (e) 6 EC on stoichiometric Li$_2$CO$_3$/Au; (f) 5 EC, 1 PF$_6^-$ on Li$_2$CO$_3$/Au. F is in pink; see Fig. 2 caption for color key. (The figures are removed due to file size limitations – they can be found in the JPCC paper or are available upon request.)

Li$_2$CO$_3$. However, this “spectator” EC layer leads to a large $\mathcal{V}_e$ decrease. They carry sufficiently large dipole moments, even when tilted almost flat in the adsorption geometry, to reduce $\mathcal{V}_e$ by $>1$ V compared to vacuum interfaces. At liquid-solid interfaces, thermal fluctuations should modify the $\delta$ value predicted for the monolayer EC in vacuum at T=0 K. Nevertheless, liquid EC at finite temperature has also been shown to change the PZC of the LiC$_6$ edge plane by more than 1 V. EC molecules are highly asymmetric; they bind strongly to cations, including Li$^+$ ions at material surfaces, but weakly to anionic species. The
resulting dipole layer decreases the vacuum $\mathcal{V}_e$ on both anodes and cathodes unless the surfaces are sufficiently highly charged to force reorientation of the molecules.

The DOS of Fig. 8b may superficially seem to suggest Li$_2$CO$_3$ oxidation can occur at a very low $\mathcal{V}_e=2.31$ V. However, $\mathcal{V}_e$ predicted with no Li vacancy is already lower than $\mathcal{V}_i$ computed for removing one Li. The correct interpretation of the first 3 columns of Table 3 is that the Li content needs to increase in the direction of $\mathcal{V}_e$ until all Li-sites are occupied (Sec. II). It is inconsistent for (Li$^+,e^-$) pairs to be removed from the stoichiometric Li$_2$CO$_3$ slab when $\mathcal{V}_e=2.31$ V. Therefore no oxidation occurs.

So far we have considered uncharged electrodes. If a liquid electrolyte is present, net surface charges can be compensated by mobile ions in the liquid electric double layer (Fig. 1g). Fig. 7f and 8c represent a charged interface after replacing an EC molecule with a PF$_6^-$ ion. The simulation cell remains charge neutral, and the $-|e|$ charge must be largely compensated by a net positive charge on the Au(111) surface. This sets up an additional dipole moment, which increases $\Phi$ (Eq. 4). As a result, $\mathcal{V}_e$ rises to 3.53 V, very close to $\mathcal{V}_i$ under these conditions (Table 3). The DOS (Fig. 8c) shows that, while the PF$_6^-$ valence band remains well below $E_F$, some Li$_2$CO$_3$ orbitals on the outer surface has been raised almost to the Fermi level due to the close proximity of the anion. Although the extent of the surface charge depletion is difficult to quantify, Fig. 8c suggests that oxidation may initiate at the outer surface of Li$_2$CO$_3$ in liquid electrolyte if PF$_6^-$ coordinates to the carbonate surface in an inner-shell configuration (i.e., they are in physical contact), and if the carbonate film is thin enough to allow electron transport.

A thicker carbonate film will increase $\delta$ at the same PF$_6^-$ surface density because of the larger charge separation. This means that fewer PF$_6^-$ ion near the surface would be needed to generate the same voltage increase (Eq. 4). We speculate that net charges on

| $\Delta N(Li), N(PF_6^-)$ | (0,0) | (-1,0) | (-2,0) | (0,1) | (-1,1) |
|---------------------------|------|-------|-------|------|-------|
| $\mathcal{V}_e$           | 1.73 | 2.07  | 2.31  | 3.53 | 3.45  |
| $\mathcal{V}_i$           | 3.47 | 3.61  | NA    | 3.57 | NA    |

TABLE 3: Electronic ($\mathcal{V}_e$) and ionic ($\mathcal{V}_i$) voltages for the Li$_2$CO$_3$ basal plane/Au(111) interface as the number of Li vacancies at the inner surface of the Li$_2$CO$_3$ slab varies. The outer surface is coated with 6 EC and/or 5 EC and a PF$_6^-$. 

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FIG. 8: Kohn-Sham orbitals of EC/Li$_{2-x}$CO$_3$/Au decomposed on to atoms at their coordinates perpendicular to the interface. (a): stoichiometric; (b): 2 Li$^+$ vacancies inside; (c): a PF$_6^-$ replacing one EC in panel (a). The vacuum levels are at 3.12, 3.68, and 4.91 eV in the three panels. Au, Li$_2$CO$_3$, and EC-/PF$_6^-$-based orbitals are depicted in black, red, and blue, respectively. $\rho_c=0.005$. thick film surfaces are sparse and can be treated as isolated defects. The anions may also be farther away inside the liquid region and be screened by solvent molecules. As a result, the center of negative charge may or may not become more distant from the surface, and a quantitative estimate of the effect of anion-surface separation on the voltage needs to be explicitly computed. Whether thin film-coated electrodes exhibit net charges compensated by counterions in the liquid (Fig. 1f), or whether the voltage increase can be accommodated entirely by changes in Li$^+$ configurations in the solid region (Fig. 1g), depends on which option minimizes the Gibbs free energy.

