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Density functional theory screening of gas-treatment strategies for stabilization of high energy-density lithium metal anodes

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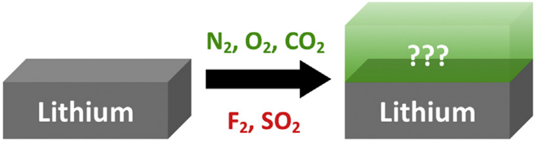
HIGHLIGHTS

- DFT suggests energetically viable gas-induced reconstructions of metal Li surfaces.
- Gas decomposition can change the work function of metal Li by more than 1 eV.
- SO_2 treatment modeled to lead to insulating ultra-thin passivation layers.
- N_2, CO_2, O_2, F_2 treatment with ≤1 monolayer leads to metallic passivation layers.
- N_2 treatment leads to the most elastically compliant ultra-thin passivation layers.

GRAPHICAL ABSTRACT



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ABSTRACT

To explore the potential of molecular gas treatment of freshly cut lithium foils in non-electrolyte-based passivation of high-energy-density Li anodes, density functional theory (DFT) has been used to study the decomposition of molecular gases on metallic lithium surfaces. By combining DFT geometry optimization and Molecular Dynamics, the effects of atmospheric (N_2, O_2, CO_2) and hazardous (F_2, SO_2) gas decomposition on Li(bcc) (100), (110), and (111) surfaces on relative surface energies, work functions, and emerging electronic and elastic properties are investigated.

The simulations suggest that exposure to different molecular gases can be used to induce and control reconstructions of the metal Li surface and substantial changes (up to over 1 eV) in the work function of the passivated system. Contrary to the other considered gases, which form metallic adlayers, SO_2 treatment emerges as the most effective in creating an insulating passivation layer for dosages ≤1 monolayer. The substantial Li → adsorbate charge transfer and adlayer relaxation produce marked elastic stiffening of the interface, with the smallest change shown by nitrogen-treated adlayers.

1. Introduction

The increasing demand for stable, high energy density rechargeable batteries for long-range electric vehicles motivates the growing interest in developing alternative chemistry and cell

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strategies to replace existing Li-ion insertion-based technologies [1,2]. Driven by the substantial theoretical increase in energy density, great efforts are currently being devoted to the development of Li-air and Li-sulfur batteries [3–9], which depend on the (to date hypothetical) availability of stable, highly reversible, lithium metal anodes, capable of delivering a nearly ten-fold increase in theoretical capacity (3860 mAh g^{-1}) over commercially used graphite anodes (372 mAh g^{-1}) [2].

The highly electropositive nature of Li (−3.04 V redox-potential vs. SHE [10]) is responsible for its extreme (reducing) reactivity towards exposed molecular media. Similarly to graphite anodes, initial decomposition of the electrolyte and the ensuing formation of a protective solid-electrolyte interphase (SEI), which should be Li^+-ion permeable yet mostly electronically insulating, is a beneficial process for the stabilization of Li anodes [1–9]. However, the repeated removal (stripping) and re-insertion (plating) of Li atoms beneath the SEI upon electrochemical cycling is known to cause cracks in the SEI and ensuing exposure of the electrolyte to metallic Li, leading to progressive electrolyte decomposition [11]. Another unresolved issue affecting the stabilization of Li metal anodes is the formation and growth, through cracks in the SEI, of highly reactive lithium metal protrusions (a.k.a. dendrites) during cycling. Lithium-dendrite growth eventually short-circuits the battery electrodes, which might cause an organic solvent electrolyte to ignite, leading to catastrophic failure of the battery [12–24]. Recent work indicates that besides cracking in the SEI during cycling, the presence of subsurface impurities (nitrides and other compounds depending on the preparation/storage of the Li foil) at the Li anode can be critical for dendrite formation and growth [25].

Prevention of Li dendrites has so far focused on physical and chemical strategies to block their formation by controlling the SEI composition and morphology via use of pressure, SEI-stabilizing additives, ionic liquid-based electrolytes, as well as copolymer (solid) electrolytes and mixtures of liquid and polymeric electrolytes [14,15,18,19,23,26–30]. Stabilization of Li anodes is made even more challenging by the simultaneous need for the electrolyte to decompose into an electron-insulating SEI with sufficiently high diffusivity of Li^+ ions, allowing the flow of Li^+ ions to the cathode through a thermally and electrochemically stable electrolyte with a low boiling point. Although promising advances have been very recently shown to be possible via combination of carefully chosen liquid and polymer electrolytes with low reduction potential, high viscosity and large size anions [30], addition of halogenated salts (especially LiF) to the electrolyte [31], and hollow carbon nanosphere coating [32], stable cycling of Li anodes for several hundred cycles at room temperature at competitive (dis) charge rates (similar to those achieved with graphite) has, to the best of our knowledge, been achieved only once in laboratory cells [33].

