

Electric field induced formation of a two-dimensional adatom gas on cryogenic Li surfaces

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Intense electrostatic fields, such as those able to break bonds and cause field-ion emission, can fundamentally alter the behavior of atoms at and on the surface. Using density functional theory calculations on the Li (110) surface under high electrostatic fields, we identify a critical field strength at which surface atoms occupying a kink site become thermodynamically unstable against adatom formation. This mechanism leads to the formation of a highly concentrated two-dimensional adatom gas on the surface. Moreover, the applied field reverses the stability of preferred adsorption sites, enabling barrierless diffusion of lithium atoms even well below the threshold required for field evaporation. The here identified mechanisms offer a unified explanation for experimental observations in atom probe tomography and for understanding high electric field phenomena at battery interfaces and electrochemical environments, especially formation of Li rich dendrites.

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I. INTRODUCTION

Electric fields critically influence the adsorption and diffusion energies of adatoms, directly impacting surface dynamics and phase stability [1]. At sufficiently high electric fields, surface atoms may undergo field desorption, ionization and evaporation—phenomena that are the basis for advanced characterization techniques such as field ion microscopy [2–4] and atom probe tomography (APT) [5,6]. These materials characterization techniques enable near-atomic resolution imaging and compositional analysis.

Previous studies have shown that electric fields can induce surface phase transitions in metals like lead (Pb) [7] and gold (Au) [8]. For Au, electric fields act as reversible triggers to induce surface roughening, as observed via *in-situ* transmission electron microscopy. Estimated electric fields of 10^9 V/m were applied to Au nanocones, resulting in a disordered phase occurring at room temperature or higher. *Ab initio* molecular dynamics calculations, including electric fields, confirmed surface roughening in Au nanoparticles, although the underlying mechanism remained poorly understood. Electrostatic fields are also known to cause surface reconstructions, as theoretically analyzed for platinum (Pt) and Au (110) surfaces [9],

where reconstruction resulted from the interaction between surface charge and the work function. Additionally electric fields and its gradients on surfaces are known to alter the surface diffusion paths and barriers [10–18].

In the present study, we will focus on the impact of high electric fields on Li surfaces. Li is widely used in modern technology due to its unique properties and wide-ranging applications involving high electric fields. As the active charge carrier in lithium-ion batteries, Li is critical for energy storage solutions, i.e., batteries that are both viable and scalable [19]. Li is also proving to be an unmatched element for most energy efficient production of ammonia [20]. These Li ion batteries power devices—from portable electronics to electric vehicles—are essential for integrating renewable energy sources into the grid. However, Li-ion batteries face significant challenges, such as dendrite formation during charging cycles. Dendrites are needlelike Li-rich deposits that can grow inside the battery, potentially causing short circuits and reducing battery life [21–23]. Additionally, the limited cycle life and safety concerns associated with dendrite-induced failures hinder the effectiveness of these batteries. The effect of electric fields is also crucial in understanding dendrite formation, where electric fields can reach $10^6 - 10^7$ V/m and even higher orders of magnitude in the early growth stage [24,25]. In addition, the low-melting point of Li makes it suitable for a liquid metal ion source in a focused ion beam (FIB) [26–29]. FIB systems are used for precise material removal and nanoscale imaging in semiconductor fabrication and materials science research. Despite its potential, using Li in FIB technology presents challenges, including the instability of Li ion sources due to its high reactivity and low melting point, and difficulty in controlling Li ion beams, which affects resolution and precision [30,31].

