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H₂O and CO₂ surface contamination of the lithium garnet Li₇La₃Zr₂O₁₂ solid electrolyte†

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Understanding the reactivity of ubiquitous molecules on complex oxides has broad impacts in energy applications and catalysis. Garnet-type Li₇La₃Zr₂O₁₂ is a promising solid-state electrolyte for lithium (Li)-ion batteries, and it readily reacts with H₂O and CO₂ when exposed to ambient air. Such reactions form a contamination layer on Li₇La₃Zr₂O₁₂, which is detrimental to the battery operation. The strong interactions of Li₇La₃Zr₂O₁₂ with H₂O and CO₂, however, make Li₇La₃Zr₂O₁₂ a promising support to catalyze H₂O dissociation and CO₂ adsorption. Here, using first-principles calculations, we investigate the adsorption and reactions of H₂O and CO₂ on a Li₇La₃Zr₂O₁₂ surface. We show that H₂O reacts through the exchange of protons and Li⁺ and produces metal hydroxide species. At high H₂O coverage, half of the H₂O molecules dissociate, while the other half remain intact. CO₂ reacts with the Li₇La₃Zr₂O₁₂ surface directly to produce carbonate species. We clarify that the individual reactions of H₂O and CO₂ with Li₇La₃Zr₂O₁₂ are more thermodynamically favorable than the co-adsorption of H₂O and CO₂. Finally, we demonstrate that low temperature and high partial pressure promote the reactions of H₂O and CO₂ with Li₇La₃Zr₂O₁₂. For the energy storage application of Li₇La₃Zr₂O₁₂, our study provides processing conditions to minimize surface contamination. From a catalysis point of view, our findings reveal the potential of using complex oxides, such as Li₇La₃Zr₂O₁₂, as a support for reactions requiring H₂O dissociation and strong CO₂ adsorption.

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1. Introduction

Energy storage and conversion devices relying on complex oxides are central to the decarbonization of our planet.^{1–4}

On one hand, lithium(Li)-ion batteries based on oxide chemistries^{1,5} offer an appealing strategy to store green energy produced by photo-voltaic panels, wind turbines, hydropower and/or hydroelectric means. Li batteries suffer from safety issues, mostly due to the flammability of liquid electrolytes.¹ Solid-state batteries, replacing the flammable electrolyte with a solid “ceramic” – solid electrolytes – are safer alternatives.^{6–9} When suitably doped, the garnet-type quaternary oxide Li₇La₃Zr₂O₁₂ as a solid electrolyte achieves unprecedented Li⁺ conductivities (~10⁻⁶–10⁻³ S cm⁻¹).^{10–24} Importantly, Li₇La₃Zr₂O₁₂

is claimed to be stable against high-energy density Li-metal anodes, which is an appealing feature for high-energy density batteries enabling vehicular transportation.^{20,22–25}

On the other hand, complex oxides catalyze the decomposition of abundant molecules, such as H₂O and CO₂.^{26–30} Water dissociation during the water-gas shift reaction is a vital elementary step that is promoted by oxide supports, such as Al₂O₃, CeO₂, CuO, La₂O₃, Mn₂O₄, TiO₂, Y₂O₃, ZrO₂, *etc.*^{31–37} Complex oxides are extensively studied as catalytic supports to adsorb CO₂ from dilute gas streams and subsequently transform CO₂ into valuable chemicals.^{36,38–43}

Here, using Li₇La₃Zr₂O₁₂ as an example, in the framework of *ab initio* thermodynamics, we investigate the reactivity of this complex oxide with two ubiquitous molecules: H₂O and CO₂. Previous work by Sharafi *et al.* using Raman and X-ray photo-emission spectroscopy (XPS) revealed the existence of thick layers (~5–10 nm) of Li₂CO₃ on the Li₇La₃Zr₂O₁₂ surfaces, upon exposure to air.^{21,23} The same authors also detected LiOH on the Li₇La₃Zr₂O₁₂ particles. The cartoon of Scheme 1 shows the reaction pathways of CO₂ and H₂O with Li₇La₃Zr₂O₁₂, as proposed in previous bulk-material calculations by Sharafi *et al.*¹⁹ using density functional theory (DFT).

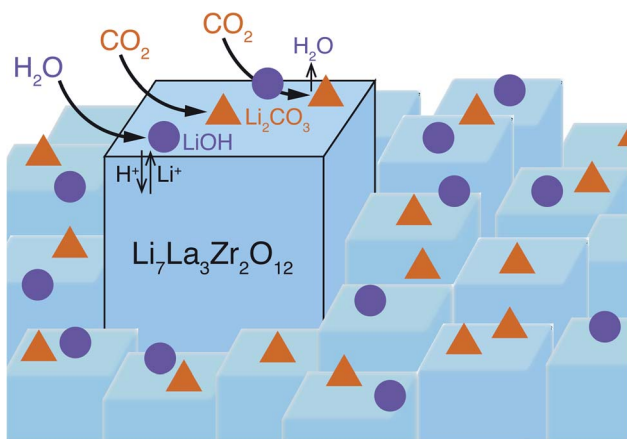
Nevertheless, the complexity of Li₇La₃Zr₂O₁₂ (and other garnets) in general suggests that considering the reactions of CO₂ and H₂O beyond the bulk structure is necessary.¹⁹ Specifically, the structural heterogeneity of active sites on low index

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† Electronic supplementary information (ESI) available: (i) benchmark tests on the effect of vdW corrections, (ii) convergence tests of slab calculations, (iii) structure of the slab unit cell, (iv) tests on single-point energy cutoffs, (v) the description of the metal sites' local environment and H₂O dissociation, (vi) calculation results for forced H₂O dissociation at high coverage, (vii) geometry of surface carbonates formed at the surfaces and Li₂CO₃, and (viii) Mulliken charges of sites post-adsorption. See DOI: 10.1039/d1ta10228a



Scheme 1 Possible reaction pathways for $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ particle contamination when exposed to H_2O and CO_2 .

crystal planes, which contributes to activating closed shell species such as CO_2 and H_2O , requires detailed exploration of the reactions on surface. Here, we investigate this complex reactivity using DFT calculations of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ slabs interacting with H_2O and CO_2 . The computed surface phase diagrams reveal that at room temperature and ambient pressures H_2O is adsorbed vigorously on the exposed Li sites at the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ surface, nucleating LiOH and protons. These protons are then exchanged with the highly mobile Li^+ ions and may “intercalate” in the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ bulk.¹⁴ Likewise, our simulations demonstrate that CO_2 is adsorbed on the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ surface and readily transforms into carbonate species.

If $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is to be used in battery devices, our simulations provide guidelines to curb its degradation by CO_2 and H_2O . In contrast, spontaneous H_2O dissociation on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ makes it potentially relevant for the water-gas shift reaction,^{44,45} while the strong chemisorption of CO_2 makes $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ a promising dual functional material for CO_2 capture and conversion.^{46,47} Hence, in the context of catalysis, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ appears to be an excellent catalyst support to investigate the reactions of CO_2 activation and water splitting, respectively. These results are important to chart the reactivity of this complex quaternary oxide, which may be extended to other complex oxides.

2. Computational methods

The chemical reactions at the surface of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ were probed with Kohn–Sham DFT simulations⁴⁸ and approximated by the Perdew–Burke–Ernzerhof (PBE) functional.⁴⁹ van der Waals (vdW) interactions were treated with the D3 method with a Becke–Johnson (BJ) damping term.^{50–52} The wavefunctions were expanded as plane waves and core electrons by the projector-augmented wave (PAW) method as in VASP.^{53–56} The PAW potentials and the recommended cutoff energies were: C 08 Apr 2002 400 eV, H 15 Jun 2001 250 eV, La 06 Sep 2000 219 eV, Li_sv 23 Jan 2001 272 eV, O 08 Apr 2002 400 eV, and Zr_sv 07 Sep 2000 230 eV. Slab optimization was performed in two steps: (i) a preliminary PBE and Γ -point optimization, and (ii) optimization

with PBE + D3-BJ with a $2 \times 2 \times 1$ k -mesh and a cutoff energy of 440 eV. The total energy was converged to 1×10^{-5} eV per cell and forces acting on atoms to within $0.01 \text{ eV } \text{\AA}^{-1}$. We concluded with final single-point energy calculations at a higher cut-off of 520 eV and integrated over a $4 \times 4 \times 1$ k -point grid.