E. Au/LiMn$_2$O$_4$/vacuum and Au/LiMn$_2$O$_4$/EC/vacuum (Fig. 3d for Summary)

In previous work, we have considered EC oxidative decomposition on Li$_2$Mn$_2$O$_4$ (100) and (111) surfaces, in both UHV conditions and in explicit liquid electrolyte. The liquid is found not to strongly affect the rate-determining reaction barrier on the (100) surface. The voltage dependence of EC decomposition was not considered there because
Li$_x$Mn$_2$O$_4$, like most transition metal oxides, does not have a readily-defined $E_F$.

In this work, $E_F$ is made unambiguous by putting a thin, reconstructed LMO (111) slab on a Au (111) “current collector” (Fig. 2c). Removing an $e^-$ from the system, without removing an accompanying Li$^+$, does not immediately lead to a change in any Mn ion charge state, strongly suggesting that the $e^-$ is removed from the Fermi level straddling Au orbitals (not shown). This confirms that $E_F$ is relevant for voltage estimate via Eq. 1. Allowing geometry optimization after $e^-$ removal yields a localized hole polaron which is now in equilibrium with $E_F$.

In contrast to Li$_2$CO$_3$ and Li$_3$PO$_4$, successive removal of Li$^+/e^-$ pairs from the stoichiometric LMO slab occur most favorably from the outer surface (Fig. 9a, see also the S.I.), not the LMO/Au interface. A Mn(III) turns into a Mn(IV) to accompany each $e^-$ removal. Table 4 indicates that the voltage increases with decreasing surface Li content, and $V_e=V_i$ is achieved at $\Delta N$(Li)=$-2$ under UHV conditions.

Next we add EC to the LMO surface. If the system were a liquid-solid interface, the surface Li content, net surface charge, and surface density of EC molecules which directly coordinate to available Li ions should be self-consistently deduced using AIMD simulations at finite temperature. Here we confine ourselves to $T = 0$ K and to adding one EC, yielding the surface used in Ref. 17. $\Delta N$(Li)=$-4$ in this model (Fig. 9b), and $V_e=4.23$ V, in reasonably agreement with $V_i=4.19$ V for this configuration (Table 4). The voltage is within the experimental LMO operating range. Except for the shift in $V_e$, and hence in the vacuum level, the DOS is almost unchanged from the case where no EC is present (Fig. 10a-b). With no anion on the surface, the EDL structure should resemble Fig. 1a.

### Table 4: Electronic ($V_e$) and ionic ($V_i$) voltages for the Li$_x$Mn$_2$O$_4$(0001)/Au(111) interface as the number of Li vacancies at the outer surface varies.

| $\Delta N$(Li),N(EC),N(PF$_6^-$) | (-2,0,0) | (-3,0,0) | (-4,0,0) | (-5,0,0) |
|---------------------------------|--------|--------|--------|--------|
| $V_e$                           | 3.28   | 4.33   | 4.71   | 5.24   |
| $V_i$                           | 3.27   | 3.58   | 4.40   | NA     |

| $\Delta N$(Li),N(EC),N(PF$_6^-$) | (-3,1,0) | (-4,1,0) | (-5,1,0) | (-4,1,1) |
|---------------------------------|--------|--------|--------|--------|
| $V_e$                           | 4.02   | 4.23   | 4.78   | 6.39   |
| $V_i$                           | 3.86   | 4.19   | NA     | NA     |
Fig. 9: EC and PF$_6^-$/Li$_{1-x}$Mn$_2$O$_2$/Au. Au atoms are not shown. (a) $\Delta N$(Li)=-5; (b) $\Delta N$(Li)=-4; with 1 intact EC; (c) $\Delta N$(Li)=-4; with 1 intact EC and 1 PF$_6^-$; (d) $\Delta N$(Li)=-4; with 1 broken EC; (e) $\Delta N$(Li)=-4; with 1 broken EC and 1 PF$_6^-$. $\Delta N$(Li) is the number of surface Li vacancies compared to the stoichiometric slab. See Fig. 2 caption for color key.