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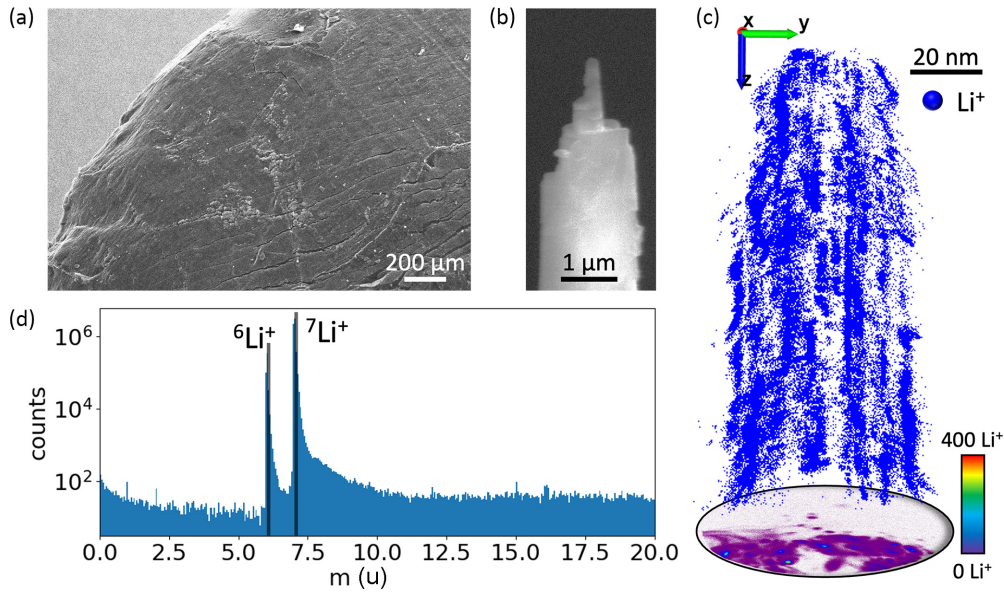


FIG. 1. (a) SEM image of a sliced Li bulk. (b) APT specimen of cryo-FIB prepared pure Li sample. (c) Reconstructed 3D atom map with a detector contour map (0 to 400 ion counts) map in a bottom. (d) The corresponding mass spectrum with two naturally occurring Lithium isotopes, with a measured isotope ratio of 13.2 (theoretical 12.2).

II. METHODS

Motivated by these findings and the challenges in Li applications, we investigated the electrostatic field effects on Li surfaces by APT experiments and state-of-the-art *ab initio* simulations that directly incorporate the electrostatic field [32,33]. An important step in bringing theory and experiment together is the development of an approach to extend the powerful concept of density functional theory (DFT) constructed surface phase diagrams to include the electric field as a state variable. Using this approach, we explore the high-field behavior of Li surfaces and show that electrostatic fields can drive a phase transition from a conventional, largely adatom-free surface to a two-dimensional (2D) adatom gas. The formation of such a dense adatom gas naturally explains the formation of Taylor cones in the APT experiments, a feature that has only been observed when probing liquids such as water [34]. By demonstrating that electrostatic fields effectively induce and regulate surface phenomena in Li, our results lay the ground for manipulating atomic-scale properties and advancing Li-based technologies. This encompasses not only more reliable APT analyses but also potential enhancements in battery performance and focused ion beam applications, ultimately underscoring the strategic importance of Li as a critical resource.

First, specimens for APT were prepared from a pure Li foil (Alfa Aesar, 99.9%) using a dual beam scanning electron microscope (SEM)/Xe-plasma focused ion beam (PFIB), FEI Helios PFIB, following the protocol proposed for pure Na [see Figs. 1(a) and 1(b)] [35]. The prepared samples were transported to a CAMECA 5000 XS atom probe through an ultrahigh vacuum (UHV) suitcase [36]. APT measurements were conducted at a base temperature of 60 K, using laser mode with an energy of 15pJ and a frequency of 100 kHz at a detection rate of 0.4%. The detector event histogram, bottom inset in Fig. 1(c), shows concentrated spots of ion hits, which

when reconstructed look like the elongated plumes seen in Fig. 1(c), resembling those reported in Li-containing oxides [37–39]. This is in stark contrast to “normal” APT datasets, which typically show uniform field evaporation [40–44]. There is no measurable influence of this field evaporation behavior on the time-of-flight measurements. The mass-to-charge-ratio can hence be properly calculated, Fig. 1(d), and the two isotopes of Li are correctly identified.