As in this study we probe the adsorption and reactivity of molecules at the surface of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, it is crucial to treat explicitly the effect of vdW forces. vdW interactions were determined by the D3 + BJ method.^{50–52} Using these settings, the lattice constants ($a = 13.085 \text{ \AA}$ and $c = 12.579 \text{ \AA}$) of tetragonal ($Ia4_1/acd$) $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ were used to rescale the (010) slab models from ref. 24. The (010) Li-terminated off-stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ model contains 248 atoms and has a surface energy of $\sim 1.34 \text{ J m}^{-2}$. The dispersion corrections (D3-BJ) increase the stability of the bulk structure, resulting in an increased surface energy by $\sim 0.50 \text{ J m}^{-2}$ compared to ref. 24. A well-converged vacuum size of 15 \AA was used to eliminate spurious slab–slab (and adsorbate–adsorbate) interactions along the direction orthogonal to the surface plane.

A bulk-like region of the slab where all atomic positions are fixed was introduced in the middle of the slab models. A 40% bulk-like region was determined from convergence tests on slab total energies (see Fig. S1 in the ESI[†]), at which the total energy is converged to $\sim 7 \text{ meV}$ with relatively modest computational costs. Note that this procedure is commonly applied in surface science and catalysis to reduce significantly the computing time of structure optimization of large slab models.⁵⁷ Benchmark tests on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ bulk lattice constants and surface energies were performed to compare the effects of DFT functionals, *i.e.*, PBE, PBE + D3 without damping, and PBE + D3 with BJ damping (see Table S1 of the ESI[†]).

The coordination numbers and Mulliken charges were derived from the crystal orbital Hamilton populations (COHP) available in the Lobster code.⁵⁸ For the COHP calculations, the energy range is set to -15 to 10 eV , and the same basis functions as those in the PAW potentials are used for projections.

The adsorption energy (ΔE_{ads}) was calculated using eqn (1):⁵⁹

$$\Delta E_{\text{ads}} = \frac{1}{2n} [E(\text{slab}|2n\text{H}_2\text{O}^{\text{ads}}) - E(\text{slab}) - 2nE(\text{H}_2\text{O}^{\text{g}})], \quad (1)$$

where $n = 1$ is the number of adsorbed molecules on each side of the slab model. In eqn (1), we approximated the Gibbs energy of each term by the DFT total energy (*i.e.*, $G \approx E$), thus neglecting the zero point energy, pV and entropy contributions. $E(\text{slab}|2n\text{H}_2\text{O}^{\text{ads}})$ is the total energy for the slab adsorbed with $n\text{H}_2\text{O}$ (on each surface side), $E(\text{slab})$ is the total energy for the clean-surface slab, and $E(\text{H}_2\text{O}^{\text{g}})$ is the total energy for H_2O in the gas phase. From eqn (1), a more negative ΔE_{ads} value indicates a more favorable interaction of the adsorbate with the surface.

The energy changes computed as a function of H_2O (and CO_2) coverage are calculated in terms of the Landau grand-potential energy, Ω of eqn (2).

$$\Omega(x/5 \text{ ML}) = \frac{1}{2A} [G(\text{slab}|2x\text{H}_2\text{O}^{\text{ads}}) - (12 - 2x)\mu^{T,P}(\text{H}_2\text{O}^{\text{g}})], \quad (2)$$

$$\approx \frac{1}{2A} [E(\text{slab}|2x\text{H}_2\text{O}^{\text{ads}}) - 2xTS_{\text{vib}}^T(\text{H}_2\text{O}^{\text{ads}}) - (12 - 2x)\mu^{T,P}(\text{H}_2\text{O}^{\text{g}})], \quad (3)$$

where x is the number of sites adsorbed on each surface, A is the surface area, and T and P are the temperature and partial pressure of H_2O , respectively. $G(\text{slab}|2x\text{H}_2\text{O}^{\text{ads}})$ is the Gibbs free energy of the adsorbed slab and approximated as in eqn (3), by $E(\text{slab}|2x\text{H}_2\text{O}^{\text{ads}})$, the DFT total energy of the slab adsorbing $x\text{H}_2\text{O}$ molecules on each surface. $S_{\text{vib}}^T(\text{H}_2\text{O}^{\text{ads}})$ is the vibrational entropy of the adsorbed H_2O (in either a dissociated or an intact form), which is calculated by fixing all atoms except the adsorbate. $\mu^{T,P}(\text{H}_2\text{O}^{\text{g}})$ is the chemical potential of H_2O gas approximated by its DFT total energy in vacuum, corrected by the zero-point energy, and scaled to given T and P conditions using the Shomate equation.⁶⁰ Then, the change of grand-potential energy ΔQ ($x/5$ ML) at different water coverage is computed using eqn (4) with respect to the clean surface (0/5 ML).

$$\Delta Q(x/5 \text{ ML}) = Q(x/5 \text{ ML}) - Q(0/5 \text{ ML}). \quad (4)$$

3. Results

3.1. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (010) surface and selection of adsorption sites

Our analysis begins by selecting the energetically most favorable surface cut of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ from ref. 24. The off-stoichiometry Li-terminated (010) surface (and identical to the (100) and the (001) surfaces) displays the lowest surface energy ($\sim 0.87 \pm 0.02 \text{ J m}^{-2}$) and remains stable even at high temperatures ($\sim 1000 \text{ K}$), targeted by typical thermal treatments of these oxides. The (010) surface corresponds to the dominant surface in the computed Wulff shapes of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, and it is representative of the real $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ particles, either in sintered powders or sheet composites. Here, off-stoichiometric surfaces refer to surfaces where the stoichiometry deviates in composition from the bulk. As described in the Computational methods (Section 2), the (010) surface from ref. 24 was rescaled and recalculated in this study with the incorporation of vdW interactions.

When studying the adsorption of molecules on surfaces, a non-negligible challenge is selecting chemically sound adsorption configurations from the sheer number of imaginable adsorption conformations. This is especially true in complex oxides, such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, which contains three chemically distinct cations with varying local coordination environments of the oxygen atoms. We used pymatgen to ease the identification of unique adsorption sites and subsequently construct the initial structure of adsorbates bound to these sites.⁶¹ To prevent the well-known convergence problems of slab calculations in the presence of fictitious electrical dipoles from polar adsorbates (H_2O here), we adsorbed molecules on both surface sides.⁶²

In order to clarify the mechanisms of H_2O and CO_2 reactions with $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, it is first necessary to create appropriate adsorption models by understanding the characteristics of

different active sites on this structurally heterogeneous surface. These characteristics include the proximity of active sites to the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ surface, their local environment, their Mulliken charges, and their coordination numbers.

Fig. 1(a) and (b) show the side and top views of the off-stoichiometric Li-terminated (010) surface of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. By defining a range of search, along the non-periodic direction of the slab of $\sim 0.9 \text{ \AA}$ from the most exposed atom at the surface, we identified 10 on-top surface adsorption sites. These sites show different proximity to the surface; we denote each site according to its element followed by all species bonded to it. Thus, in Fig. 1 seven unique sites out of the 10 were identified: two types of Li sites Li[2O] and Li[3O]; two types of La sites La[5O] and La[6O]; three types of O sites O[LiLaZr], O[Li2La], and O[3Li2La], respectively.

Nominally, positively charged ions, such as Li^+ and La^{3+} , at the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ surface will attract negatively polarized parts of the adsorbing molecules and *vice versa*.

Fig. 1(c–e) show the computed Mulliken charges and coordination numbers for all seven types of adsorption sites. Mulliken analysis is an intuitive (but not unique) way of repartitioning the electron charge density on each atom (and orbital) by projecting it onto individual orthonormalized atomic orbitals.⁶³ The surface sites of each species show similar Mulliken charges, albeit distinct coordination numbers. As expected, Li and La metal sites show positive Mulliken charges. From an adsorption point of view, these sites will behave as Lewis acids in favor of accepting electrons from the oxygen lone pair of H_2O . Indeed, the reactivity of these cations follows the scale of absolute hardness, η : Li^+ ($\sim 35.1 \text{ eV}$) $>$ La^{3+} ($\sim 15.4 \text{ eV}$) \gg Zr^{3+} ($\sim 5.68 \text{ eV}$),^{64,65} with Li^+ , the most electrophilic cation of the three. Since Zr^{3+} is the least reactive metal of the three, we will not consider its reactivity in the remainder of this study. Oxygen sites reveal their basic character, potentially driving the CO_2 adsorption *via* the C atom. We use this knowledge to guide our understanding of the adsorption and dissociation of H_2O and CO_2 on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$.

3.2. H_2O adsorption and hydroxide formation on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

Here, we provide the mechanistic insights into H_2O adsorption and reactions on the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (010) surface to form hydroxide species.