It is also important to elucidate the EDL structure of a charged, polaron-conducting LMO surface, not considered previously. As in the Li$_2$CO$_3$ example, we impose a positive charge by optimizing the geometry of a PF$_6^-$ anion on the LMO surface in the overall charge-neutral simulation cell (Fig. 9c). The DOS (Fig. 10c) reveals that PF$_6^-$ retains its excess electron and is not oxidized. A net +|e| compensating charge is found in the LMO slab, on a second layer Mn ion (“Mn 14”) below the LMO/vacuum interface. This layer contains Mn(II) ions, exchanged with Li$^+$ in the Persson group’s reconstruction, which may be the reason a Mn(III) ion there can lose an e$^-$ most readily. The dipole moment created by the Mn(IV)-PF$_6^-$ charge separation raises $V_e$ dramatically, from 4.25 V to 6.41 V. Comparing the DOS with (Fig. 10b) and without (Fig. 10c) the PF$_6^-$, an occupied d-orbital on “Mn 14” is indeed seen to be depopulated; its orbital energy level now moves above $E_F$. The EDL in this redox-active material now resembles Fig. 1h. A lower surface anion density will yield smaller shifts $V_e$ but will require a simulation cell with a much larger lateral surface area.
Finally, we re-examine EC decomposition on the $\Delta N(\text{Li}) = -4$ LMO slab, now with Au(111) present. Fig. 9d depicts a partially decomposed EC molecule on this LMO surface. A H$^+$ is transferred to the LMO slab without breaking any C-O bond in the EC. Its energy is $+0.35$ eV above the intact EC configuration (Fig. 9b), in good agreement with that of the reaction intermediate depicted in Fig. 5c of Ref. 17 where the Au slab was absent. A subsequent, C-O bond-breaking step is needed to render EC oxidation favorable.

Examining the spin states reveals that a Mn(IV) ion ("Mn 16") immediately below the oxide surface gains an $\text{e}^-$ to become a Mn(III). Consistent with this analysis, the DOS shows an unoccupied Mn $d$-orbital (Fig. 10b for intact EC) becoming occupied (Fig. 10d for broken EC), moving from above $E_F$ to below it due to polaronic relaxation. Some orbitals on the decomposed EC fragment reside near $E_F$, suggesting further oxidation can readily occur.

Regardless of whether an $\text{e}^-$ is added to LMO from an oxidized EC, or is removed by imposing a $+|e|$ charge due to a counter-anion nearby, only Mn redox states change. Charge localization on Mn ions, accompanied by polaronic relaxation and a compensating PF$_6^-$ or EC$^+$ fragment nearby, ensures that $\text{e}^-$ and hole never access the Fermi level which lies on Au orbitals (Fig. 10). The Au current collector only serves to establish $E_F$, with which polaron formation in LMO must remain in equilibrium. Therefore the effect of the applied voltage is indirect. Increasing $V_i$ and $V_e$ consistently requires the loss of surface Li$^+$ (Table I), which leaves the surface with more oxygen ions that are under-coordinated, and increases its reactivity towards EC molecules. Adsorbed PF$_6^-$ ions also increases the voltage.

Since $V_i$ controls the Li content at equilibrium in this voltage range (Li-sites are not fully depopulated yet), one can arguably ignore both the Au slab and $V_e$ while performing simulations of parasitic reaction on such redox-active surfaces. As discussed above, the same reaction intermediate energetics is predicted with or without the Au slab. However, $V_e$ also controls the PF$_6^-$ surface density. Anions in proximity of the electrode surface constitute spatial inhomogeneities or "hot spots" where parasitic or Li$^+$ insertion reactions may preferentially occur. Indeed, when a PF$_6^-$ is adsorbed near the EC, the deprotonated EC intermediate (Fig. 9e) is found to be $0.1$ eV more favorable than the intact EC, instead of $0.35$ eV less favorable when the PF$_6^-$ is absent. Thus voltage-dependent anion adsorption can affect interfacial processes. If the cathode material is metallic rather than polaronic,
FIG. 10: Kohn-Sham orbitals of EC and PF$_6^-$/Li$_{1-x}$Mn$_2$O$_4$/Au, decomposed on to atoms at their coordinates perpendicular to the interface. (a) No adsorbed species. (b) 1 intact EC; (c) 1 intact EC and 1 PF$_6^-$. (d) 1 broken EC. $\Delta N$(Li)=-4 in all cases. The vacuum levels are at 6.08, 5.60, 7.75, and 4.86 eV in the four panels. Au, LMO, and EC-/PF$_6^-$-based orbitals are depicted in black, red, and cyan, respectively. The filled green and violet circles refer to $d$-orbitals localized on Mn 14 and Mn 16 (see text). $\rho_e$=0.005.$^{28}$

the surface charge is more uniformly distributed,$^{72,73}$ $\rho_e$ is more relevant, and qualitatively different behavior may be observed.

V. CONCLUSIONS

Both electrons and Li$^+$ can move in the surface films covering the electrodes in lithium ion battery (LIB), and in the electrodes themselves, in response to voltage variations. This
makes LIB rather unique among electrochemical devices. The structures of electric double layers (EDL), and the atomic lengthscale manifestations of voltages, become much more complex than on pristine noble metal electrodes.