III. RESULTS AND DISCUSSION

The formation of hotspots on the detector has previously been associated to the formation of so-called Taylor cones [34,45–47]. These conical protrusions can form on liquid surfaces under strong electric fields, and the locally higher curvature at the apex of the cone enhances the electric field, facilitating field evaporation. Similar patterns have been reported in the APT analysis of water [34]. By virtue of field evaporation these sharp features smoothen out, and field evaporation continues by formation of new cones at a different location. As the reconstruction is built sequentially from the ion impact positions [41], this leads to the appearance of individual plumes, that each correspond to the formation and exhaustion of a cone.

Based on these experimental observations, we hypothesize that the Li surface undergoes a dramatic change from its stable crystal structure under these high electrostatic fields. To investigate this hypothesis, we conducted systematic DFT calculations that explicitly include high electrostatic fields [32] to investigate the behavior of Li metal surfaces. On the surface, steps and kinks are the relevant sites for field ion imaging and field evaporation due to their lower coordination and thus weaker bonding. To represent such features using periodic slab models that are computable within DFT, carefully chosen high-index surface orientations are employed.

To set up the simulations, we designed a tool to generate metallic slabs of a high Miller index [48] with selected terrace, length, and direction of steps and kinks, inspired by the work by Van Hove and Somorjai [49]. This tool and all the DFT calculations we discuss later are set up and analyzed in pyiron [50], which is an integrated development environment for atomistic simulations. We created a bcc Li (110) surface with 65 atoms. To apply an electrostatic field on one side of the slab, we use the generalized dipole correction implemented in the DFT library S/PHI/nX [32,51]. For the calculations, we use the projector augmented wave pseudopotentials taken from the Vienna *Ab initio* Simulation Package (vasp) library and the Perdew-Burke-Ernzerhof [52] exchange-correlation functional. We ensured a careful convergence with respect to the $\mathbf{k}$ points and the energy cutoff for plane waves to yield an accuracy of 10^{-3} eV in the relevant energies. A $\mathbf{k}$ -point sampling of $6 \times 6 \times 1$ for (110) cells and equivalent $\mathbf{k}$ -density sampling for (952) with a plane-wave energy cutoff of 550 eV was used. *Ab initio* molecular dynamics (AIMD) simulations were performed using vasp VASP with a timestep of 1 fs, with an energy convergence threshold of 10^{-4} eV. Temperature control was achieved using a Langevin thermostat set to 300 K and a friction coefficient of 5 ps^{-1} . For the application of an electric field of $1.25 \text{ V/\AA}$, a Python plugin was used in conjunction with vasp VASP 6.5.0, which allows users to modify vasp through Python scripting, thereby allowing for the application of an electric field via the generalized dipole correction [32]. The electrostatic field provides a degree of freedom for phase stability and has two dominant effects when applied at sufficient strength. First is the atomic scale charge (electronic) redistribution, which either softens or strengthens some bonds. Second is the induction of a tensile stress on the slab, called Maxwell stress that requires an additional convergence criterion—namely, the total thickness of the slab ($\approx 18 \text{ \AA}$) and the height of the fixed layers ($7.5 \text{ \AA}$) in the slab—to yield converged interlayer relaxations to within 0.1%. Additional care must be taken for electronic occupancy smearing methods and widths used, as the charge distributions under these high electrostatic fields proved to be sensitive to them. We used Fermi-Dirac smearing with first-order entropy corrections with a width of 0.1 eV.

To understand how the electrostatic field impacts the surface phases, we chose to compute the adsorption surface phase diagram for the (110) surface of Li. For bcc Li (110) is a close-packed surface and has only slightly higher surface energy than the most stable (100) surface under field free conditions [53,54]. The self-adsorption energy of Li-on-Li is calculated in the presence of an electric field ε as

$$E_{ad}^{Li}(\varepsilon) = E_{tot}^{slab+Li^{ad}}(\varepsilon) - E_{tot}^{slab}(\varepsilon) - E_{ref}^{Li}(\varepsilon), \quad (1)$$

where $E_{tot}^{slab+Li^{ad}}$ is the total DFT energy of a metal surface with Li adatom, E_{tot}^{slab} is the total energy of the clean (110) surface, and E_{ref}^{Li} is the reference state to define the reservoir of Li adatom. On this particular Li surface, we see two possible adsorption sites, namely on-top and bridge. All these energies have been calculated as a function of electrostatic field, to get the adsorption surface phase diagram shown in Fig. 2. We note, that in contrast to common surface phase diagrams the state variable is not chemical potential or temperature but

