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Facilitated Dissociation of Water in the Presence of Lithium Metal at Ambient Temperature as a Requisite for Lithium-Gas Reactions

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ABSTRACT The high reactivity of lithium with gas molecules under ambient conditions plays a key role, negative or positive depending on the purpose, in its wide applications. However, the underlying mechanism is still unclear. A facilitated dissociation of water in the presence of lithium (Li) at ambient conditions is revealed using molecular simulations. The subsequent reactions with other gases are investigated to elucidate the role of water in enabling lithium-gas
reactions. The in-depth understanding of controlled lithium reactively opens up a new avenue of designing highly selective gas separation processes. A controlled exclusive reaction of lithium with nitrogen in the nitrogen/methane mixture would provide infinite selectivity of nitrogen over methane revolutionizing natural gas purification industry.

INTRODUCTION

Lithium (Li) is a highly reactive element and never found in its pure form in nature.\textsuperscript{1} It reacts with moisture/water (H\textsubscript{2}O) and produces lithium hydroxide (LiOH), hydrogen (H\textsubscript{2}), and heat at ambient temperature.\textsuperscript{2} However, at ambient temperature no reaction would occur or the reaction kinetics are negligibly slow between Li metal and dry common gases, such as methane (CH\textsubscript{4}), carbon dioxide (CO\textsubscript{2}), oxygen (O\textsubscript{2}), nitrogen (N\textsubscript{2}), and hydrogen (H\textsubscript{2}). Nevertheless, some of these reactions could occur readily upon exposing Li to moist gas streams.\textsuperscript{3} For example, a Li anode reacting with O\textsubscript{2} and N\textsubscript{2} under ambient environment leads to the undesirable Li corrosion throughout Li battery manufacturing.\textsuperscript{4} Through the analysis of the final products of lithium-gas reactions,\textsuperscript{2} it is acknowledged that the presence of lithium hydroxide or lithium hydride might be responsible for those reactions.\textsuperscript{5} These observations indicate that H\textsubscript{2}O plays an indispensable role in enabling Li reaction with gases, although the underlying atomic-scale mechanism at ambient temperature is still unclear. The interplay among water molecules, gases, and lithium surface needs to be addressed more precisely in order to elucidate how such an exposure could lead to low-temperature lithium-gas reactions. Indeed, it is unclear why such reactions showed direct relationship with water content and higher water content reverses/lowers the reactivities.\textsuperscript{2}
unclear how and when, in the course of reaction, lithium hydroxide is generated and how it participates in the progress of reaction or whether it plays any critical role in these reactions or it’s just a prominent byproduct.

Understanding the interaction and/or reaction between Li metal and H$_2$O at ambient conditions is crucial to establish the Li reactivity with other gases in a moist environment.\textsuperscript{6} It in turn allows for rationally designing and optimizing applications of Li involving gases. For example, Li combustion evolution for energy storage applications\textsuperscript{7-11} involve Li reacting with various gases, such as O$_2$, H$_2$O, CO$_2$, and N$_2$. An in-depth understanding of the Li-H$_2$O reaction will benefit the design of this system. For another example, controlling specific Li-gas reactions could enable to develop highly selective and thus efficient gas separation processes. A manipulated exclusive reaction of Li with N$_2$ will find potential applications in the separation of N$_2$ from pretreated natural gas streams (mainly containing N$_2$ and CH$_4$) – among the most challenging and important gas separation applications.\textsuperscript{12} In such gas streams, N$_2$ is regarded as an impurity that needs to be removed.\textsuperscript{13} The state-of-the-art technology for N$_2$ removal from natural gas is cryogenic distillation, a process being highly energy intensive.\textsuperscript{14} A material capable of reacting with N$_2$ but not with CH$_4$ at ambient temperature and thus exclusively removing N$_2$ would afford an exceptionally high selectivity and thus efficient route for natural gas purification.

