First-principles studies on the atomistic properties of metallic magnesium as anode material in magnesium-based batteries

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ABSTRACT

Rechargeable magnesium-ion batteries (MIBs) are a promising alternative to commercial lithium-ion batteries (LIBs). They are safer to handle, environmentally more friendly, and provide a five-time higher volumetric capacity (3832 mAh·cm⁻³) than commercialized LIBs. However, the formation of a passivation layer on metallic Mg electrodes is still a major challenge towards their commercialization. Using density functional theory, the atomistic properties of metallic magnesium, such as bulk, surface, and adsorption properties, were examined. Well-selected self-diffusion processes on perfect and imperfect Mg surfaces were investigated to better understand the initial surface growth phenomena. Subsequently, rate constants and activation temperatures of crucial diffusion processes on Mg(0001) and Mg(1011) were determined, providing preliminary insights into the surface kinetics of metallic Mg electrodes.
1. INTRODUCTION

Rechargeable batteries are of outstanding importance in achieving global climate goals as they play a key role in electronic applications, in the mobility sector for the electrification of cars, or stationary grid energy storage systems for surplus wind and solar power. The most prominent representatives are Lithium-ion batteries (LIBs)\(^1\text{--}^5\), which are facing controversy due to the use of critical raw materials such as lithium, cobalt, nickel, or graphite.\(^6\) Metallic lithium anodes have a high theoretical capacity (3861 \(\text{mAh} \cdot \text{g}^{-1}\)), the lowest negative electrochemical potential (-3.04 \(\text{V vs. standard hydrogen electrode (SHE)}\)), and a low density (0.59 \(\text{g} \cdot \text{cm}^{-3}\)), however, are prone to form dendrites.\(^7\) Dendrites are needle-shaped structures leading to short circuits, thermal runaways, and even battery failures, although promising approaches such as the electrostatic shielding of the lithium surface through additives have been proposed to tackle this problem.\(^8\) Due to these safety concerns, graphite with intercalated lithium ions is still used as anode material in commercial LIBs, reducing its theoretical capacity by roughly one order of magnitude to 372 \(\text{mAh} \cdot \text{g}^{-1}\) in present day commercial LIBs.\(^9\)

Therefore, rechargeable multivalent magnesium-ion batteries (MIBs) have emerged as a promising alternative, mainly due to the bivalency of the magnesium atom, which allows it to carry twice the charge resulting in a higher volumetric capacity (3833 \(\text{mAh} \cdot \text{cm}^{-3}\) vs. 777 \(\text{mAh} \cdot \text{cm}^{-3}\) of graphite anodes in commercial LIBs).\(^10\) Additionally, magnesium has a low electrochemical potential (-2.37 \(\text{V vs. SHE})\), is highly abundant, of low cost, and is environmentally friendly. These benefits are reflected in the exponentially increasing number of publications that have recently been dedicated to the topic of MIBs, as shown in Figure 1 from the publication by Li et al.\(^11\) On the other hand, a great deal of effort is required to find suitable electrolytes that allow reversible magnesium deposition while at the same time providing a broad electrochemical window.\(^9,12\) Conventional carbonate electrolytes cannot be used for rechargeable MIBs because the solid electrolyte interface (SEI) formed by decomposition products of the electrolyte is not permeable to magnesium-, in contrast to lithium-cations.\(^10,13\) Proposed solutions are electrolytes based on Grignard reagents, \(\text{Mg}(\text{TFSI})_2\) salts or ionic liquids, as well as the use of polymeric interlayers as artificial SEI.\(^13,14\) Nevertheless, the structure and growth mechanism of SEI formation remains poorly understood due to its high complexity, highlighting the need for adequate theoretical modeling on different time and length scales.\(^15\)

The second controversial issue is whether dendrite formation is possible on metallic magnesium anodes. On the one hand, the tendency of occurrence is significantly lower than for the lithium equivalent,\(^16\) yet dendrites have been demonstrated under harsh deposition
conditions, as shown by the Banerjee group.\textsuperscript{[17]} As a result, there have been requests to conduct experiments to determine critical current densities\textsuperscript{[18]} and to define precise voltage windows\textsuperscript{[19]} for dendrite-free regions. In a recently published study, the critical overpotential of dendrite formation on lithium, sodium, and magnesium was calculated using a grand-canonical density functional theory (DFT) approach, indicating a combination of high surface tension, low surface capacitance, and low potential of zero charge (PZC) as indicators for mitigated dendrite growth.\textsuperscript{[20]} Another explanation for enhanced dendrite growth on lithium compared to magnesium surfaces includes the accumulation of negative excess charges at the peaks of protrusions of the lithium electrodes inducing a strong electric field that attracts further lithium cations.\textsuperscript{[21]} In addition, lower step-down and terrace self-diffusion barriers of magnesium compared to lithium are considered responsible for the reduced dendrite growth.\textsuperscript{[22,23]}