Initially, we investigated the adsorption of a single H_2O molecule on the Li-terminated $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (010) surface. This low coverage analysis enables us to probe the surface characteristics of the surface. For every Li or La site, one H_2O was adsorbed on each side of the slab model, which eliminates any potential electrical dipoles caused by polar H_2O .⁶² The adsorption energies (ΔE_{ads}) of eqn (1) were computed for all five Li and La sites of Fig. 1.⁵⁹

Notably, the calculated ΔE_{ads} indicates a higher tendency of a H_2O molecule to adsorb on Li^+ sites ($\Delta E_{\text{ads}} = -1.21 \text{ eV}$) compared to La^{3+} sites (-0.85 eV), clearly following the scale of cation absolute hardness reported by Parr and Pearson, with Li^+ ($\sim 35.1 \text{ eV}$) $>$ La^{3+} ($\sim 15.4 \text{ eV}$).

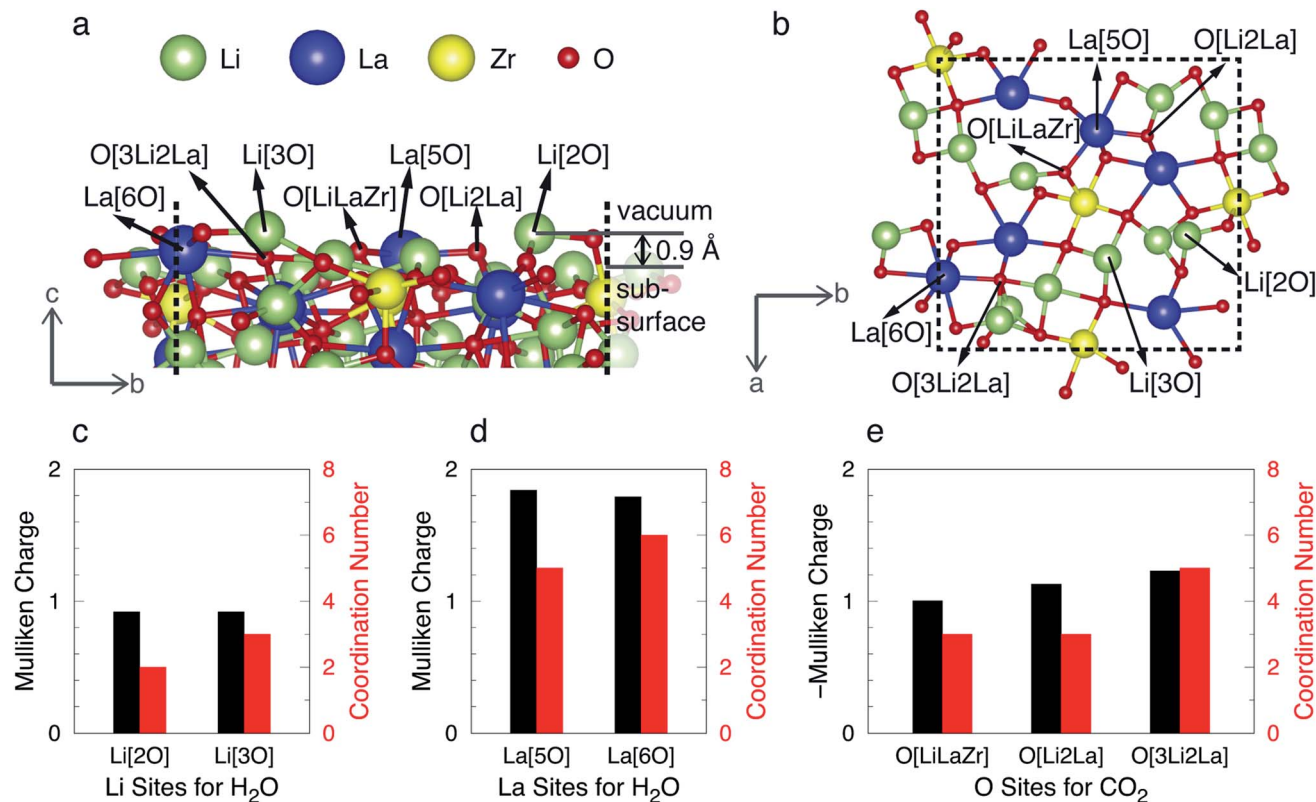


Fig. 1 Properties of the adsorption sites on a $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ surface. (a) Side view and (b) top view of the off-stoichiometry Li-terminated (010) surface of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. The boundary of the slab unit cell is marked with dashed lines. Li, La, Zr, and O species are shown in green, blue, yellow, and red, respectively. The surface adsorption sites are identified within an $\sim 0.9 \text{ \AA}$ vertical range (panel (a)). The double headed arrow marks the surface range, outside of which are the vacuum and subsurface. Sites are denoted by the element followed by ions immediately bonded to the site. The 7 unique sites are: 2 types of Li ($\text{Li}[3\text{O}]$ and $\text{Li}[2\text{O}]$), 2 types of La ($\text{La}[6\text{O}]$ and $\text{La}[5\text{O}]$), and 3 types of O ($\text{O}[\text{Li}_2\text{La}]$, $\text{O}[\text{Li}_2\text{La}]$, and $\text{O}[\text{LiLaZr}]$), respectively. For a clearer view of the sites local environments, we concealed atoms far away from the surface. Mulliken charges (black bars) and coordination numbers (red bars) for Li sites in (c), La sites in (d), and O sites in (e). Li and La sites show positive Mulliken charges, indicating their electro-positive character, and vice versa for O sites.

Fig. 2 shows the diagram of the computed adsorption energies and a magnification of the adsorption sites for the two most favorable adsorption cases, which always occur on exposed Li sites.

For the most favorable $\text{Li}[3\text{O}]$ site (dark green line), H_2O dissociates accompanied by a significant ΔE_{ads} ($\sim -1.21 \text{ eV}$), and reacts with the Li site to form LiOH (see the lower inset of Fig. 2). Upon H_2O dissociation, a OH^- group is formed between the proton released and an adjacent oxygen atom of the surface; the OH^- group forms a hydrogen bond with the O of the LiOH formed on the $\text{Li}[3\text{O}]$ site. In the 2nd most favorable $\text{Li}[2\text{O}]$ site (see the upper inset of Fig. 2), the adsorbed H_2O remains intact, yielding still a non-negligible ΔE_{ads} of $\sim -1.14 \text{ eV}$, but comparatively less favorable than the $\text{Li}[3\text{O}]$ site by $\sim 70 \text{ meV}$. Notably, we attempted the dissociation of H_2O on the $\text{Li}[2\text{O}]$ site with a calculated ΔE_{ads} of $\sim -1.18 \text{ eV}$, indicating that the dissociation is thermodynamically favorable by $\sim -40 \text{ meV}$ with respect to non-dissociative adsorption at these sites.

It is important to unearth the causes behind the significant magnitudes of ΔE_{ads} s and dissociation behaviors of H_2O on different metal sites. We observed that if the coordinates of the surface sub-layers and the inner region of the surface (making

$\sim 80\%$ of the slab) are held frozen to those of the bulk slab, the adsorbed H_2O will not dissociate on any site, regardless of its chemical activities. Clearly, with such a constraint in place, the adsorption energy does not benefit from the reorganization of

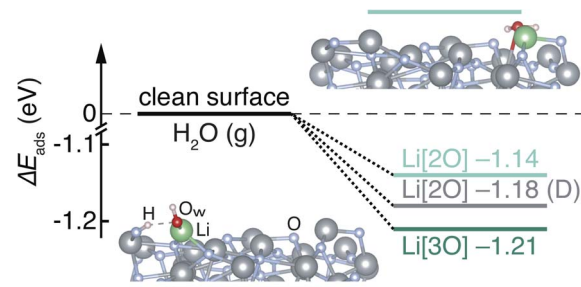


Fig. 2 Adsorption energy for H_2O on the two most favorable sites $\text{Li}[2\text{O}]$ (light green) and $\text{Li}[3\text{O}]$ (dark green) on the Li-terminated $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (010) surface. The H_2O molecule on $\text{Li}[2\text{O}]$ remains intact after adsorption (upper inset), while H_2O on $\text{Li}[3\text{O}]$ dissociates to form LiOH (lower inset). The grey $\text{Li}[2\text{O}]$ level marked with a "D" shows adsorption energy for a model where we forced H_2O dissociation on the $\text{Li}[2\text{O}]$ site. Atomic species not directly involved in the adsorption are greyed out.

the surface atoms, which promotes the dissociative adsorption of H₂O. Thus, the adsorption energy follows the trend of the site exposure to the surface, with the top (bottom) site showing the most negative adsorption energy. In contrast, by constraining only 40% of the slab model, as in the rest of this study, the adsorbed H₂O on specific sites readily dissociates during the geometry optimization. Note that such preference for dissociation caused by the rearrangement of atoms in the surface sub-layers is rarely seen in metals.