The presence of lithium hydroxide in the final product of most of these reactions\textsuperscript{5} suggests the release/generation of hydroxide group (-OH) is necessary which can be hypothesized to occur
via a water dissociation ($\text{H}_2\text{O}^* \rightarrow \text{OH}^* + \text{H}^*$) over the lithium metal surface. It is acknowledged that a water dissociation reaction could occur at any temperature but at different scales depending on the how the energy barrier is overcome.\(^{15}\) This dissociation reaction can be enhanced in the presence of appropriate catalysts.\(^{16,17}\) Various metal catalysts have been studied on promoting water dissociation using experimental measurements and density functional theory (DFT) calculations,\(^{18-36}\) addressing the water-gas shift reaction\(^{37}\) where the water dissociation needed to be enhanced in Fischer–Tropsch process.\(^{38}\) Due to the high reactivity of Li, we contend that Li can promote water dissociation via interacting with $\text{H}_2\text{O}$ and the species generated. In other words, Li could lead to a facilitated dissociation of water. However, the interaction/reaction of Li metal with water at near-ambient temperature and the subsequent dissociation of $\text{H}_2\text{O}$ have not been studied yet.

This study for the first time establishes the water dissociation process in the presence of Li metal surface at near-ambient temperature (i.e., $35 - 100 \, ^\circ\text{C}$) using computational chemistry calculations. We reveal that the generated OH and H species react with Li metal and other $\text{H}_2\text{O}$ molecules and produce mostly LiOH, small amount of LiH, $\text{H}_2$ gas, and water complexes in the form of Zundel\(^{39,40}\) and Eigen-like complexes.\(^{41}\) We conclude that this water dissociation is a facilitated process in that Li pushes $\text{H}_2\text{O}$ molecules to dissociate favorably. The fundamental knowledge established in this study shed light on advancing Li applications involving the participation of gases.
Computational Procedures

The analysis of reactivities were carried out using density functional theory calculations as follows. The linear and quadratic synchronous transition methods were employed for identifying transition-state structures using Dmol\textsuperscript{3} package\textsuperscript{42}. In transition-state search, ultrafine quality (tolerances: displacement = 10\textsuperscript{-5} Å, energy = 10\textsuperscript{-4} kJ/mol, force = 0.001 kJ/mol·Å, self-consistent field criteria = 10\textsuperscript{-6}) was applied. In the density functional theory calculations, the generalized-gradient approximations (GGA) and perdew-becke-ernzerhof (PBE) functionals were used\textsuperscript{43}. The Hamiltonian and double numerical basis including d-polarization function level of theory (version 4.4) was implemented. The thermal smearing\textsuperscript{44} was applied to control the convergence behavior in which the Fermi level energies are populated according to a thermal distribution resulting in enhanced self-consistent field calculations convergence\textsuperscript{45}. A transition-state optimization step was utilized to refine the transition-state structures. A vibrational analysis was performed to obtain frequencies spectra, identify optimal transition-state structures, and determine activation free energies\textsuperscript{46}. To calculate the minimum energy path (MEP)\textsuperscript{47} where a transition-state is identified in the prior step, and to identify other possible minima on MEP missed in transition-state search, the nudged elastic band (NEB) method\textsuperscript{48} was employed. In this method, the neighboring points on the path are connected by a fictitious spring force so that the continuity of the path and projection of the force can be ensured and the MEP can be achieved. The transition-state confirmation tool of Dmol\textsuperscript{3} package\textsuperscript{42} was then used for other minima on MEP missed. After identifying all the transition state structures as well as reactants and products,
the next step for free energy of activation calculations is an extra ensuring energy optimization step for each structure. The energy optimization was performed using the DMol³ package where GGA and becke-lee-yang-parr (BLYP) functionals were employed with aforementioned ultrafine quality. In all calculations, the solvation effect was considered using COnductor-like Screening MOdel (COSMO). The reason why we used perdew-becke-ernzerhof (PBE) functionals in transition-states search and becke-lee-yang-parr (BLYP) functionals for final energy optimization is that the possible electron/charge transfer in the course of reactions can be handled by perdew-becke-ernzerhof (PBE) functionals reliably, while in the energy optimization of finally confirmed structures where such phenomenon is not of concern, the becke-lee-yang-parr (BLYP) functionals provide a fast and reliable option. The free energy of activation of each step from state $i$ toward the neighboring state $j$ in the course of reaction coordinate is defined as difference of respective free energies. The free energy of activation is defined as the difference between reactants free energy and free energy of the transition state with the highest energy. In this case, the calculated free energies of structures were retrieved from outmol files.