In this work, periodic DFT calculations have been performed to determine the atomistic properties of magnesium and to explain the initial stages of surface growth. This technique has previously been applied for lithium\textsuperscript{[24]} and sodium\textsuperscript{[25]} in our group. For this purpose, the bulk, surface, and adsorption properties of magnesium were first calculated. Based on the obtained surface energies, the corresponding equilibrium shape of a magnesium crystal was determined within the framework of the Wulff construction.\textsuperscript{[26]} Subsequently, a wide variety of two- and three-dimensional diffusion processes on perfect and imperfect Mg(0001) and Mg(10\bar{1}1) surfaces were investigated and analyzed concerning surface growth phenomena. Finally, the obtained DFT results provide a data set for parametrizing a force field for metallic Mg or performing corresponding kinetic Monte-Carlo studies.\textsuperscript{[27,28]}
2. METHODOLOGY

Periodic DFT calculations were performed with the plane-wave based Vienna *ab initio* simulation package (VASP)\(^{[29,30]}\). The core electrons were described using the projector augmented wave (PAW)\(^{[31]}\) method of Blöchl as implemented in VASP.\(^{[32]}\) Exchange correlation effects were described within the generalized gradient approximation (GGA) of Perdew, Burke, and Enzerhof (PBE).\(^{[33]}\) Additionally, the Bayesian error estimation functional with van der Waals correlation (BEEF-vdW) was applied to determine the standard deviation of the investigated quantities.\(^{[34]}\) A plane-wave cutoff energy of 400 eV was employed after detailed convergence studies (SI Figure 1), where Mg 2s electrons were described as valence electrons. Following the scheme of Monkhorst and Pack, a \(k\)-point mesh density of at least 0.14 Å\(^{-1}\) was applied for all total energy calculations.\(^{[35]}\) Thermal smearing of one-electron states was allowed using the Gaussian smearing method (\(\sigma = 0.1\) eV) to determine the partial occupancies of each orbital and acquire faster convergence with respect to the number of \(k\)-points. The electronic self-consistent field (SCF) was considered converged when the total energy difference was less than \(10^{-5}\) eV, and the norms of all the forces were smaller than \(10^{-3}\) eV·Å\(^{-1}\). Surface energies were calculated on symmetrical \((1 \times 1)\) cells with a minimum slab thickness of 30 Å and a minimum vacuum region of 20 Å (SI Table I). A single atom in the middle of the slab was fixed to avoid net translations.\(^{[24]}\) Adsorption energies, dimer interaction, diffusion barriers, and frequencies were generally calculated on converged slabs with 6 surface layers, where the two uttermost layers were fixed to emulate bulk properties. If it became necessary, vicinal slabs were used. The exact surface characteristics are summarised in SI Table II. The minimum energy path (MEP) was determined with the climbing image nudged elastic band (CI-NEB) method as implemented in the transition state tools for VASP (VTST) with generally 7 images between the initial states separated by a spring constant of 5.0 eV·Å\(^{-2}\).\(^{[36,37]}\) As an initial guess for the MEP the image-dependent pair potential (IDPP) was applied.\(^{[38,39]}\) To confirm the transition state and to determine rate constants, we calculated vibrational frequencies with the dynamical matrix method from the VTST package. For this purpose, the electronic and ionic convergence criteria were increased to \(10^{-8}\) eV and \(10^{-8}\) eV·Å\(^{-1}\), respectively, and the diffusing as well as the nearest neighbor atoms along the diffusion pathway were symmetrically displaced by 0.007 Å in each spatial direction.

The cohesive energy \(E_{\text{coh}}\) is defined as the energy gain an isolated atom receives when it is embedded in a certain crystal structure. It was calculated by subtracting the energies of the isolated atoms \(E_{\text{atom}}\) from the energy of the bulk crystal structure \(E_{\text{bulk}}\), divided by the total number of atoms \(N\) in the bulk structure:
\[ E_{\text{coh}} = -\frac{1}{N}(E_{\text{bulk}} - N \cdot E_{\text{atom}}) \]  

(1)

Bulk moduli were calculated based on the jellium equation of state.\[^{[43]}\] In order to be able to compare the theoretical cohesive energy with the experimental reference, the zero-point vibrational energy \( E_{\text{ZPVE}} \) was estimated as follows.\[^{[41]}\]

\[ E_{\text{ZPVE}} = \frac{9}{8} k_B \theta_D \]  

