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Supporting Information

# Atomistic Studies on Water-Induced Lithium Corrosion

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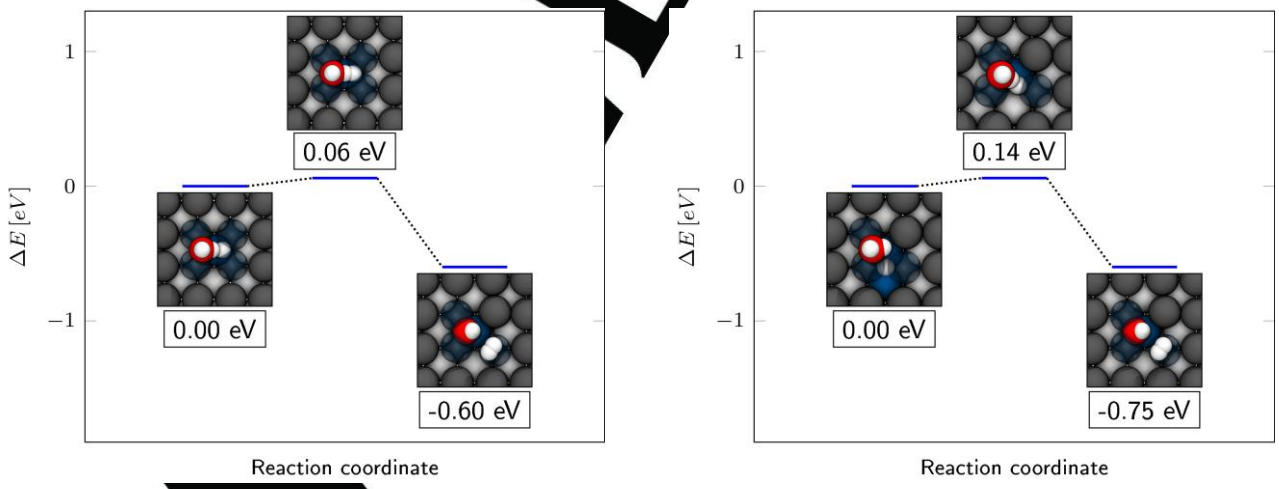
## Convergence studies

**Table 1.** Convergence study for the energy cutoff and number of ***k***-points. Shown are the binding energies per molecule $E_{bind.}$ on Li(100) for the respective settings. The Li(100)-$H_2O_{bri.}$ structure corresponds to a Li(100) surface with a single water molecule on the bridge position. On the Li(100)-$OH_{sidebri.}$ + $H_{bri.}$ structure the water molecule dissociated in a OH molecule in the *sidebridge* and a H atom in the *bridge* position. The energies were related to a single water molecule in the gas phase and are reported in eV.

| Structure | ***k***-points | ENCUT 300 eV | ENCUT 400 eV | ENCUT 500 eV |
|---|---|---|---|---|
| Li(100)-$H_2O_{bri.}$ | 2x2x1 | -0.788 | -0.777 | -0.780 |
| | 3x3x1 | -0.783 | -0.773 | -0.775 |
| | 4x4x1 | -0.783 | -0.772 | -0.774 |
| | 5x5x1 | -0.784 | -0.772 | -0.774 |
| | 6x6x1 | -0.783 | -0.771 | -0.775 |
| | 7x7x1 | -0.783 | -0.772 | -0.774 |
| Li(100)-$OH_{sidebri.}$ + $H_{bri.}$ | 2x2x1 | -2.744 | -2.668 | -2.661 |
| | 3x3x1 | -2.745 | -2.665 | -2.657 |
| | 4x4x1 | -2.740 | -2.663 | -2.655 |
| | 5x5x1 | -2.741 | -2.662 | -2.654 |
| | 6x6x1 | -2.743 | -2.661 | -2.655 |
| | 7x7x1 | -2.741 | -2.661 | -2.655 |

## Barriers and frequency analysis of transition states




(a) Energy profile for the reaction of $H_2O$ and a hydrogen atom in the front.

(b) Energy profile for the reaction of $H_2O$ and a hydrogen atom at the side.

**Figure 1.** The energy profile in **(a)** shows the hydrogen evolution through the reaction of a hydrogen atom in the *bridge* position in the front of a $H_2O$ molecule and in **(b)** the reaction path with a hydrogen atom at the side. Both profiles show the dissociation of the respective molecule under the release of one of their hydrogen atoms towards the adsorbed hydrogen atom. The framed relative energies are related to the respective undissociated structures.

**Table 2.** Summary of the $\Delta E_{\mathrm{for}}$ and $\Delta E_{\mathrm{back}}$ barriers in eV for the backward and forward diffusion, dissociation and reaction processes on Li(100) and the imaginary frequency of the respective transition states in $cm^{-1}$.