Unsurprisingly, H₂O dissociation lowers the adsorption energy. With a stabilizing contribution arising from H₂O dissociation, the adsorption energy no longer follows the trend of sites proximity to the surface. From top to sub-layer sites in the surface, the adsorption energies are: -1.14 eV (Li[2O]), -1.21 eV (Li[3O]), -0.85 eV (La[5O]), -0.80 eV (La[6O]), and -0.65 eV (Li[3O]). Furthermore, our results clearly indicate that the dissociation behavior depends on the local environment of the adsorption site. If a specific adsorption configuration displays oxygen atoms in the vicinity of the adsorption site, protons from adsorbed H₂O readily dissociate to bond with the surface oxygen species. The dissociative adsorption of H₂O is well understood in previous studies of metal oxides including rutile-TiO₂, anatase-TiO₂, and rutile-RuO₂.^{66–68} In general, we find that adsorbed H₂O tends to dissociate when there are oxygen atoms within ~ 1.9 Å of the cation site (Table S2[†]), unless there are metal ions that can better stabilize H₂O adsorption *via* bonding with O in H₂O (see the inset for Li[2O] in Fig. 2). Therefore, the values of ΔE_{ads} in Li₇La₃Zr₂O₁₂ are clearly affected by (i) the site proximity to the surface and (ii) H₂O dissociation driven by the local environment.

We are also interested in the bonding character of H₂O adsorption (or dissociation) on the Li₇La₃Zr₂O₁₂ surface since H₂O, a closed shell species, has significantly favorable ΔE_{ads} . First, we determined the dispersion contribution to the adsorption energy by comparing our predictions with (PBE-D3) and without van der Waals contributions, and hence just with GGA PBE.⁴⁹ The results show that there is a consistent dispersion contribution of only ~ 15 – 20% to the total DFT energies. This means that dispersion interactions are not a major source of bonding and indicates a more dominant nature of chemisorption-driven reactions instead of physisorption.

Next, we compared the changes of the Mulliken charges of all Li and La sites and O of H₂O before and after H₂O adsorption (Fig. S3(a and b) in the ESI[†]). Unlike on reducible oxides (with open-shell d or f transition metals),^{69,70} there is no charge transfer between H₂O and the surface sites, which indicates the electrostatic nature of the interaction. These insights agree with previous findings that intrinsic surface electrostatics in an insulating ‘ionic’ system play a critical role in stabilizing the dangling lone pair of H₂O.⁷¹

We now investigate the adsorption of multiple H₂O molecules to simulate reactions at high water coverage on the Li₇La₃Zr₂O₁₂ surface. All five Li and La sites were first ordered according to their individual H₂O adsorption energy, from more negative to more positive. In particular, the order of adsorption energies is Li[3O] (-1.21 eV) < Li[2O] (-1.14 eV) \ll La[5O] (-0.85 eV) < La[6O] (-0.80 eV) < Li[3O] (-0.65 eV). Following

this order of stability, we adsorbed H₂O on available metal sites achieving a complete H₂O monolayer (ML). For each additional molecule, the structure was relaxed before the next H₂O was adsorbed. After all five sites were adsorbed, we identified an additional Li site, which emerged from the surface re-organization upon increasing water coverage. Eventually, six H₂O molecules were adsorbed on each side of the slab (12 in total).

Table 1 reports the ΔE_{ads} for H₂O on the (010) Li₇La₃Zr₂O₁₂ surface as the exposed metal sites are progressively saturated. We denote the H₂O coverage as the fraction of one monolayer ($x/5$ ML). ΔE_{ads} for the same adsorption but with all H₂O forced to dissociate is reported in Table S3.[†]

Table 1 shows that the addition of subsequent H₂O molecules to the Li₇La₃Zr₂O₁₂ (010) surface from $1/5$ ML to $6/5$ ML gradually increases ΔE_{ads} to more positive values. This progressive increase is mainly caused by the more positive adsorption energy of each site, from -1.21 to -0.65 eV, dependent on their proximity to the surface and whether H₂O spontaneously dissociates. This increase is also likely due to additional H₂O–H₂O interactions as a result of crowding the Li₇La₃Zr₂O₁₂ surface, and the progressively neutralized and less reactive surface. Simultaneously, specific adsorption arrangements favor hydrogen bonding with the surface.

Fig. 3(a) shows the energy diagram for all adsorption steps towards high H₂O coverage beyond one monolayer. ΔQ was calculated using eqn (2)–(4) for increasing H₂O coverage at a partial pressure of 1 bar and at 300 K. A negative ΔQ means that H₂O adsorbs favorably on the Li₇La₃Zr₂O₁₂ surface. As more H₂O molecules adsorb, ΔQ continuously becomes more negative, indicating that increasing coverage is favorable up to $6/5$ ML. This trend also suggests that H₂O can probably adsorb beyond $6/5$ ML. We also found a decreasing trend for the absolute difference of ΔQ between consecutive H₂O adsorptions. For example, the absolute difference between ΔQ of $6/5$ ML and $5/5$ ML is 8.7 meV Å⁻², less than 10.1 meV Å⁻² between $1/5$ ML and $0/5$ ML. This decreasing difference is primarily attributed to the adsorption energy trends of individual sites, as less favored adsorption sites become occupied at higher coverages.

As we only consider adsorption sites within ~ 0.9 Å from the surface top (bottom), more adsorption sites may be available. Electrostatic repulsion between adsorbates should have only

Table 1 H₂O adsorption energy (in eV per molecule) at an increasing number of molecules (ML). The site is the adsorption site. $\delta\Delta E_{\text{ads}}$ indicates the change of ΔE_{ads} upon the addition of a H₂O molecule. The number of dissociated H₂O molecules (H₂O) is also indicated. MOH (M = Li/La) indicates whether the addition of a new H₂O molecule promotes metal hydroxide formation

ML	Site	ΔE_{ads}	$\delta\Delta E_{\text{ads}}$	H ₂ O	MOH
1/5	Li[3O]	-1.21	—	1	Yes
2/5	Li[2O]	-1.19	$+0.02$	1	No
3/5	La[5O]	-1.19	0.00	2	Yes
4/5	La[6O]	-1.10	$+0.09$	2	No
5/5	Li[3O]	-1.09	$+0.01$	3	Yes
6/5	Li[3O]	-1.07	$+0.02$	3	No