(2)

\( k_B \) corresponds to the Boltzmann constant and \( \theta_D \) to the Debye temperature, which is 400 K for magnesium.\[^{[41]}\]

The surface energy \( \gamma \) is defined as the surface excess free energy per unit area and was calculated by subtracting a multiple of the bulk energy \( N \cdot E_{\text{bulk}} \) from the energy of the slab \( E_{\text{slab}} \), divided by the area of the surface \( A \) times two (because of the symmetric slab configuration):

\[ \gamma = \frac{1}{2A} (E_{\text{slab}} - N \cdot E_{\text{bulk}}) \]  

(3)

All surface energies were employed to carry out the Wulff construction.\[^{[26]}\] The area fractions of the facets were calculated using the Python package WulffPack for a nanocrystal with 5000 atoms.\[^{[42]}\]

Adsorption energies \( E_{\text{ad}} \) were obtained by subtracting the energy of the pure surface \( E_{\text{slab}} \) plus the energy of an isolated magnesium atom \( E_{\text{Mg-atom}} \) from the energy of the relaxed system \( E_{\text{tot}} \) containing the slab with the adsorbed atom:

\[ E_{\text{ad}} = E_{\text{tot}} - (E_{\text{slab}} + E_{\text{Mg-atom}}) \]  

(4)

The interaction energy \( E_{\text{int}} \) was calculated by subtracting two times the adsorption energy of a monomer \( E_{\text{ad}}^{\text{monomer}} \) from the adsorption energy of a dimer \( E_{\text{ad}}^{\text{dimer}} \):

\[ E_{\text{int}} = E_{\text{ad}}^{\text{dimer}} - 2 \cdot E_{\text{ad}}^{\text{monomer}} \]  

(5)

The Ehrlich–Schwoebel barrier \( E_{\text{ES}} \) was determined for all step-down diffusion processes.\[^{[43,44,45]}\] It corresponds to the additional energy barrier that a diffusing atom has to overcome when descending a step and was calculated by subtracting the terrace self-diffusion barrier \( E_{\text{a}}^{\text{for(Terrace)}} \) from the barrier of the step-down process \( E_{\text{a}}^{\text{for(Step-down)}} \):

\[ E_{\text{ES}} = E_{\text{a}}^{\text{for(Step-down)}} - E_{\text{a}}^{\text{for(Terrace)}} \]  

(6)
The reaction rate $k_{@RT}$ at room temperature ($T = 293.15 \, K$) was calculated for each diffusion process by means of transition state theory as given by the Arrhenius equation:

$$k_{@RT} = \nu \cdot \exp \left( - \frac{E_a}{k_B T} \right)$$

(7)

where the pre-exponential factor $\nu$ was determined based on the Einstein approximation\textsuperscript{[46]} with the vibrational frequencies of the diffusing adatom and the nearest surface atoms along the migration pathway for the initial and the transition state. $E_a$ equals the activation energy and $k_B$ is the Boltzmann constant.

The activation temperature $T_a$ above which a process runs at the rate $\Gamma$ was calculated with the equation used by Bogicevic et al.\textsuperscript{[47]} Above $T_a$, a process is considered to be ‘activated’ following the formula:

$$T_a = \frac{E_a/k_B}{\ln (\nu/\Gamma)}$$

(8)

Since the rate $\Gamma$ depends on the experimental growth rate, $\Gamma = 1 \, s^{-1}$ was set, which is valid for a deposition rate of about $0.001 – 0.1 \, \text{ML} \cdot s^{-1}$. As indicated, $E_a$ corresponds to the activation energy, $k_B$ to the Boltzmann constant, and $\nu$ to the pre-exponential factor. For some processes ($D_0 \leftrightarrow D_1$, $D_2 \leftrightarrow D_3$, $T_0 \leftrightarrow T_1$, $E_2 \leftrightarrow E_3$ (Ex.)) with very small activation barriers ($<0.02 \, \text{eV}$), the pre-exponential factor could not be determined due to imaginary frequencies in the TS. In these cases, a value of $\nu = 5.0 \cdot 10^{12} \, s^{-1}$ was assumed, which corresponds to the average value of the pre-exponential factor, usually in the range between $10^{12} – 10^{13} \, s^{-1}$.
3. RESULTS AND DISCUSSION