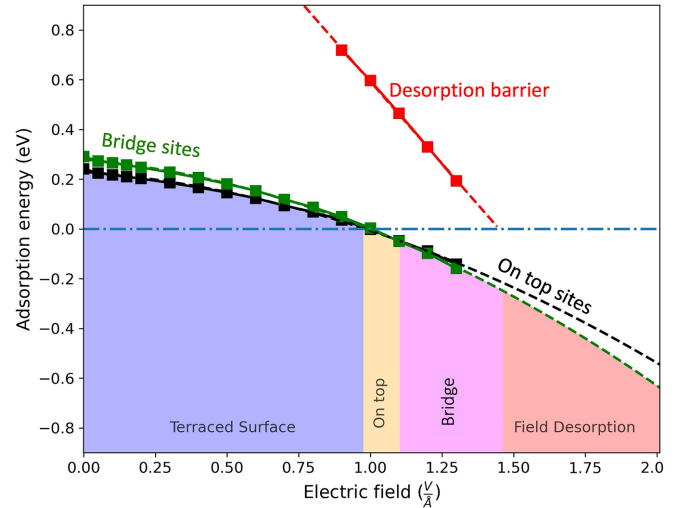


FIG. 2. The adsorption surface phase diagram of Li calculated as a function of the applied electrostatic field. The adsorption energies for the on-top (black) and bridge (green) sites are plotted as a function of electrostatic field. The field desorption barrier (for on-top) as a function of field is also plotted (red).

electric field, allowing us to directly identify the thermodynamically preferred surface phase for a given electric field.

The choice of reference is important for calculation of such a diagram. We considered the kink sites of a stepped Li surface as the reservoir for Li adatoms. These kink sites are a consequence of the hemispherical end-form of APT specimens. Kink sites represent extended reservoirs because removing an atom from such a site merely shifts the kink position along the step. Field evaporation usually occurs mainly from such kink sites due to the amplification of local electric fields [55–57] compared to terraces and straight steps. For calculations, we chose a surface of high Miller indices, namely (952). This stepped-kink surface has a (110)-type terrace with steps along the (100) direction and kinks along (111). Hence, the E_{ref}^{Li} is calculated as

$$E_{ref}^{Li}(\varepsilon) = E_b^{Li-kink}(\varepsilon) = E_{tot}^{slab+kink}(\varepsilon) - E_{tot}^{slab-kink}(\varepsilon) \quad (2)$$

where, $E_b^{Li-kink}(\varepsilon)$ is the binding energy of Li kink atom as function of electrostatic field, which is the difference of total energy of slab containing a Li kink site [$E_{tot}^{slab+kink}(\varepsilon)$] and total energy of the slab after removing the kink atom [$E_{tot}^{slab-kink}(\varepsilon)$]. Using this reference, the adsorption energies of Li on two sites, i.e., on-top and bridge sites are calculated at different electrostatic fields. In the field-free case, the kink-site reference is identical to the chemical potential of the bulk because the surfaces before and after removal are translationally equivalent. In the presence of the field, there is a small difference due to the extra field-induced energy in the volume of the atom. For periodic surfaces considered in our computations, it can be expressed directly as

$$\Delta E = \frac{1}{2}\epsilon_0\varepsilon^2\Delta\Omega = \frac{1}{2}Q\varepsilon\Delta z,$$

where ϵ_0 is the dielectric constant of the vacuum, $\Delta\Omega$ the volume per atom of bulk Li, Q the charge per surface unit cell and Δz the displacement of the periodic surface along the surface normal when the atom is removed. The equivalence of