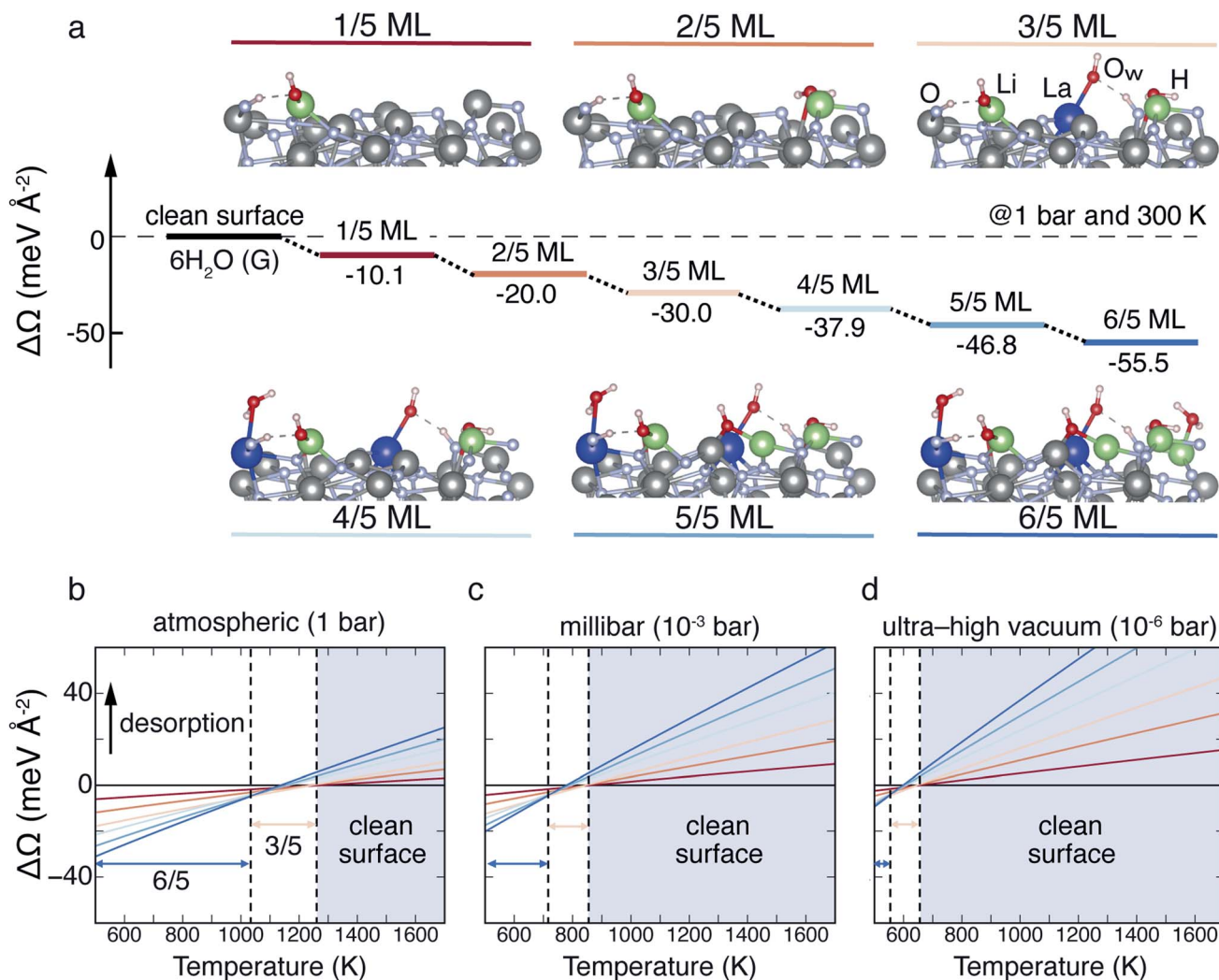


Fig. 3 Change of grand-potential energy $\Delta\Omega$ relative to the clean $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ surface and gas-phase H_2O at variable temperatures and pressures of technological relevance. In panel (a), the H_2O coverage is denoted by the fraction of a monolayer (ML) of H_2O on the surface. Full coverage is achieved at 6/5 ML when all the five original sites plus an additional site are adsorbed. Increasing coverage is marked by divergent colors from red to blue. $\Delta\Omega$ as a function of temperature for different H_2O coverages and partial pressures of 1 (b, atmospheric regime), 1×10^{-3} (c, mbar regime), and 1×10^{-6} bar (d, ultra-high vacuum regime). Double arrows show the most favorable coverage within temperature ranges. Atomic species not directly involved in the adsorption are greyed out.

secondary effects on the increasingly more positive values of ΔE_{ads} . Furthermore, a progressive addition of H_2O molecules contributes to gradually neutralizing the highly reactive Li^+ sites. Indeed, at a very high water coverage, beyond 6/5 ML, newly adsorbed H_2O molecules may not dissociate, even if dissociation is favored in a single H_2O adsorption on the same site.

For coverage up to 6/5 ML, half of the adsorbed H_2O molecules dissociate and react with the surface to form LiOH (see Table 1). The same happens when all adsorbed H_2O molecules are forced to dissociate before relaxation (see Table S3†). This “half-dissociation” trend was also observed for simple metal oxides like RuO_2 ,^{72,73} but a different water dissociation fraction of 75% was observed for the (101) surface in anatase- TiO_2 .⁷⁴ Note that the H_2O dissociation is spontaneous during geometry optimization, and thus it is not necessary to calculate its kinetic

barriers explicitly (expected to be barrier-free). In terms of hydrogen bonding for adsorbates, the dissociated proton always forms hydrogen bonds with the oxygen atom in the original H_2O molecule. All H_2O adsorbates that remain intact form hydrogen bonds with adjacent surface O atoms.

Our analysis of the H_2O reactivity with the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ surface extends to conditions of technological relevance of this material. This analysis is relevant for the optimization of synthesis and heat treatment conditions in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and common oxides. Fig. 3(b–d) show $\Delta\Omega$ as a function of temperature at atmospheric (1 bar), millibar (10^{-3} bar), and ultra-high vacuum (10^{-6} bar) partial pressures, respectively. The temperature range explored in Fig. 3(b–d) spans those of typical synthesis and sintering temperature (~ 1000 °C) of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$.¹⁶

Under atmospheric conditions (Fig. 3(b)), ΔQ at different coverage is plotted in the same color scheme as in Fig. 3(a). A positive ΔQ indicates that adsorbed H_2O is favourable for desorption. We mark the most favorable coverage in different temperature ranges using double headed arrows. In general, as the temperature increases, the H_2O coverage of the surfaces decreases until the surface of $Li_7La_3Zr_2O_{12}$ is water free. This situation is achieved for temperatures above ~ 1260 K (Fig. 3(b)). At lower temperatures (up to ~ 1030 K), the most favorable coverage is 6/5 ML $Li_7La_3Zr_2O_{12}$, whereas the 3/5 ML coverage is the most favorable condition in the temperature range 1030–1260 K. Considering even higher coverage, one would expect steeper lines than for 6/5, resulting in a water-rich surface of $Li_7La_3Zr_2O_{12}$. However, such conditions cannot change the scenario for higher temperature ranges (≥ 1260 K), exhibiting a water-free $Li_7La_3Zr_2O_{12}$ surface.

Under millibar (Fig. 3(c)) and ultra-high vacuum (Fig. 3(d)) H_2O partial pressures, one can find the same general trends for coverage vs. temperature as under atmospheric pressure (Fig. 3(a)). However, the temperature range for a water-free clean surface of $Li_7La_3Zr_2O_{12}$ increases as the H_2O partial pressure decreases. For example, in situations of ultra-high vacuum (Fig. 3(d)), we predict an onset temperature of ~ 650 K, at which the $Li_7La_3Zr_2O_{12}$ surface will be water-free. These findings indicate that low partial pressures are beneficial to minimize surface contamination by H_2O and $LiOH$.

3.3. CO_2 adsorption and carbonate formation on $Li_7La_3Zr_2O_{12}$

We now focus on CO_2 adsorption on $Li_7La_3Zr_2O_{12}$ and its subsequent transformation into carbonate CO_3^{2-} species. We probed CO_2 adsorption on five oxygen sites of the Li-terminated $Li_7La_3Zr_2O_{12}$ surface, as shown in Fig. 1. The adsorption is achieved by placing the carbon atom of CO_2 close (~ 1.17 Å) to the O site, to induce the formation of a C–O bond. The most favorable site is O[LiLaZr], and its ΔE_{ads} is strikingly high ~ -2.21 eV – a clear indication of CO_2 chemisorption. The other sites show comparable (~ -1.65 to -1.31 eV) but more positive adsorption energies. The least favorable site is O[3Li2La], still with a sizeable ΔE_{ads} of ~ -1.31 eV.

Regardless of the binding oxygen site, the adsorbed CO_2 species reorganize into carbonate CO_3^{2-} species after structural optimization. In detail, two oxygen atoms in CO_2 form bonds with metal ions available in the vicinity, with the carbonate species organizing in a polydentate conformation (Fig. S1†).⁷⁵ For all carbonates formed on the five sites, there are 13 bonds formed between surface metal ions and O of CO_2 , including eight Li–O bonds and five La–O bonds. The higher number of Li–O bonds shows a clear preference for Li^+ over La^{3+} ions. In particular, the surface carbonates show an average C–O bond length of ~ 1.31 Å, comparable to ~ 1.28 Å in bulk Li_2CO_3 .⁷⁶

The adsorption of CO_2 consists of two types of bonds: one between the carbon atom of CO_2 and a surface oxygen site, and the other between the oxygen atoms of CO_2 and metal ions of the surface. We observe that the incipient bond between O and metal ions on $Li_7La_3Zr_2O_{12}$ has major contributions to the

values of ΔE_{ads} . On different adsorption sites, the strength for the O and metal ion bonding depends on which metal ions are proximal to the site.

We also determined the bonding nature for CO_2 chemisorbed on $Li_7La_3Zr_2O_{12}$. Indeed, the dispersion contributions are calculated to be only ~ 15 – 20% , similar to the cases of H_2O adsorption discussed earlier. Charge transfer is then analyzed through the changes of Mulliken charges upon adsorption. Fig. S3† shows that the average changes are ~ 0.30 for the surface O sites and ~ -0.26 for C in CO_2 . Besides, the average change upon adsorption is ~ -0.22 for O in CO_2 , ~ -0.01 for surface Li ions bonded to O, and ~ 0.12 for La ions. These changes are slightly larger than those for H_2O adsorption (~ -0.05 for Li sites, ~ 0.07 for La sites, and ~ 0.03 for O in H_2O , see Fig. S3 in the ESI†). Taken together, this analysis confirms that the structural heterogeneity of surface sites on $Li_7La_3Zr_2O_{12}$ (010) enables strong adsorption of H_2O and CO_2 , which are otherwise known to physisorb on metals and ionic oxides. While such robust adsorption events are detrimental for the application of $Li_7La_3Zr_2O_{12}$ in energy storage, they indicate that $Li_7La_3Zr_2O_{12}$ is a potentially interesting catalyst support for H_2O activation and adsorbing CO_2 from dilute streams.