a. Bulk properties

The bulk properties of magnesium, including lattice constants, binding energies, and bulk moduli, were calculated for the following crystal structures with the PBE and the BEEF-vdW functional: hexagonal-close-packed (hcp), double-hexagonal-close-packed (dhcp), body-centered-cubic (bcc), face-centered-cubic (fcc), simple cubic (sc), β-tungsten (a15) and diamond (dia). The calculated values for both functionals for all crystal structures and a comparison with experimentally obtained data are shown in Table I. Magnesium crystallizes in accordance with experimental studies in a hcp structure under ambient conditions. The calculated cohesive energy of 1.50 eV·atom$^{-1}$ from the PBE functional is in almost perfect agreement with the experimental value (Table I) and with other theoretical studies (SI Table III). The BEEF-vdW functional slightly underestimates the cohesive energy, but it is within its estimated error. Moriarty et al. first predicted a phase transformation from the hcp to the bcc structure at around 50 GPa from generalized pseudopotential theory$^{[48–50]}$, which Olijnyk and Holzapfel later confirmed by X-ray diffraction (XRD)$^{[51]}$. This is contradicted by the study of Erandonea et al., who assumed the dhcp instead of the bcc structure at high pressures and temperatures.$^{[52]}$ Moriarty et al. also predicted a second phase transformation from the bcc to the fcc structure at even higher pressures$^{[49]}$, which could not be observed experimentally.$^{[53]}$

Table I. Calculated and experimentally observed physical constants for different bulk phases of magnesium. The lattice constants $a_0$ and $c_0$ are given in Å, bulk moduli $B_0$ in GPa, and the cohesive energy $E_{coh}$ in eV·atom$^{-1}$. For the BEEF-vdW functional, the calculated standard deviation of the cohesive energy is given in parenthesis. The experimental results were taken from Ref. [54]. The influence of the zero-point vibrational energy $E_{ZPVE}$ on the experimental values is given in parentheses. The values were adapted from Alchagirov et al. for $a_0$, $c_0$, and $B_0$ and calculated with equation (2) for $E_{coh}$.$^{[41]}$

| Bulk properties | This work | Other works |
|-----------------|-----------|-------------|
|                 | PBE       | BEEF-vdW    | Experiment |
| hcp             | $a_0$     | 3.18        | 3.19        | 3.21 (0.00) |
|                 | $c_0$     | 5.21        | 5.21        | 5.21 (0.00) |
|                 | $B_0$     | 36.5        | 37.1        | 35.4 (-0.04) |
|                 | $E_{coh}$ | 1.50        | 1.33 (0.27) | 1.51 (0.04) |
| dhcp            | $a_0$     | 3.19        | 3.18        |             |
|                 | $c_0$     | 10.43       | 10.43       |             |
|                 | $B_0$     | 36.1        | 36.7        |             |
|                 | $E_{coh}$ | 1.49        | 1.33        |             |
| bcc             | $a_0$     | 3.57        | 3.58        |             |
|                 | $B_0$     | 35.3        | 35.4        |             |
|                 | $E_{coh}$ | 1.48        | 1.30 (0.28) |             |
| fcc             | $a_0$     | 4.52        | 4.52        |             |
|                 | $B_0$     | 35.9        | 36.66       |             |
|                 | $E_{coh}$ | 1.49        | 1.32 (0.27) |             |
b. Surface properties

The surface energy is regarded as a measure for the stability of a surface and determines the equilibrium shape of a crystal.\textsuperscript{[55]} In agreement with literature\textsuperscript{[56–58]}, Mg(0001) is the most stable crystal surface, followed by Mg(10\textbar{}10)A and Mg(10\textbar{}11), which differ in our calculations by less than 1 meV\cdot\text{Å}^2 (Table II). Mg(0001) lies in the basal plane of the \textit{hcp} unit cell, which is characterized by a particularly high packing density, resulting in thermodynamic stabilization.\textsuperscript{[54]} At this point, we refer to the work of Tang et al., who established a model to predict the relative stability of magnesium surfaces based on the number of broken basal and non-basal bonds.\textsuperscript{[59]} They also showed that Friedel oscillations are especially present on low-index Mg surfaces, influencing surface relaxation. On the other hand, on high index surfaces, relaxation is driven by charge depletion and charge smoothing effects. In an embedded atom method (EAM) potential study, Mg (10\textbar{}11) was considered to be the second most stable surface, which is not the case according to our DFT calculations.\textsuperscript{[60]} Caution is required for Mg(10\textbar{}10) since there are two possible surface terminations Mg(10\textbar{}10)A and Mg (10\textbar{}10)B, which are shown in SI Figure 2. Mg(10\textbar{}10)B differs from Mg(10\textbar{}10)A by one missing row and is characterized by parallel atomic lines making deep channels. Mg(10\textbar{}10)A also has channels, but not as distinct as in Mg(10\textbar{}10)B. Surface energies calculated with the BEEF-vdW functional are generally lower but have the same stability sequence. All PBE results are within the error range of the BEEF-vdW functional. Further surface energies (that also entered the following Wulff construction) and a literature data summary are provided in SI Table IV.