In practice, the calculations are performed as follows. The calculation starts with creating the plausible reaction related documents, i.e. reactant (Li and H₂O) and products (H₂ and LiOH). Then using reaction preview tool, the atoms were matched and balanced followed by generation of an initial pathway trajectory between the reactant and product. Then the aforementioned transition-state search method as implemented in Dmol³ package was applied on the generated trajectory file while the “bond monitoring” was requested using the keyword asking for
Frequency properties of trajectory file. At a transition state, one imaginary frequency appears in the IR spectrum. The frequencies were calculated by using Vibrational Analysis tool of Dmol³ package. For each identified frequency, to make sure of approaching the correct transition-state structure, a transition-state optimization step was performed followed by a transition-state Confirmation step which uses NEB calculations. This is to guarantee that no transition-state structure is missed.

To study the interactions between solid structures, water, and water dissociation species, the adsorption energies were determined by using the configurational bias Monte Carlo techniques according to a simulated annealing schedule and compared with the activation free energies determined by DFT (Dmol). A unit cell of lithium contains 5 lithium atoms. The substrate for Monte Carlo calculations were constructed as 3 times in thickness and 15 times in width and length. This corresponds to 1800 lithium atoms in substrate. The structures were optimized in DMol³ package using the generalized gradient approximations (GGA) and perdew-becke-ernzerhof (PBE) functionals first and then used for adsorption studies. In the adsorption simulations, the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field was used following a relaxation step and charge assignment. Adsorption orientations and energies were calculated for water molecules varied from 1 to 100 for ten different runs.

Results and discussion
To elucidate the water dissociation process, we calculated the energy landscape of this process on Li (Figure 1). The computed activation free energy ($\Delta G$) of water dissociation is 2.715 kJ/mol. Note that the scaling factor for energy in molecular-scale systems with a large number of molecules $^{53} (RT = k_B T \cdot N_A$, $N_A$ being Avogadro number) at the investigated temperature range (35 – 100 °C) corresponds to $\approx$1 kJ/mol. As the $\Delta G$ of water dissociation is a bit larger than the scaling factor, extra energy must be supplied to enable this reaction to occur. We hypothesized that the released heat from the initial adsorption of H$_2$O molecule on Li surface affords the extra energy for propelling the water dissociation reaction. To examine this, the adsorption energy of H$_2$O on Li was computed to be -76.013 kJ/mol. The magnitude of this value is reasonable with respect to similar systems reported. For example, the energy released upon H$_2$O adsorption on copper was measured to be -40.524 kJ/mol, $^{54}$ sufficient for water molecules to undergo dissociation and form OH and H species. $^{32}$ Thus, we justified our hypothesis. Note that the metal surface tends to have higher water coverage at lower temperatures due to the nature of physisorption, $^{20}$ implying water dissociation occurs more readily at near-ambient conditions. $^{54, 55}$
Figure 1. Energy landscape of water dissociation on Li: red, white, purple colors correspond to oxygen, hydrogen and lithium, respectively. (A) induction stage, (B) water dissociation, (C) close contact between Li and dissociation species, (D) formation of LiH and LiOH, (E) late stage interactions between LiH, LiOH, and water leading to LiOH and H2 generation as final products, (F) products stable state. ΔG in kJ/mol for (1) 2.175, (2) 0.410, (3) 3.820, (4) 8.170, (5) 9.360, and (6) 24.470. Total energy release is 375 kJ/mol, as indicated by (7).

The evolution of water dissociation on the Li surface is presented in Figure 2. Upon moving close to Li surface, a H2O molecule orients itself with its molecular plane perpendicular to the metal surface and the oxygen atom of this H2O molecule pointing downward. A slight elongation
of O–H bonds (to 1.12 Å) is caused by the strong attractive interaction between the oxygen atom of this molecule and Li as well as the attractive interaction between the hydrogen atoms of this molecule and oxygen atoms of other H₂O molecules. Subsequent interactions of the Li with hydrogen atoms of this H₂O molecule result in the titling of the H₂O molecule, making the axis of one of the O–H bonds orient perpendicularly to the surface normal and breaking this O–H bond. The separated hydrogen atom (hydride) moves away and then binds to the Li surface (not instantaneously). The left O–H bond in parallel to the surface normal binds to the Li surface, too.