the two expressions is a direct consequence of the relation of surface charge density and electric field,

$$\frac{Q}{A} = \epsilon_0 \epsilon.$$

In field-free cases, the on-top site is energetically favored over the bridge site for Li by about 50 meV. This agrees with an earlier DFT study on Li adsorption energies [53]. This contrasts with the common adsorption site preference in other metals, where either bridge or hollow sites are preferred due to their higher coordination number. The application of electrostatic field shows a further stabilization of adsorption sites [1] compared to the kink-site reference. This is expected as the additional charge due to electrostatic field can be localized on a single atom closer to the counterelectrode, leading to the stabilization of the adsorption sites.

Interestingly, at fields above ~ 1 V/Å, both adsorption sites are thermodynamically preferred over the kink site, as the adsorption energies becomes negative. This implies a spontaneous dissolution of kink sites, to move to the adsorption sites, preferentially to the on-top sites. Thus, the region marked by the blue-colored “terraced surface”, is the most stable surface configuration for fields up to ~ 1 V/Å. Further increase in the electrostatic field lowers the adsorption energies. Up to ~ 1.1 V/Å, the on-top adsorption site continues to be more stable than the bridge site. However, the energetical differences among them are very small compared to the thermal energy at 60 K, which is ~ 5 meV. At electrostatic fields greater than 1.1 V/Å, the bridge site adsorption energy is lower than the on-top adsorption energy, leading to a switch in the favoured adsorption site from on-top to bridge site. These regions are marked in the adsorption-surface phase diagram where the on-top and bridge site adsorption regimes are marked in yellow and pink, respectively. The concentration of the adsorbed Li atoms remains finite, however, due to a repulsive interaction between them, which would raise the adsorption energy and thus require higher fields to become thermodynamically competitive. To verify this, we calculated the surface phase diagram for adsorption as a function of both electric field and the coverage of Li adatoms, see Supplemental Material Fig. S2 [58]. These calculations show the repulsive interactions between the adatoms increase the “critical” electric fields for thermodynamically spontaneous dissolution of kinks with increasing adatom coverage. At higher coverages the “critical” field becomes comparable to the field desorption strength. Our focus however is on the low-coverage regime where Li adatoms behave as independent particles and rarely occupy neighboring sites, allowing us to neglect global coverage effects. At higher coverages, repulsive interactions limit adatom density, but these do not significantly affect local bonding changes during diffusion.

Under such high electrostatic fields, field-induced desorption of the adatoms becomes prevalent. Usually, the adatoms have higher propensity to get field desorbed than atoms embedded into the surface, so it is relevant to evaluate the field desorption barriers for the adatom. For this we have calculated the potential energy profile as seen by an on-top adatom, as it is gradually moved away from the (110) surface. On this path, the atom is gradually acquiring a positive net charge [32,33,59]. In other words, the adatom gradually turns into

an ion, also known as the charge-draining mechanism of field desorption [60]. At a given sub-critical field, this results in a 1D potential energy curve with a barrier that must be overcome by the adatom to become a free ion. These field evaporation/desorption curves are calculated at each electric field strengths, by gradually moving the atom of interest only along the direction of the electric field to compute the energy of the system, as detailed in Refs. [32,33]. Figure 3(a) shows the field desorption curves for the on-top adatom for fields ranging from 0.9 V/Å to 1.3 V/Å, with a significant barrier for field desorption. Even at a field strength of 1.3 V/Å, the barrier is estimated to be 0.15 eV, positioned at 2.3 Å away from the adatom site. Field desorption is therefore unlikely under these conditions, and stable adatoms should be seen on the Li surface even at these high electrostatic fields. The field desorption barriers are extracted from these curves and are plotted in Fig. 2, to show the relevant electrostatic field strengths where field desorption is to be expected. A linear extrapolation to the “zero” barrier is found to be at ~ 1.43 V/Å. Thus, the on-top site for adsorption continues to be stable till ~ 1.43 V/Å, after which the adatom is expected to field desorb. The field desorption barriers for bridge site adatom show a very similar profile (see Fig. S1).