Table II. Calculated surface energies $\gamma$ (given in meV\cdot\text{Å}^2) for selected magnesium surfaces. For the BEEF-vdW functional, the calculated standard deviation of the surface energy is given in parenthesis.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$\gamma$ & This work & Other works & \\
& PBE & BEEF-vdW & Experiment\textsuperscript{[61]} \\
\hline
Mg(0001) & 33.9 & 38.7 (9) & 51.0 \\
Mg(10\textbar{}10)A & 40.3 & 44.9 (9) & \\
Mg(10\textbar{}11) & 40.9 & 45.8 (8) & \\
Mg(10\textbar{}10)B & 55.5 & 59.4 (11) & \\
\hline
\end{tabular}
\end{table}
Interestingly, and as already shown in literature\cite{56,57}, the Wulff construction (Figure 1) reveals for both functionals (PBE, BEEF-vdW) a reverse order of the area fractions versus surface energies. Our calculations confirm that Mg(10\overline{1}1) has the largest area share with 48.6%, although it is only the third most stable surface, followed by Mg(10\overline{1}0)A (27.9%) and Mg(0001) (23.7%) as shown in Table III. Other publications also assign Mg(11\overline{2}0) area fractions in the Wulff construction, which was not observed in our case.\cite{60,62} It is important to mention that even over a wide potential range, the shape of the magnesium crystal behaves almost constant, which suggests that in the working potential range of magnesium batteries, our calculated surface area fractions are still valid.\cite{63} The calculated area fractions emphasize the need to study the diffusion properties of all three surfaces collectively, rather than looking at one surface termination individually.

Table III. Calculated (PBE and BEEF-vdW) and literature area fractions of the respective magnesium surface Mg(0001), Mg(10\overline{1}0)A, and Mg(10\overline{1}1) from the calculated Wulff construction shown in Figure 1.

| Area fraction | Functional | Mg(0001) | Mg(10\overline{1}0)A | Mg(10\overline{1}1) |
|---------------|------------|----------|---------------------|---------------------|
| This work     | PBE        | 23.7%    | 27.9%               | 48.6%               |
|               | BEEF-vdW   | 22.4%    | 25.8%               | 50.5%               |
| Other works   | PBE\cite{56} | 22.5%    | 27.2%               | 49.5%               |
|               | PBE\cite{57} | 25.0%    | 33.0%               | 42.0%               |

Figure 1. The thermodynamic equilibrium shape of a magnesium crystal is determined by the calculated Wulff construction. All surface energies (PBE) from SI Table IV were included in the evaluation of the Wulff shape.
c. Adsorption energies

The adsorption energy provides information about which positions are preferentially populated. Consequently, adsorption of Mg was studied on the surfaces present according to the Wulff shape (Mg(0001), Mg(10\bar{1}0)A, Mg(10\bar{1}1)) as well as, for the sake of completeness, on Mg(10\bar{1}0)B. The respective adsorption energies (PBE/BEEF-vdW) and available literature data (PBE) are summarized in Table IV. In addition, a schematic representation of all adsorption sites studied is provided in SI Figure 3.

The highest energy gain results from adsorption on the bridge-bottom position on Mg(10\bar{1}0)B (-1.64 eV), which is also the only stable adsorption site on this surface. The high adsorption energy seems logical since Mg(10\bar{1}0)B, the surface termination with the highest surface energy, aims for its stabilization by a transformation into the much more stable counterpart Mg(10\bar{1}0)A. In fact, this becomes even more evident when comparing the structural environments of the adsorption sites in SI Figure 3. Mg(10\bar{1}0)B is characterized by deep channels running parallel. Adsorption at the bridge-bottom position coordinates the adsorbate to six adjacent neighbors, more than in any other site, regardless of the surface. The second highest adsorption energy was found for Mg(10\bar{1}0)A at the ontop-bottom site (-1.00 eV), significantly lower than on Mg(10\bar{1}0)B. Mg(10\bar{1}0)A also exhibits channels, although they are not as deep as in Mg(10\bar{1}0)B, and the number of coordination partners of an adsorbate is reduced to five. Following closely behind with a 0.03 eV lower adsorption energy (-0.97 eV) is the hollow site on Mg(10\bar{1}1), where the adsorbate has a coordination number of four. These two sites have the highest adsorption energies for the surfaces present in the Wulff shape, indicating primary adsorption to occur on Mg(10\bar{1}0)A and Mg(10\bar{1}1).