A similar behavior was also observed on transition and noble metals (Cu, Au, Ni, Pd, and Pt²³, ³², ⁵⁶–⁵⁸) and their dimers M₂ (M = Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au),²⁶ and metal ions (Al³+, Cr³+, and Fe³+).³³ We identified different species generated during water dissociation, i.e., molecular water (H₂O), hydride (H), hydroxyl group (OH), and a small number of hydroxyl and hydride groups interacting with H₂O molecules (in the form of Zundel (H₂O₂⁺)³⁹, ⁴⁰ and Eigen (H₉O₄⁺)-like (as interactions with H from OH group is involved) complexes⁴¹), as shown in Figure 3. Observation of these species is consistent with those on other metals reported in literature,²², ⁵⁵, ⁵⁹–⁶⁴ validating our simulation framework.
Figure 2. Schematic representation of the evolution of intermediates in water dissociation on Li (legends are the same as in Figure 1): (A) water molecule moving towards metal surface, (B) water rotating due to the close contact (oxygen-metal distance upon H$_2$O adsorption being 2.1 Å), (C) O-H bond elongates due to oxygen-metal interactions, (D) OH and H release, and (E) OH and H binding to metal surface generating LiOH and LiH.

Figure 3. Schematic representation of the observed formation of Zundel and Eigen-like complexes.

We observed different movement behavior for H and OH groups, as shown in Figure 4. While OH groups bind onto the Li surface immediately upon generation, H groups do after traveling a short distance. Such a different movement behavior between H and OH groups was also observed in literature,$^{23, 26, 33, 65}$ validating our simulation framework. The higher movability of H in comparison with OH on metal surfaces is related to the relative bond strength.$^{66, 67}$ The metastable bond (of both ionicity-covalency nature) forms between H and metal, weaker than the ionic bond between OH and metal, making H less strongly sticking to$^{68, 69}$ and move further on$^{70-72}$ the metal surface.
Figure 4. Schematic representation of different movement behavior of H and OH groups (legends are the same as in Figure 1).

At the final stage of water dissociation, LiOH is generated as the major product with a $\Delta G$ of 0.410 kJ/mol and LiH as the minor product with a $\Delta G$ of 3.820 kJ/mol. The $\Delta G$ for LiH
generation is just a bit higher than scaling factor (i.e., ≈1 kJ/mol) but would be suppressed by the parallel competing LiOH generation which associates with a lower $\Delta G$ than scaling factor. The higher $\Delta G$ leads to a lower reaction rate based on the transition state theory of chemical reactions ($k \equiv \exp(-\Delta G)$). Thus one would expect a higher frequency of LiOH generation over LiH.

This is consistent with the reported observations. These interactions/reactions consume OH and H and thus promote water dissociation to proceed. In other words, water molecules experience facilitated or autocatalytic dissociation in the presence of Li surface. The first observation of lithium hydride in our simulation is worthy to be further investigated by experiments as this could provide a complete picture of lithium-water reaction and have implications in subsequent reactions with other molecules. As seen from Figure 1, for the overall Li-H$_2$O reaction, the $\Delta G$ equals to 24.470 kJ/mol. This computed value is in excellent agreement with the experimentally measured value (25.940 kJ/mol), validating our simulation framework.

From Figure 1, the overall heat release of reaction is determined to be $375 + 76.013 - 24.470 \approx 427$ kJ/mol. This value is consistent with experimentally measured heat release, i.e., ≈ 480 kJ/mol, validating our simulation framework.

The ease of Li reaction with any compound, including water and other gases of interest, is governed by the relative magnitude of the $\Delta G$ with respect to the scaling factor. For instance, the large difference between the calculated $\Delta G$ of the overall reaction of Li-H$_2$O and scaling factor suggests that such Li-H$_2$O reaction is not straightforward and involves intermediate steps. Accordingly, we established that water dissociation occurs and the thus dissociated species
further react with Li to propel Li-H$_2$O reaction. To explain the observed reactivity of Li with other gases (including O$_2$, H$_2$O, CO$_2$, and N$_2$) in presence of H$_2$O, we hypothesized that the produced LiOH and LiH, as a consequence of water dissociation on Li, must play the key role instead of the Li itself. To confirm this hypothesis, we calculated the $\Delta G$ of Li, LiH, and LiOH reacting with each aforementioned gas with the results shown in Figure 5-7, respectively. A detailed discussion of these reactions is beyond the scope of the current work and will be communicated elsewhere.