Other relevant information to be considered is the field evaporation curves for kink site Li atoms as these kink sites are shown to dissolve and move to adatom sites from our calculations shown in Fig. 2. The field evaporation curves for a kink atom on the (952) Lithium surface for fields ranging from 0.8 V/Å to 1.5 V/Å are shown in Fig. 3(b). The field evaporation curves for the kink atoms are computed similarly as the field desorption curves. A barrier of 0.13 eV is still seen at 1.3 V/Å indicating that the field evaporation is less likely to occur. We also observed the roll over motion of kink Li atom on to the terrace in some cases. This also suggests that the kink atoms would either dissolve and diffuse on the terrace or can become adatoms on the terrace due to roll over motion. These calculations indicate that the dissolution of kink atoms to adatom sites is a very likely phenomenon to occur before either field desorption or field evaporation can occur.

To understand these peculiar effects of the electrostatic field on Li, we looked at the interatomic distances between the adsorbed Li atom and its first nearest neighbor. When adsorbed on an on-top site and despite a change to the charge of only approximately 5%, Li tends to form a dimer-like bond with the surface atom, with an interatomic distance of 2.65 Å. We also performed a DFT calculation for the Li₂ molecule and obtained a bond distance of 2.7 Å, which is comparable to the observed first neighbor distance for on-top adsorption site. We therefore conclude that the on-top lithium atom forms a covalent bond with the surface atom. Such unique bonding character for the on-top site also leads to a reduced height of the on-top adatom compared to the bridge site adatom. Figure 4(a) shows the heights of atoms for on-top and bridge configurations, respectively. Due to the difference in the heights of the adsorbed atoms and the possible formation of “dimer”-like bonds for the on-top site (evaluated from bond lengths), the on-top atom can develop a smaller positive charge. This smaller charge is confirmed by computing the Hirshfeld charge [61] on the adatoms. Figure 4(b) shows the Hirshfeld charge of the adatom at 1.2 V/Å field for either

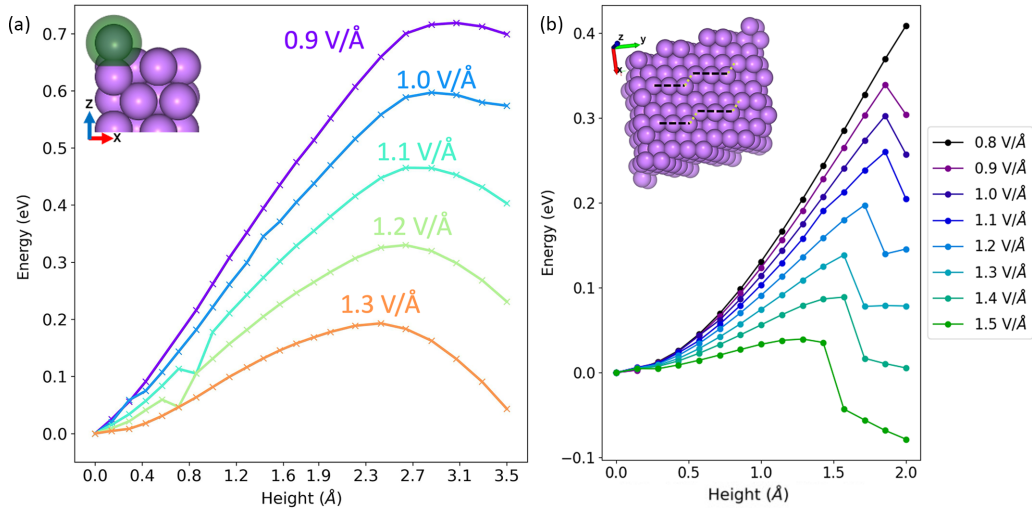


FIG. 3. (a) Field desorption curves for on-top adatom on Lithium (110) surface showing the presence of barrier. (b) Field evaporation curves for the kink atom evaporation from a (952) stepped Lithium surface. The insets show the corresponding surface configurations.