There are two stable adsorption sites in the case of the most stable surface Mg(0001). Preferred adsorption occurs at the fcc site (-0.58 eV), which is energetically slightly favored compared to the hcp site (-0.56 eV). Thus, both adsorption energies are approximately 40% lower than the corresponding adsorption energies on Mg(10\bar{1}0)A and Mg(10\bar{1}1). Clarification may be found again by considering the morphology. Mg(0001) has a flat surface with a high packaging density. The coordination of the adsorbate occurs only to three surface atoms. Moreover, the energetically similar but unstable bridge site already allows the prediction of a low terrace self-diffusion barrier. At this point, we refer to the work of Lautar et al. in which potential energy surfaces (PES) were calculated, clearly showing the varying energy landscapes for Mg(0001), Mg(10\bar{1}0)A, and Mg(10\bar{1}1).\cite{56} We also want to reference two EAM potentials for magnesium by Liu et al.\cite{64} and Sun et al.\cite{65} However, in the potential of Liu et al., only the bridge position on Mg(0001) is stable, which is not the case according to our DFT calculations.\cite{60} We also want to point to the section Diffusion barriers, which further clarifies...
why fcc sites are energetically favored over hcp sites, although this contradicts the nature of the hcp lattice, which should follow the ABABAB-stacking sequence.

All calculated adsorption energies are consistent with previously published theoretical results (on PBE level).\textsuperscript{[22,56,66,67]} The error range for the BEEF-vdW functional varies between 0.10 and 0.31 eV, indicating a strong dependence on the chosen functional. However, all PBE results are within the BEEF-vdW standard deviation, and the energy ratios are equal for both functionals.

Table IV. Calculated (PBE and BEEF-vdW) and theoretical reference adsorption energies $E_{ad}$ of an adsorbed Mg atom on Mg(0001), Mg(1010) and Mg(1011). All values are given in eV·atom$^{-1}$. For the BEEF-vdW functional, the calculated standard deviation of the adsorption energy $E_{ad}$ is given in parenthesis. A schematic representation of all adsorption sites studied is given in SI Figure 3.

| $E_{ad}$ | Adsorption site | This work | Other works |
| --- | --- | --- | --- |
|  |  | PBE | BEEF-vdW | PBE |
| Mg(0001) | fcc | -0.58 | -0.48 (0.15) | -0.58\textsuperscript{[56]}, -0.59\textsuperscript{[22]} |
|  | hcp | -0.56 | -0.47 (0.14) | -0.56\textsuperscript{[56]}, -0.57\textsuperscript{[22]} |
|  | bridge* | -0.56 | -0.46 (0.14) | -0.57\textsuperscript{[22]} |
|  | ontop* | -0.45 | -0.38 (0.12) | -0.44\textsuperscript{[22]} |
| Mg(1010)A | ontop-bottom | -1.00 | -0.86 (0.23) | -1.03\textsuperscript{[56]} |
|  | bridge-bottom* | -0.97 | -0.84 (0.21) |
|  | ontop-up* | -0.46 | -0.42 (0.10) |
|  | bridge-up* | -0.58 | -0.51 (0.12) |
| Mg(1010)B | ontop-bottom* | -1.23 | -1.04 (0.25) |
|  | bridge-bottom | -1.64 | -1.45 (0.31) |
|  | ontop-up* | -0.42 | -0.38 (0.10) |
|  | bridge-up* | -0.52 | -0.50 (0.12) |
| Mg(1011) | hollow | -0.97 | -0.83 (0.19) | -0.97\textsuperscript{[56]} |

* unstable configuration; fixed with constraints.