This work considers Au(111) slabs coated with Li-conducting solid electrolytes or cathode oxide materials under ultra high vacuum (UHV) conditions. The applied voltage is shown to be strongly correlated with the surface dipole density at the interface, reminiscent of photovoltaics studies. In relatively electrochemically inert thin films like Li$_3$PO$_4$ and Li$_2$CO$_3$ coated on Au(111), dipole moments responsible for voltage increase are established by creating negatively charged Li$^+$ vacancies at the interface between cathode surfaces and the thin solid films, compensated with positive charges on the cathode. The phosphate example highlights the crucial role of dipole density. The carbonate case emphasizes that organic solvent molecules like ethylene carbonate (EC) can dramatically modify the predicted voltage even in the absence of charged species (salt). A corollary is that the Poisson-Boltzmann theory for liquid electrolytes, which ignores solvent dipole moments, may not quantitatively describe battery interfaces.

With Li$_x$Mn$_2$O$_4$ (LMO) cathode oxide thin films coated on Au current collectors, charge transfer occurs at the outer LMO surface and involves changes in Mn redox states. The Au slab only indirectly determines the surface Li content and the anion surface density. Modeling of electrolyte decomposition on such electrode surfaces arguably does not require explicitly including the current collector. However, the voltage-dependent surface density of PF$_6^-$ creates inhomogeneities and hot spots where fast electrolyte decomposition can occur.

We also critically examine the definitions of “applied voltage” in DFT calculations at interfaces. We distinguish two voltages: electronic ($\mathcal{V}_e$), due to electronic motion, and ionic ($\mathcal{V}_i$), due to Li$^+$ redistribution. In any atomic configuration, $\mathcal{V}_e$ is well defined in a metallic electrode and should coincide with the experimental voltage imposed via a potentiostat. $\mathcal{V}_i$ is a self-consistency criterion. At equilibrium, the system is pinned by Li$^+$ insertion redox reactions, and $\mathcal{V}_e=\mathcal{V}_i$. It can be efficiently computed using the “lithium metal cohesive energy” method widely used in the battery theoretical literature, although most previous work neglects the possibility of net surface charges, compensated by ions inside the liquid electrolyte, which may affect parasitic reactions and Li$^+$ insertion kinetics.

But out-of-equilibrium conditions are also critical to many battery-related phenomena such as SEI formation and electroplating. Here $\mathcal{V}_e$, which governs electron content at battery
interfaces, is the correct definition of voltage. However, the work function-derived definition of $V_e$ does not fully account for spatial inhomogeneities. Our solid state modeling considerations form the basis for future AIMD simulations of thin film-coated electrode/liquid electrolyte interfaces.

**Supporting Information**

A supporting information (S.I.) document provides more details about the model systems used, reports calculations on Li$_2$CO$_3$(001)/Au(111) interfaces and Li$_2$CO$_3$ bulk crystal decomposition thermodynamics considerations, and gives a brief comparison between aqueous interfaces and battery electrolyte interfaces. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

**Acknowledgement**

We thank Steve Harris, Sang Bok Lee, John Cumings, Yue Qi, Peter Feibelman, and Ismaila Dabo for useful discussions, and Nitin Kumar for performing preliminary CO$_3^{2-}$ breakdown simulations. This work was supported by Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DESC0001160. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

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88 The spatially decomposed DOS plots Fig. 3, 5, 7, and 9 follow Refs. 72. They are constructed from the VASP PROCAR output file which approximately decomposes $e^-$ spatial distributions onto individual atoms. Contributions above $\rho_e=0.07$ and $\rho_e=0.05$ are included for Li$_3$PO$_4$/Au and Li$_2$CO$_3$ plots. Different criterion are used because $e^-$ are delocalized to different extent at different interfaces; we stress all DOS decomposition schemes are approximate.
Eq. 4 implies that a small, $-0.01 \, |e|/\text{Å}$ interfacial dipole density is sufficient to reduce the voltage by 1.8 V.

Most monatomic anions like $\text{Cl}^-$ would lose an $e^-$ to the electrode under UHV conditions. Fortunately, the highest occupied molecular orbital (HOMO) of $\text{PF}_6^-$ lies far below the Fermi level in all cases and permit this strictly illustrative test.

Transferring one $e^-$ to the LMO surface does change $V_e$ due to the small lateral surface area of the simulation cell. In the limiting case of one EC decomposition on an infinite LMO surface, such voltage changes should be minimal. We also note that the $\Delta N(\text{Li})=-4$ voltage of $\sim 4.2$ V should in reality induce some loss of Li from the bulk LMO regions. This effect has been omitted in Ref. 17 for simplicity; it should make EC decomposition occur even more readily because it will produce more Mn(IV) ions in the near-surface region.