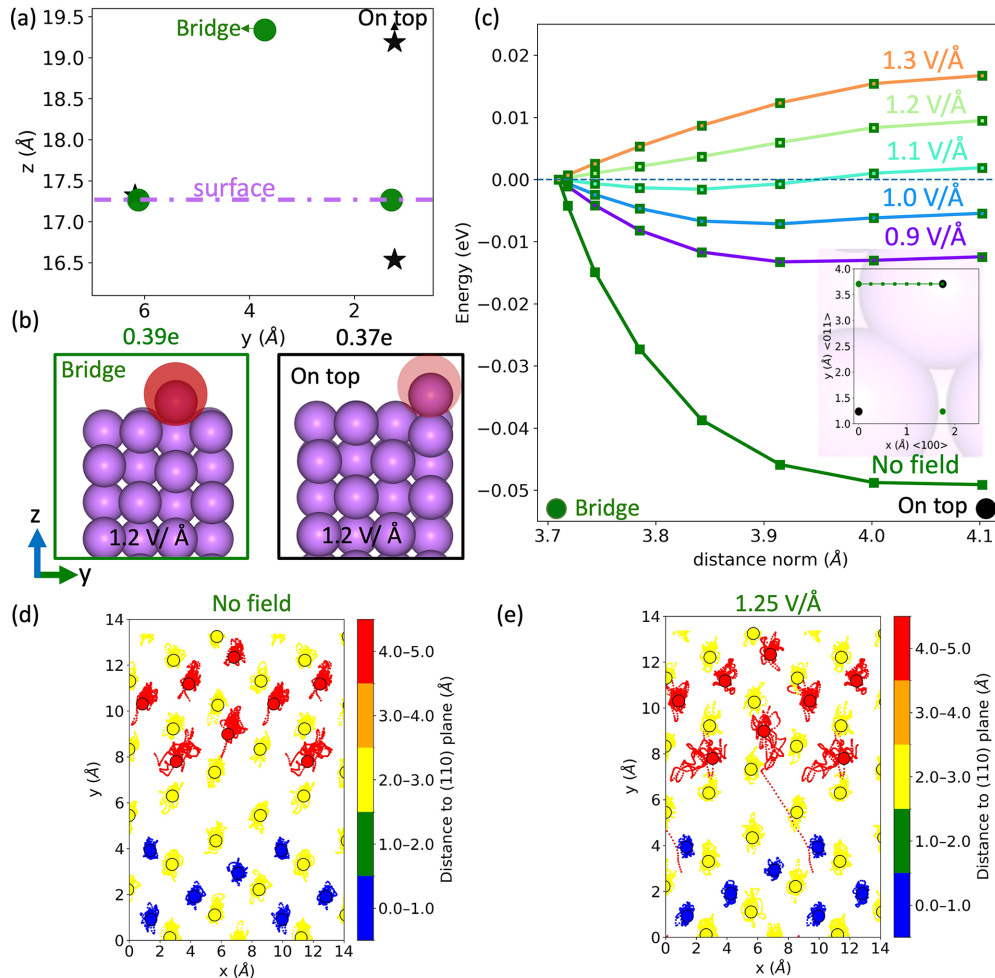


FIG. 4. (a) z-y positions of the atoms in bridge configuration (in green, circles) and on-top configuration (in black, stars), indicating that bridge site protrudes slightly outwards compared to the on-top atom. (b) The Hirschfeld charge acquired by the bridge atom and on-top atom at $1.2 \text{ V/\AA}$ field. (c) The energy profile along the green path from bridge site to on-top shown in the inset, for the various fields. The switch in the preferred adsorption site as a function of field and the reduction in diffusion barrier is seen. (d) AIMD trajectories of the atoms from top 3 layers of the kinked (952) surface, repeated twice along x, at 300K without any external field, the atoms are coloured according to the distance from the (110) plane forming the terrace and in (e) the trajectories are shown with a field of $1.25 \text{ V/\AA}$, where spontaneous dissolution of kink atom is seen.

configuration. The on-top site develops an overall lower charge of $0.37e$ than the bridge site atom's charge of $0.39e$.