We then studied CO_2 adsorption as a function of CO_2 coverage. CO_2 was sequentially adsorbed on all five O sites available on the $Li_7La_3Zr_2O_{12}$ surface. The sequential adsorption follows the order of their individual adsorption energies, from more negative to more positive (O[LiLaZr] (-2.21 eV) \ll O[Li2La] (-1.65 eV) $<$ O[LiLaZr] (-1.58 eV) $<$ O[LiLaZr] (-1.34 eV) $<$ O[3Li2La] (-1.31 eV)). In the process to adsorb the last CO_2 onto the $Li_7La_3Zr_2O_{12}$ surface, the O[3Li2La] site was found unfavorable, as adsorbed CO_2 on this site was too close (~ 1.20 Å) to La^{3+} on the reconstructed surface. Eventually, there are only four out of five oxygen sites available for CO_2 adsorption, which set the highest CO_2 coverage to 4/5 ML. Besides the original five sites, less exposed O surface sites could increase the CO_2 coverage beyond 4/5 ML.

Table 2 shows the computed ΔE_{ads} for increasing the CO_2 loading up to the condition of 4/5 ML.

Fig. 4(a) shows the structure schematics and ΔQ diagram for each adsorption step toward the 4/5 ML coverage. ΔQ is defined as in eqn (3) and (4), and here it is calculated at 300 K and a CO_2 partial pressure of 1 bar.

In regimes of high-coverage, multiple CO_2 molecules interact with the surface in the same way as singly adsorbed CO_2 molecules, transforming into CO_3^{2-} units. At the highest calculated coverage of 4/5 ML, all adsorbed CO_2 molecules react with the surface and form carbonates. As the coverage increases, ΔQ continuously decreases, indicating that the reaction between the surface and an increasing amount of CO_2 (up to 4/5 ML) is thermodynamically favorable. However, from Fig. 4, one observes that the absolute difference of ΔQ between consecutive steps decreases progressively, similar to the trends of Fig. 3(a). Fig. 4 and Table 2 show that each oxygen species at the $Li_7La_3Zr_2O_{12}$ surface becomes increasingly less reactive as the CO_2 coverage increases, which contributes to a progressive decrease of ΔE_{ads} and ΔQ .

Table 2 CO₂ adsorption energy (in eV per molecule) with increasing coverage of molecules (ML). The site is the adsorption site. $\delta\Delta E_{\text{ads}}$ indicates the change of ΔE_{ads} upon the addition of a CO₂ molecule. CO₃²⁻ indicates whether the addition of a new CO₂ molecule promotes carbonate formation

ML	Site	ΔE_{ads}	$\delta\Delta E_{\text{ads}}$	CO ₃ ²⁻
1/5	O[LiLaZr]	-2.21	—	Yes
2/5	O[Li2La]	-1.85	+0.36	Yes
3/5	O[LiLaZr]	-1.75	+0.10	Yes
4/5	O[LiLaZr]	-1.62	+0.13	Yes

Fig. 4(b-d) show $\Delta\Omega$ at technologically relevant temperature and CO₂ partial pressures. As the temperature increases, the adsorption and reaction of CO₂ become less favorable, and the preferred coverage decreases from 4/5 ML to the

conditions of CO₂-free surfaces. Similarly to the H₂O case, at low temperature even higher CO₂ coverage than 4/5 ML may become accessible. However, this does not change significantly the situation of low CO₂-free surfaces at high temperature, as shown in Fig. 4(b-d). As the CO₂ partial pressure decreases from atmospheric to ultra-high vacuum, the formation of carbonate species at the Li₇La₃Zr₂O₁₂ surface appears less favorable, with the stability ranges of temperature expanding accordingly. This indicates that low CO₂ partial pressures are beneficial to minimize the carbonate contamination of the Li₇La₃Zr₂O₁₂ surface.

3.4. CO₂ and H₂O co-adsorption on Li₇La₃Zr₂O₁₂

Having previously demonstrated the pronounced reactivity of the Li₇La₃Zr₂O₁₂ surface with H₂O and CO₂, we verify the

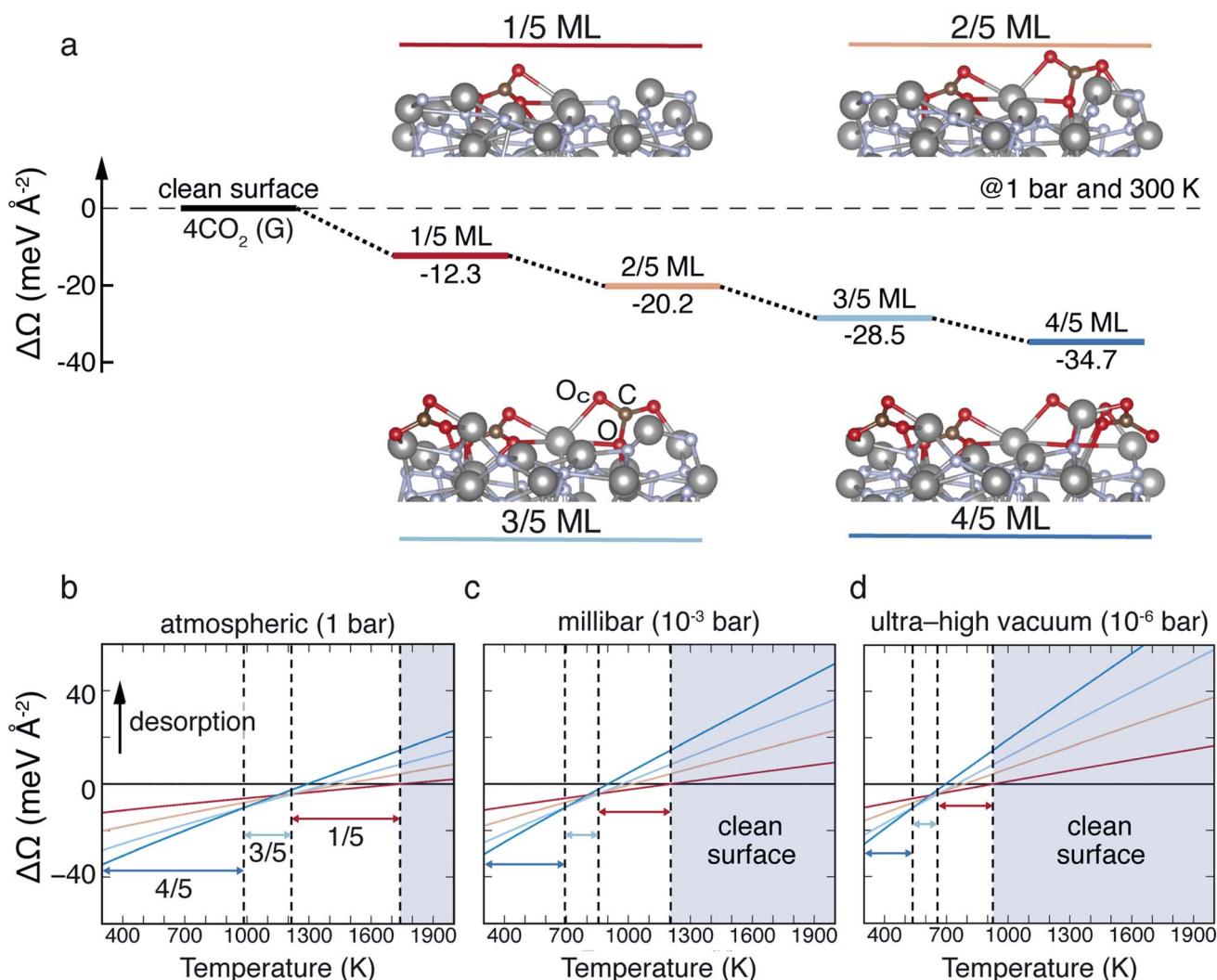


Fig. 4 Change of grand potential $\Delta\Omega$ relative to a clean surface and gas-phase CO₂ at variable temperatures and pressures of technological relevance. In panel (a), the CO₂ coverage is denoted by a fraction of the CO₂ monolayer (ML) of the surface. $\Delta\Omega$ (in $\text{meV } \text{\AA}^{-2}$) as a function of temperature for different CO₂ coverage and partial pressures of 1 (b, atmospheric regime), 1×10^{-3} (c, millibar regime), and 1×10^{-6} bar (d, ultra-high vacuum regime), respectively. Double arrows denote the most favorable coverage within each temperature range. The structures and $\Delta\Omega$ for different coverage are marked using the same color scheme of four divergent colors. Atomic species not directly involved in the adsorption are greyed out.

possibility of H₂O and CO₂ reacting concurrently with the off-stoichiometric Li-terminated (010) cut.