d. Diffusion barriers

**Terrace self-diffusion on Mg(0001), Mg(10\overline{1}0)A, and Mg(10\overline{1}1)**

To understand the mobility of Mg atoms on defect-free surfaces, we examined the terrace self-diffusion barriers on the three thermodynamic most stable surfaces Mg(0001), Mg(10\overline{1}0)A, and Mg(10\overline{1}1). A schematic illustration of the initial (atoms marked in green) and final (atoms marked in red) positions is shown in Figure 2. The respective barriers are summarized in Table V. Additionally, estimated prefactors and room-temperature reaction rates are provided for the PBE and the BEEF-vdW functionals in the supporting information, as well as the energy profiles of the respective processes (SI Table V, SI Table VI, SI Figure 4).
Diffusion of a single Mg adatom on Mg(0001) occurs almost barrier-free from the thermodynamic most stable fcc to the slightly increased hcp position in a hopping mechanism \([\text{fcc}_0 \rightarrow \text{hcp}_1, E_a = 0.02 \text{ eV}]\). Roe et al. justified the low terrace self-diffusion barrier on Mg(0001) with the small coordination number of 3 of the migrating atom, an intrinsic property of the hexagonally close-packed \(\{0001\}\)-facet.\[^{[88]}\] A possible exchange process for Mg(0001) seems highly unfavorable \([\text{fcc}_0 \rightarrow \text{hcp}_2 (\text{Ex.}), E_a = 0.74 \text{ eV}]\), which is also true for all investigated Mg surfaces in contrast to the alkali metal Na(100) in which the exchange process is dominating.\[^{[25]}\] The morphology of Mg(1010)A is characterized, as mentioned earlier, by channels running parallel to each other. Diffusion within a channel has a minor barrier \([\text{ob}_0 \leftrightarrow \text{ob}_1, E_a = 0.02 \text{ eV}]\), while transitions across channels have approximately 20-fold higher barriers for hopping and exchange processes \([\text{ob}_0 \leftrightarrow \text{ob}_2, E_a = 0.42 \text{ eV}; \text{ob}_0 \leftrightarrow \text{ob}_2 (\text{Ex.}), E_a = 0.46 \text{ eV}]\). In the case of Mg(1011), diffusion between adjacent and opposite hollow positions was studied. Adjacent diffusion \([h_0 \leftrightarrow h_1, E_a = 0.30 \text{ eV}]\) is more likely than diffusion between opposing sites \([h_0 \leftrightarrow h_2, E_a = 0.42 \text{ eV}]\). The PBE and BEEF-vdW calculations are consistent and in agreement with literature.\[^{[23,56,62,68]}\] Recently, Jäckle et al. suggested that the low terrace self-diffusion barrier of magnesium may indicate the lack of dendrite growth.\[^{[23]}\] This is valid for Mg(0001), partially for Mg(1010)A but rather less for Mg(1011), the surface with the largest area fraction of the Wulff particle.

Table V. Calculated (PBE and BEEF-vdW) and theoretical reference activation energies \(E_a\) for forward and backward terrace self-diffusion processes. The values are given in eV. For the BEEF-vdW functional the calculated standard deviation of the activation energy \(E_a\) is given in parenthesis.

| Terrace   | Pathway                  | \(E_a^{\text{for}}\) | \(E_a^{\text{rev}}\) |
|-----------|--------------------------|------------------------|------------------------|
|           | This work | Other works | This work | Other works |
|           | PBE       | BEEF-vdW    | PBE       | BEEF-vdW    | PBE |
| Mg(0001)  | \text{fcc}_0 \leftrightarrow \text{hcp}_1 | 0.02 | 0.02 (0.02) | 0.02 \[^{[23,56,68]}\], 0.03 \[^{[62]}\] | 0.01 | 0.01 (0.01) | 0.02 \[^{[23,56,68]}\], 0.03 \[^{[62]}\] |
| Mg(0001)  | \text{hcp}_0 \leftrightarrow \text{hcp}_1 (\text{Ex.}) | 0.74 | 0.79 (0.23) | 0.79 \[^{[56]}\] | 0.72 | 0.77 (0.23) | 0.79 \[^{[56]}\] |
| Mg(1010)A | \text{ob}_0 \leftrightarrow \text{ob}_1 | 0.02 | 0.02 (0.04) | 0.02 \[^{[56]}\] | 0.02 | 0.02 (0.04) | 0.02 \[^{[56]}\] |
| Mg(1010)A | \text{ob}_0 \leftrightarrow \text{ob}_2 | 0.42 | 0.35 (0.15) | 0.45 \[^{[56]}\] | 0.42 | 0.35 (0.15) | 0.45 \[^{[56]}\] |
| Mg(1010)A | \text{ob}_0 \leftrightarrow \text{ob}_2 (\text{Ex.}) | 0.46 | 0.47 (0.14) | 0.56 \[^{[56]}\] | 0.46 | 0.47 (0.14) | 0.56 \[^{[56]}\] |
| Mg(1011)  | \text{h}_0 \leftrightarrow \text{h}_1 | 0.30 | 0.27 (0.06) | 0.29 \[^{[56]}\] | 0.30 | 0.27 (0.06) | 0.29 \[^{[56]}\] |
| Mg(1011)  | \text{h}_0 \leftrightarrow \text{h}_1 (\text{Ex.}) | 0.59 | 0.62 (0.16) | 0.57 \[^{[56]}\] | 0.59 | 0.62 (0.16) | 0.57 \[^{[56]}\] |
| Mg(1011)  | \text{h}_0 \leftrightarrow \text{h}_2 | 0.42 | 0.38 (0.08) | 0.41 \[^{[56]}\] | 0.42 | 0.38 (0.08) | 0.41 \[^{[56]}\] |
Figure 2. Schematic representation of terrace self-diffusion processes on Mg(0001), Mg(10\bar{1}0)A, and Mg(10\bar{1}1). Green-colored atoms mark the initial, while red-colored atoms mark the final positions.