In Fig. 2, we also saw that the adsorption energies of both sites are very similar near the critical field, where kinks can spontaneously dissolve. To understand the surface diffusion behavior of the adatom, we calculated the energy profile along the green path from the bridge site to the on-top site, shown in the inset of Fig. 4(c). The calculation follows a similar procedure as the field evaporation curves, with the difference being the adatom is moved laterally on the surface at each electric field, while its z coordinate is allowed to relax. The energy profiles are referenced with respect to the bridge site and are calculated for various magnitudes of electrostatic fields. As seen previously when the electrostatic field is absent the on-top site is the stable site compared to the bridge site. The relative stability of the on-top site changes with the introduction of the electrostatic field. Above $1.1 \text{ V/\AA}$, the bridge site becomes relatively more stable than the on-top site. Apart from that, in Fig. 4(c) it is evident that the energy profile becomes almost flat at $1.1 \text{ V/\AA}$ and further increase of the electrostatic field destabilizes the on-top site. The almost flat energy surface indicates a barrier less surface diffusion of Li adatoms could occur on the Li surface. The electrostatic field thus affects not only the relative stabilities of the adsorbed sites, but also the surface diffusion barriers.

The electrostatic field is known to reduce the surface diffusion barrier [1]. In addition, the field evaporation and desorption strength being greater than the field at which the switch in the preferred adsorption sites happens, leads to a very mobile layer on the surface of Li under electrostatic field. This allows for the Li surface to undergo a phase transformation from a kink/stepped surface to a 2D adatom gas phase (due to no surface diffusion barriers), which is stable. The energy profile along two different paths on a kinked surface (952) for the kink atom at $1.25 \text{ V/\AA}$ is shown in Fig. S4. The energy profile clearly shows that a significant energy is gained as the kink atom is moved to an adatom position, with a barrier of 0.09 eV . Based on these results, we performed AIMD calculations, which demonstrate the spontaneous emission of adatoms from a kinked/stepped surface with the application of an electric field under finite temperature. Figures S5 (a), (c) and (b), (d), show the AIMD 5-ps trajectories at 300 K for the kinked surface (952) under no applied electric field and with an electric field of $1.25 \text{ V/\AA}$. The trajectories of the atoms belonging to the top three layers of the slab are shown in Figs. 4(d) and 4(e). The atoms are colored according to their distance from the (110) terrace forming plane. The 300 K

temperature was chosen based on the barrier estimated from the DFT calculations and to mimic the experimental conditions experienced due to laser pulsing in APT. In the case of an applied field, the kink atom spontaneously breaks away from the step and moves to an adatom position on the terrace, as seen in Fig. 4(e). Additional MD simulations for an ad-atom at 60 K (Fig. S6) confirm that field-supported diffusion persists even at lower temperatures. This confirms the formation of a 2D adatom gas phase for fields above a critical value.

In summary, by extending the concept of surface phase diagrams to include the electric field as a state variable, we have demonstrated the huge impact that electric fields, even below the field desorption limit, can have on surface stability and kinetics. In particular, for Li as a technologically highly relevant prototype material, we have identified regions in the phase diagram where the crystalline surface becomes thermodynamically unstable against the formation of a gas/liquid-like surface state, a state that would not be expected to form at the low temperatures encountered in a cryogenic environment. The high sensitivity of surface states and diffusion barriers to electric fields provides an important means of actively manipulating them using an easy-to-control quantity such as the electric field. Such phase diagrams are also expected to be very useful in identifying conditions where, selected phases are absent, e.g., where such phases would lead to degradation or dendrite formation. Finally, we note that the approach outlined here to construct surface phase diagrams with the electric field as a state parameter from DFT surface calculations, where the electric field has been explicitly included, is general and can be easily applied to any system and surface structure.

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DATA AVAILABILITY

Some of the data that support the findings of this article are openly available [62]. The density functional theory datasets from S/PHI/nX are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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