**Figure 5.** Computed $\Delta G$ for pure Li reaction with considered gases: Eqs. 1 – 6 stands for (1) $2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2$, (2) $2\text{Li} + \text{H}_2 \rightarrow 2\text{LiH}$, (3) $6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N}$, (4) $4\text{Li} + \text{O}_2 \rightarrow 2\text{Li}_2\text{O} + \text{Li}_2\text{O}_2$, (5) $10\text{Li} + 3\text{CO}_2 \rightarrow 2\text{Li}_2\text{CO}_3 + 3\text{Li}_2\text{O} + \text{Li}_2\text{C}_2$, and (6) $2\text{Li} + 2\text{CH}_4 \rightarrow \text{Li}_2\text{C}_2 + 4\text{H}_2$, respectively.
Figure 6. Computed $\Delta G$ for LiH reaction with considered gases: Eqs. 1 – 7 stands for (1) $\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$, (2) $\text{LiH} + \text{H}_2 \rightarrow \text{LiH} + \text{H}_2$, (3) $6\text{LiH} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N} + 3\text{H}_2$, (4) $3\text{LiH} + \text{N}_2 \rightarrow \text{Li}_3\text{N} + \text{NH}_3$, (5) $2\text{LiH} + \text{O}_2 \rightarrow 2\text{LiOH}$, (6) $10\text{LiH} + 3\text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + 3\text{Li}_2\text{O} + \text{Li}_2\text{C}_2 + 5\text{H}_2$, and (7) $2\text{LiH} + 2\text{CH}_4 \rightarrow \text{Li}_2\text{C}_2 + 5\text{H}_2$, respectively. The absolute heat release by water adsorption on Li is 76.013 kJ/mol.
Figure 7. Computed ΔG for LiOH reaction with considered gases: Eqs. 1 – 6 stands for (1) LiOH + 2H₂O → LiOH.H₂O + H₂O, (2) 2LiOH + H₂ → LiOH + LiH + H₂O, (3) 3LiOH + N₂ → Li₃N + N(OH)₃, (4) 4LiOH + O₂ → 2Li₂O₂ + 2H₂O, (5) 2LiOH + CO₂ → Li₂CO₃ + H₂O, and (6) 2LiOH + 2CH₄ → Li₂C₂ + 2H₂O + 3H₂, respectively. The absolute heat release by water adsorption on Li is 76.013 kJ/mol.

The reaction between pure Li and the gases cannot readily occur at ambient temperatures because the ΔG (Figure 5) are much larger than the scaling factor. This finding is consistent with reactivity analysis of pure Li and considered gases in literature.²⁻⁵ The spontaneous reaction between Li and H₂O releases a considerable amount of energy that affords to overcome the ΔG for the reaction between the produced LiH or LiOH and some of these gases (Figure 6 and 7). Thus, the occurrence of facile reaction would be observed upon contacting Li with these gases in a moist environment. Taking N₂ reaction as an example, it follows a reaction between LiH and N₂ producing lithium nitride (Li₃N) and H₂. In the case of CO₂, the interaction between LiOH
and CO₂ provides a route for the production of lithium carbonate (Li₂CO₃). In the case of O₂, both LiH and LiOH are responsible and contribute almost equally to the production of lithium peroxide. These computed pathways are in excellent agreement with experimental observations.

**Conclusion**

The mechanism of facilitated dissociation of water on lithium at near-ambient temperature and its subsequent role in the observed reaction with other gases are illustrated. The presence of lithium promotes the water dissociation process via consuming the dissociation products, i.e., H and OH. On the other hand, the presence of water enables lithium reaction with other gases via lithium-water reaction products, i.e., LiH and LiOH. Such an in-depth understanding promises a wide range of applications of lithium metal involving the participation of gases. The controlled mediation of water in the reaction between mixed gases and lithium metal could allow for exclusive consumption of certain gases. For example, lithium can exclusively react and thus remove N₂ from a mixture of N₂ and CH₄, implying promising highly efficient natural gas purification (infinite selectivity of N₂ over CH₄) which represents the most challenging and important gas separation application.

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