We investigate the co-adsorption of H₂O and CO₂ to mimic the hydroxide-mediated carbonation proposed in ref. 19, but here mediated explicitly by the Li₇La₃Zr₂O₁₂ surface. We adsorbed one H₂O molecule on the most favorable site Li[3O] and then found the most favorable site to adsorb one CO₂ molecule on the same slab, see the inset in Fig. 5(a). In the co-adsorption model, the most favorable CO₂ site is O[LiLaZr] as for the case of individual CO₂ adsorption (see Section 3.3).

Next, we take the individual adsorption cases of H₂O and CO₂ to represent the independent adsorption reactions (Fig. 5(b)). This situation corresponds to the infinitely separated adsorption of H₂O and CO₂ molecules, with the two molecules not interacting with each other. Fig. 5(a) shows the ΔE_{ads} of the co-adsorption of H₂O and CO₂, while Fig. 5(b) shows the ΔE_{ads} s for infinitely separated H₂O and CO₂ molecules.

The composed ΔE_{ads} of the individual adsorption energies of H₂O ($\Delta E_{\text{ads}} \sim -1.21$ eV) and CO₂ (~ -2.21 eV) is ~ -3.42 eV, which is more negative than the energy of co-adsorption, *i.e.*, ~ -3.25 eV. In the co-adsorption model of Fig. 5(a), the adsorbed H₂O does not easily deprotonate, as opposed to the incipient H₂O dissociation (at the same site) when adsorbed individually as in Fig. 5(b). This evidence clearly indicates that individual reactions of H₂O and CO₂ with Li₇La₃Zr₂O₁₂ compete favorably against the concurrent co-adsorption of H₂O and CO₂.

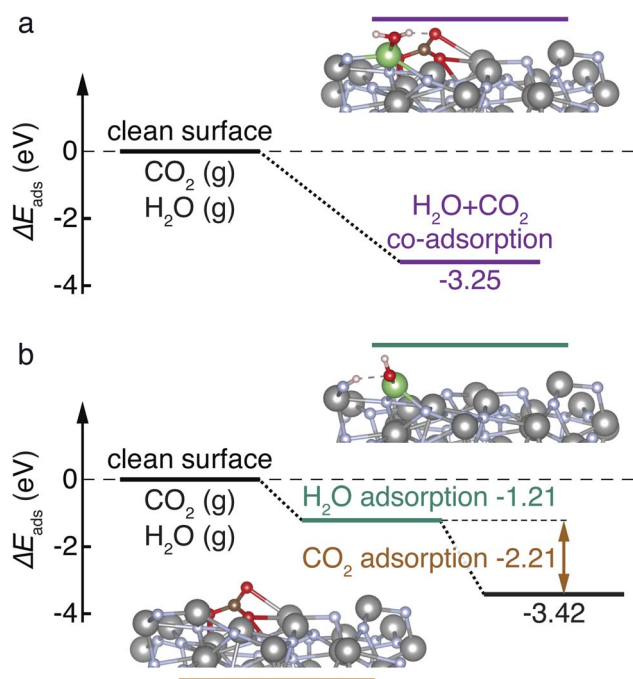


Fig. 5 ΔE_{ads} for the adsorption of H₂O and CO₂: (a) co-adsorption and (b) infinitely separated adsorption. The co-adsorption shows $\Delta E_{\text{ads}} = -3.25$ eV (in purple). The infinitely separated H₂O adsorption ($\Delta E_{\text{ads}} = -1.21$ eV, in green) and CO₂ adsorption ($\Delta E_{\text{ads}} = -2.21$ eV, in brown) shows a combined adsorption energy of $\Delta E_{\text{ads}} = -3.42$ eV, more negative than the co-adsorption. The insets show schematic diagrams for adsorption structures. Atomic species not directly involved in the adsorption are greyed out.

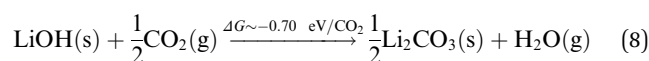
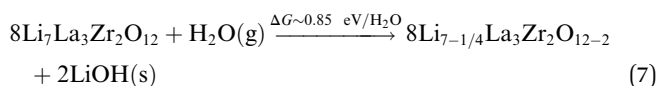
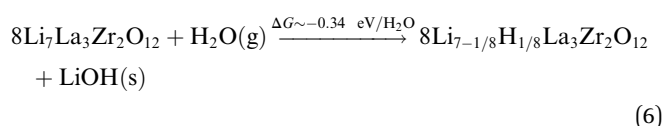
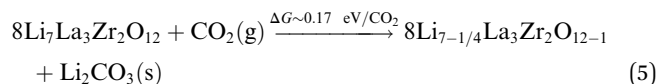
Therefore, the surface contamination of Li₇La₃Zr₂O₁₂ will be mostly driven by the independent reactions of direct hydration and direct carbonation, as opposed to the hydroxide-mediated carbonation proposed in ref. 19.

4. Discussion

Using slab calculations in the framework of *ab initio* thermodynamics, we have explored the reactivity of the complex oxide Li₇La₃Zr₂O₁₂ with two ubiquitous molecules: H₂O and CO₂. It is noted that all the adsorption processes investigated are barrier-free, which indicates the high reaction rates of H₂O and CO₂ with Li₇La₃Zr₂O₁₂. A quantitative evaluation of the reaction rates requiring microkinetic models is beyond the scope of this study.

The exposure of Li₇La₃Zr₂O₁₂ to both H₂O and CO₂ has been documented by preliminary computational and experimental studies.^{14,19,21,77}

Using X-ray photo-emission spectroscopy (XPS) depth-profiling, Sharafi *et al.* showed the formation of Li₂CO₃ layers as thick as ~ 5 – 10 nm on the exterior of Li₇La₃Zr₂O₁₂ particles.¹⁹ The authors proposed several chemical reactions (eqn 5–8) between Li₇La₃Zr₂O₁₂, CO₂ and H₂O, whose energetics (ΔG s) were verified by first-principles calculations.¹⁹ Nevertheless, the proposed reaction mechanisms of Li₇La₃Zr₂O₁₂ carbonation are still elusive requiring in-depth investigations, which justifies this endeavour.



The ΔG s in eqn (5)–(8) are from ref. 19. In eqn (5), Li₂CO₃ is directly formed *via* carbonation of Li₇La₃Zr₂O₁₂, but with a predicted positive ΔG .¹⁹ Compared to the unfavorable direct carbonation of Li₇La₃Zr₂O₁₂ (eqn (5)),¹⁹ the hydroxide-mediated carbonation was interpreted as two favorable reactions: (i) the protonation of Li₇La₃Zr₂O₁₂ (eqn (6)) with H⁺ exchanging with Li⁺, followed by (ii) the conversion of LiOH and CO₂ into Li₂CO₃ as in eqn (8). Although with unfavorable ΔG (~ -0.85 eV/H₂O), another mechanism proposed was the direct hydration of Li₇La₃Zr₂O₁₂ of eqn (7), which is followed by carbonation (of eqn (8)). Therefore, carbonate contamination on Li₇La₃Zr₂O₁₂ was proposed to form *via* the hydroxide-mediated pathway (eqn (6) and (8)) rather than direct carbonation (eqn (5)).¹⁹

In Section 3.2 and Table 1, we have amply demonstrated the favorable adsorption of H₂O on the Li₇La₃Zr₂O₁₂ surface, with

spontaneous H₂O dissociation on exposed Li_{Surface} sites as Li_{Surface}-O-H, thus forming LiOH species. Our calculations clearly suggest that the formation of LiOH in Li₇La₃Zr₂O₁₂ is mediated by its reactive surface, which “catalyzes” the nucleation process of lithium hydroxide moieties. Indeed, XPS of Li₇La₃Zr₂O₁₂ particles has detected the signatures of OH⁻ groups and LiOH even at relatively high temperatures (400–500 °C).²¹

Another pathway for LiOH formation proceeds through the protonation of Li-O moieties exposed at the Li₇La₃Zr₂O₁₂ surface, which we also predicted as a spontaneous process. The protonation of other M-O (with M = La or Zr) moieties at the Li₇La₃Zr₂O₁₂ surface may also form other adventitious species, whose signatures have not been reported yet. However, the available free protons at the surface (resulting from readily dissociated H₂O molecules) can then be exchanged with Li⁺ in Li₇La₃Zr₂O₁₂ as previously reported by thermo-gravimetric analysis mass-spectroscopy, neutron investigations, and focused ion beam secondary ion mass spectrometry.^{14,77,78} Alternatively, proton species formed on the Li₇La₃Zr₂O₁₂ surface may intercalate directly into vacant Li⁺ sites of the bulk structure. Note that the high Li-ion transport in Li₇La₃Zr₂O₁₂ facilitates Li⁺/H⁺ exchange.