The observed relationship between occurrence of cracks in the SEI and Li-dendrite formation suggests that creation of a tough (i.e. mechanical damage tolerant [34]) SEI should be beneficial in preventing dendrite formation. Recent research in damage tolerant natural and synthetic materials indicates that hierarchical multi-scale (nm to cm) structuring (extrinsic toughening [34]) of composite materials can be crucial for crack suppression [34,35]. However, the requirement of favorable Li^+ diffusivity through the SEI could be hardly meet by adoption of known extrinsic toughening strategies [34,35] leading to cm-thick SEI, which would exceed the thickness of commercial cells (both electrodes and electrolyte-soaked separator) by several orders of magnitude. These considerations make exploration of novel strategies towards formation of electrochemical and mechanical stable (nm-thick) SEI a necessity for viable stabilization of Li-anodes. To this end, the critical role of atomic relaxations for interface mechanical anomalies [36–39] and the expected substantial charge transfer involved in the SEI-formation call for atomistic insight into the structural and mechanical properties of Li anode SEI beyond available results from continuum models [24,29].

Apart from, to the best of our knowledge, one exception where gas (N_2) pretreatment of metal Li was considered [40], the explored strategies for Li anode stabilization to date have invariably targeted formation of the SEI via decomposition of the cell electrolyte or components dissolved in it [14,15,18,19,23,26–30]. Experimental work in the field has been complemented by a limited number of Density Functional Theory (DFT) studies of adatom energy and diffusion on vacuum-exposed [41] and implicitly solvated [42,43] Li surfaces, ionic liquid decomposition on defect-free Li(100) [44,45], force-field modeling of fractures in Li single crystal [46], and coarse-grained dynamic Monte Carlo studies of Li dendrites [47]. However, recent advances in the field indicate that major benefits can be achieved by pre-treating Li anodes before exposure to the cell electrolyte [40,48]. In addition, the recently established link between Li subsurface impurities and dendrite formation [25] suggests that controlled deposition of impurities in metal Li substrates could be effective in preventing dendrite formation and growth.

Qualitatively, the ideal SEI or, as we start to explore here, an alternative passivation layer created by pre-treatment of the metal Li anode, should fulfill the following conditions: **i)** it should be electronically insulating in order to prevent electron transfer from the Li anode to the electrolyte. **ii)** It should be thick enough to suppress electron tunneling from the (biased) electrode to the electrolyte. To this end, we speculate that **iii)** the occurrence of a Li-SEI interface dipole opposing (zero-bias) electron-transfer from the passivated anode to the electrolyte may be beneficial. **iv)** The SEI should be tough [34] to adapt to the volume changes of the Li anode upon cycling (stripping during discharge and plating during charge) without cracking. Alternatively, **v)** a SEI capable of quickly self-healing [49–51] the cracks created during cycling may be also highly beneficial. **vi)** The SEI should allow good diffusivity of Li^+ ions. In this respect, nm-thick SEI (favoring Li-diffusion) may be preferable, provided the SEI is sufficiently thick to keep the Li-anode and the electrolyte electronically decoupled. Ideally, **vii)** it should be possible to tune a priori the Li^+ ion diffusivity of a given SEI to match the given cathode redox chemistry and (dis)charge rate, allowing for balanced battery assembly. **viii)** The SEI should be impermeable to (and insoluble in) the electrolyte solvent and other contaminants dissolved in it. Simultaneous fulfillment of all these conditions, and stability of the SEI over several (hundred to thousand) charge–discharge cycles is clearly a formidable challenge, which can be hardly met without a thorough understanding of the atomic-scale factors governing the SEI formation and evolution upon cycling.

The SEI formation via inherently out of equilibrium chemistry during the initial contact with the electrolyte and cycling of the Li anode, and the limited atomic scale control of the pristine Li surface present severe challenges to the characterization, thence understanding and eventual optimization, of the SEI formation in controlled and reproducible conditions. These considerations, encouraging results on the beneficial role of N_2 treatment of Li metal anode [40], and the observed dependence of Li anode stability on the inert atmosphere (e.g., dehydrated air vs. argon) in which commercial Li-foils are made [48,52], make us wonder whether alternative gas–solid, equilibrium based, chemical strategies could be used to create a working (i.e. fulfilling conditions i-viii above) SEI or SEI-precursor layer on Li metal anodes, before contact with the liquid or polymeric electrolyte. To the best of this knowledge, this strategy has not been systematically studied, which motivates the present work.