| Process | | | $\Delta E_{\mathrm{for}}$ | $\Delta E_{\mathrm{back}}$ | Imaginary frequency |
|---|---|---|---|---|---|
| Li(100)-$H_{hollow}$ | → | Li(100)-$H_{bridge}$ | 0.151 | 0.12 | -202.22 |
| Li(100)-$H_{bridge}$ | → | Li(100)-$H_{subbridge}$ | 0.124 | 0.003 | -67.72 |
| Li(100)-$H_{subbridge}$ | → | Li(100)-$H_{subsurface}$ | 0.082 | 0.0 | -51.58 |
| Li(100)-$H_{2,top}$ | → | Li(100)-$H_{bridge,bridge}$ | 0.271 | 1.44 | -231.57 |
| Li(100)-$OH_{bri.}$ | → | Li(100)-$OH_{sidebri.}$ | 0.08 | 2 | -138.85 |
| Li(100)-$OH_{sidebri.}$ | → | Li(100)-$OH_{sidehol.}$ | 0.03 | 0.0 | -57.15 |
| Li(100)-$OH_{sidehol.}$ | → | Li(100)-$OH_{hol.}$ | 0.02 | 01 | -105.92 |
| Li(100)-$OH_{sidehol.}$ | → | Li(100)-$O_{hol.}$+ $H_{hol.}$ | 0.89 | 2.30 | -1420.24 |
| Li(100)-$OH_{sidehol.}$ + $H_{bri.}$ | → | Li(100)-$O_{hol.}$+ $H_{2,top}$ | 0.40 | 0.61 | -626.62 |
| Li(100)-$H_2O_{bri.,1}$ (flip-bridge) | → | Li(100)-$H_2O_{bri.,2}$ | 0.05 | 0.05 | -97.81 |
| Li(100)-$H_2O_{bri.,1}$ (twist) | → | Li(100)-$H_2O_{bri.,2}$ | 0.14 | 0.14 | -59.37 |
| Li(100)-$H_2O_{bri.,1}$ (flip-top) | → | Li(100)-$H_2O_{bri.,2}$ | 0.15 | 0.15 | -63.06 |
| Li(100)-$H_2O_{bri.}$ | → | Li(100)-$OH_{sidebri.}$ + $H_{bri.}$ | 0.22 | 1.77 | -1300.23 |
| Li(100)-$H_2O_{bri.}$ + $H_{bri.}$ (front) | → | Li(100)-$OH_{sidebri.}$ + $H_{2,top}$ | 0.06 | 0.66 | -487.62 |
| Li(100)-$H_2O_{bri.}$ + $H_{bri.}$ (side) | → | Li(100)-$OH_{sidebri.}$ + $H_{2,top}$ | 14 | 0.89 | -186.49 |

## Adsorbate-adsorbate interactions

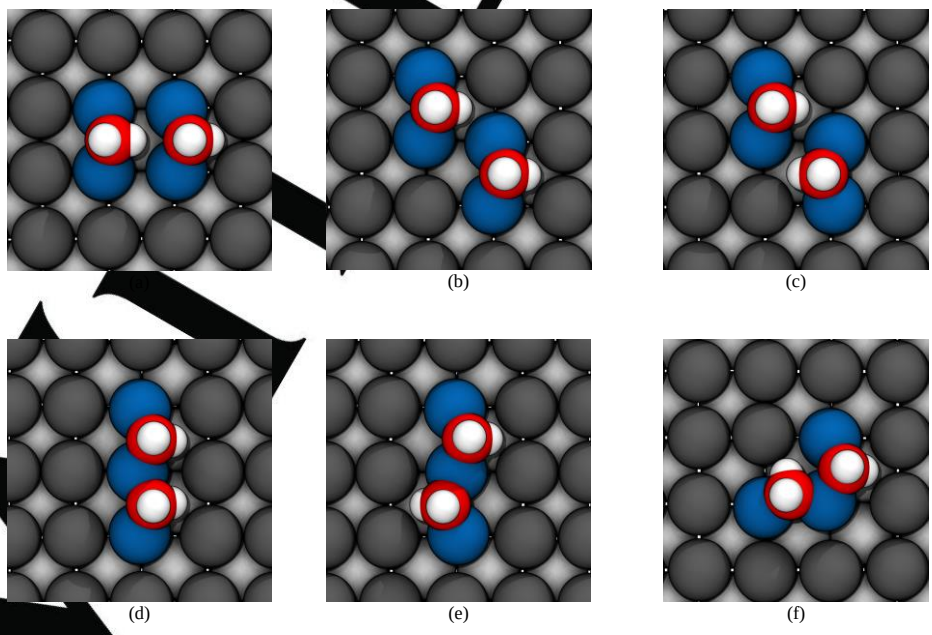



**Figure 1.** Top view of the different arrangements of $H_2O$ dimers on Li(100) in **(a)−(f)**. Hydrogen is shown in white, oxygen in red and the coordinating lithium atoms in blue.

**Table.** Binding energies per $H_2O$ molecule $E_{\mathrm{bind,mol}}^{\mathrm{dim}}$ for the respective arrangements of a water dimer on Li(100) shown in Fig. 1. The energies were related to water in the gas phase and are reported in eV. The interaction energy $E_{\mathrm{Int}}$ refers to the difference of the binding energy of the water dimers towards the one of a single water molecule $E_{\mathrm{bind,mol}}^{\mathrm{sing}}$ and is reported in meV: $E_{\mathrm{Int}} = E_{\mathrm{bind,mol}}^{\mathrm{dim}} - E_{\mathrm{bind,mol}}^{\mathrm{sing}}$.

| | Structure | $E_{\mathrm{bind,mol}}^{\mathrm{dim}}$ | |
|---|---|---|---|
| Li(100)-$(H_2O_{bri.})_2$ | (a) | -0.706 | 71 |
| | (b) | -0.767 | 9 |
| | (c) | -0.763 | 14 |
| | (d) | -0.767 | 10 |
| | (e) | -0.771 | 5 |
| | (f) | -0.729 | 48 |