CO₃²⁻ contamination of the Li₇La₃Zr₂O₁₂ particle exteriors has been previously documented through Raman and XPS measurements.^{19,21} Our calculations demonstrated spontaneous CO₂ adsorption and carbonate formation with the exposed oxygen atoms, *i.e.*, O_{Surface}-Li_{Surface} or O_{Surface}-La_{Surface} (see Section 3.3 and Table 2) at the Li₇La₃Zr₂O₁₂ surface. This is in striking contrast to the unfavorable reaction of direct carbonation proposed in eqn (5).²¹ Importantly, we show that the formation of Li₂CO₃ does not require the availability of LiOH for CO₂, but it is directly catalyzed by the Li₇La₃Zr₂O₁₂ surface. Our surface calculations show that carbonates are not limited to Li₂CO₃ species, instead incipient CO₃²⁻ species may be bonded to other metal ions exposed at the surface of Li₇La₃Zr₂O₁₂, including Li and La. Therefore, the direct carbonation of Li₇La₃Zr₂O₁₂ is thermodynamically favorable and barrier-free. Notably, the co-adsorption of H₂O and CO₂ appears less favorable than their individual adsorptions.

We have demonstrated the thermodynamically favorable processes of H₂O and CO₂ decomposition on the Li₇La₃Zr₂O₁₂

particles. We use this knowledge to prescribe external conditions (temperature and pressure), which curb the LiOH and Li₂CO₃ contamination of Li₇La₃Zr₂O₁₂ during its synthesis. Fig. 6 shows the computed surface phase diagrams of Li₇La₃Zr₂O₁₂ as functions of temperature and partial pressures of H₂O and CO₂. The derivation of the surface phase diagrams requires the minimization of the grand-potential energy of eqn (2) as the surface coverage, temperature, and pressure are varied.²⁴

From Fig. 6, one clearly sees that the scenarios of high-H₂O or CO₂ coverages are achieved at relatively high partial pressures (~2–10 bar) and low temperatures (<1000 K). Our predictions suggest that at atmospheric pressure (~1 bar) and at temperature above ~1260 K, Li₇La₃Zr₂O₁₂ particles will be free of water, protons and LiOH species. The carbonation of Li₇La₃Zr₂O₁₂ appears more pernicious, which clearly requires higher temperatures above ~1730 K for its complete elimination at atmospheric pressure (see Fig. 6(b)). These findings are representative of the real Li₇La₃Zr₂O₁₂ powder or the surface of sheets (Li₇La₃Zr₂O₁₂ composites), as the surface investigated dominates the Li₇La₃Zr₂O₁₂ Wulff shapes.^{24,79}

The synthesis of Li₇La₃Zr₂O₁₂ is commonly carried out *via* the solid-state method, by calcination in “dry” air at temperatures ~1000 °C (~1273 K).^{19,21,23} The procedures of densification of Li₇La₃Zr₂O₁₂ *via* a hot press (or spark plasma) are regularly utilized to improve the contact between particles and increase the electrolyte ionic conductivity. The surface phase diagrams in Fig. 6 clearly show that both synthesis and sintering of Li₇La₃Zr₂O₁₂ should avoid air exposure. Notably, Fig. 6 shows that post-synthesis heat treatments (above 1000 °C) are beneficial to desorb H₂O and eliminate other contaminants. Indeed, typical sintering temperatures for Li₇La₃Zr₂O₁₂ are in the range of 1000–1300 °C (~1300–1600 K).^{19,23} Higher temperatures than 1300 °C may lead to significant Li (and proton) loss.²³ However, such elevated temperatures may still prevent the full removal of Li₂CO₃ at the surface. Li loss during the Li₇La₃Zr₂O₁₂ preparation is typically mitigated by adding LiOH and Li₂CO₃. Furthermore, we speculate that the addition of LiOH and Li₂CO₃ will not be disruptive to the preparation of Li₇La₃Zr₂O₁₂, and these two compounds may also limit their formation when Li₇La₃Zr₂O₁₂ is exposed to humid air.

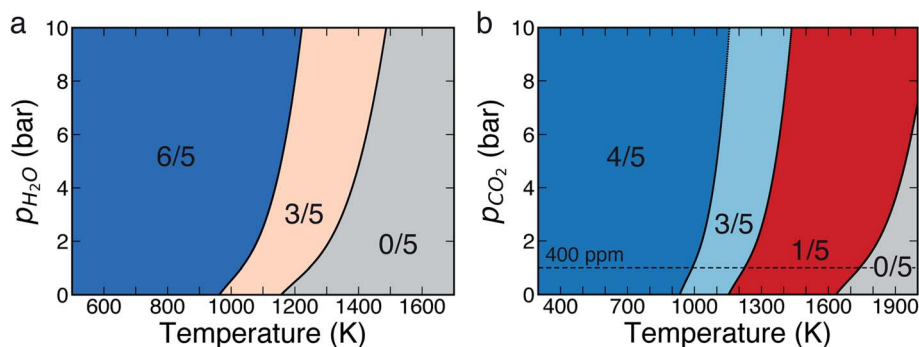


Fig. 6 Surface phase diagrams of Li₇La₃Zr₂O₁₂ at different temperatures and partial pressures of (a) H₂O and (b) CO₂, respectively. Fractions of the monolayer (ML) and solid color denote the most favorable coverage scenarios within each range of temperature (in K) and partial pressure (in bar). The dashed line marks the CO₂ level of 400 ppm at a partial pressure of 1 bar. This line is used to indicate the thermodynamic favorability of adsorbing CO₂ from dilute streams, which is of relevance in CO₂ utilization.

Although the effect of partial pressure of H₂O and CO₂ appears less significant than that of temperature with respect to Li₇La₃Zr₂O₁₂ contamination, synthesis under ultrahigh vacuum conditions ($\sim 1 \times 10^{-6}$ bar) and at ~ 800 K guarantees a water-free Li₇La₃Zr₂O₁₂ surface, which is sparsely contaminated by Li₂CO₃ species. Clearly, these conditions appear unpractical, but glove-box synthesis at pressures within mbar ranges (see Fig. 3 and 4) may be more accessible and deserve further investigations.

Fig. 6 indicates external conditions, which favor (010) Li₇La₃Zr₂O₁₂ surfaces decorated with dissociated H₂O and carbonate species. While these surfaces may not be desired for energy storage applications, the strong adsorption of CO₂ and H₂O suggests that the off-stoichiometric (010) surface of Li₇La₃Zr₂O₁₂ can serve as a support in catalysis. Using two examples of the water gas shift reaction and CO₂ utilisation, we elaborate further below. The water-gas shift reaction is typically catalyzed by noble metal nanoparticles stabilized by oxide supports. Experimental and theoretical studies have indicated that the oxide supports facilitate H₂O dissociation,^{44,45} a critical elementary step in this reaction. The favorable adsorption of H₂O and its spontaneous dissociation thus make Li₇La₃Zr₂O₁₂ a promising support for the water-gas shift reaction. Indeed, there is a concerted effort to design catalytic systems, which operate under dilute streams of CO₂.^{46,47} Fig. 6 illustrates that at 500–600 K, 4/5 ML of CO₂ is adsorbed on Li₇La₃Zr₂O₁₂ even at CO₂ pressures as low as 400 ppm. Hence, the strong adsorption strength of CO₂ on Li₇La₃Zr₂O₁₂ makes this material a promising support for dual-functional catalysts, which adsorb CO₂ from dilute streams and further hydrogenate it to chemicals, such as methanol and ethylene over metal nanoparticles dispersed on Li₇La₃Zr₂O₁₂.

5. Conclusions

In summary, using a robust *ab initio* thermodynamic framework, we investigated the complex surface reactivity of Li₇La₃Zr₂O₁₂ toward ubiquitous H₂O and CO₂. The Li-terminated off-stoichiometric surface of Li₇La₃Zr₂O₁₂ readily reacts with H₂O and CO₂, which promotes the direct formation of metal hydroxide and carbonate species. We demonstrated that synthesis within a mbar pressure range can lead to a water-free Li₇La₃Zr₂O₁₂ surface and reduce drastically the amount of carbonates formed. Our in-depth analysis provides strategies and opportunities to improve the synthesis conditions of Li₇La₃Zr₂O₁₂ and similar complex oxides with high technological relevance to batteries and catalysis. The strong adsorption of CO₂ under conditions of low partial pressure and H₂O indicates the potential of Li₇La₃Zr₂O₁₂ as a suitable catalyst support for the hydrogenation of dilute CO₂ streams and the water-gas shift reaction respectively. These findings are general and provide rules of thumb to analyze the reactivity of complex oxides toward two common molecules, *i.e.*, H₂O and CO₂.

Conflicts of interest

There are no conflicts to declare.

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