Dimer and trimer self-diffusion on Mg(0001) and Mg(10\bar{1}1)

The formation of polyatomic clusters represents the first stage of island formation. Here the question arises if attractive or repulsive interactions between adatoms are at play, resulting in a uniform distribution of the adsorbates or the formation of dimer, trimer, or cluster structures. Our calculations reveal only negative or negligible (|E_{int}| < 0.03 eV) interaction energies between two Mg adsorbates and an interaction sequence given by $E_{int,Mg(0001)} > E_{int,Mg(10\bar{1}1)} > E_{int,Mg(10\bar{1}0)A}$, as shown in detail in Table VI, Table VII and Table VIII. The corresponding dimer sites are given in Figure 3. The differences in interaction energies may be related directly to the number of nearest surface atoms of the adsorbates following the opposite order ($3_{Mg(0001)} < 4_{Mg(10\bar{1}1)} < 5_{Mg(10\bar{1}0)A}$).

On Mg(0001), only two possible dimer conformations could be detected, which are both shown in Figure 4. If both atoms were initially placed in hcp or fcc positions, the relaxed dimer ends up with both atoms in the same bridge-like position $0 \leftrightarrow 1$ with an interaction energy of 0.51 eV. In the thermodynamically more stable dimer conformation $0 \leftrightarrow 6$ (0.54 eV), one atom is located in an fcc or hcp position above a surface atom, respectively. The dimer configurations $0 \leftrightarrow 4$ and $0 \leftrightarrow 7$ are not stable and end up in dimer configuration $0 \leftrightarrow 6$. Two conformations with noticeable interaction energies are also present on Mg(10\bar{1}1). In the thermodynamically more stable conformation, both adsorbates are in adjacent hollow positions ($0 \leftrightarrow 3$) and have an interaction energy of -0.31 eV. In the thermodynamic less stable conformation, one atom sits in a hollow- and the other in an fcc-like position ($0 \leftrightarrow 1$). Since the atom sitting in fcc position coordinates to only three surface atoms, the interaction to the second adsorbate is slightly higher (-0.35 eV). For the BEEF-vdW functional, the differences in interaction energies are less pronounced for the two dimer conformations on Mg(10\bar{1}1). At greater atom distances, the interaction energy drops for all investigated surfaces to negligible values. Nevertheless, the PBE functional values are consistent with the BEEF-vdW calculations and literature.$^{23,56}$
Table VI. Calculated (PBE/BEEF-vdW) and theoretical reference dimer interaction energies of two Mg adatoms adsorbed on (6×6) Mg(0001). All interaction energies are given in eV. For the BEEF-vdW functional, the calculated standard deviation of the dimer interaction energy $E_{\text{int}}$ is given in parenthesis.

| $E_{\text{int}}$ | This work | Other works |
|------------------|------------|-------------|
| Mg(0001)         |            |             |
| 0 ↔ 1            | -0.51      | -0.40 (0.13)| -0.50\textsuperscript{[22],[56]} |
| 0 ↔ 2            | -0.05      | -0.02 (0.12)|             |
| 0 ↔ 3            | -0.04      | 0.00 (0.09) |             |
| 0 ↔ 4*           | -0.54      | -0.43 (0.11)| -0.05\textsuperscript{[56]} |
| 0 ↔ 5            | -0.03      | 0.01 (0.13) |             |
| 0 ↔ 6            | -0.54      | -0.43 (0.11)| -0.50\textsuperscript{[22]} |
| 0 ↔ 7*           | -0.54      | -0.43 (0.11)|             |
| 0 ↔ 8            | -0.04      | -0.01 (0.08)|             |

*not stable; Transition into fcc-hcp configuration.

Table VII. Calculated (PBE/BEEF-vdW) and theoretical reference dimer interaction energies of two Mg adatoms adsorbed on (6×3) Mg(1010)A. All interaction energies are given in eV. For the BEEF-vdW functional, the calculated standard deviation of the dimer interaction energy $E_{\text{int}}$ is given in parenthesis.

| $E_{\text{int}}$ | This work | Other works |
|------------------|------------|-------------|
| Mg(1010)A        |            |             |
| 0 ↔ 1            | -0.28      | -0.25 (0.06)| -0.25\textsuperscript{[56]} |
| 0 ↔ 2            | -0.01      | -0.02 (0.01)|             |
| 0 ↔ 3            | 0.02       | 0.02 (0.02) |             |
| 0 ↔ 4            | 0.01       | 0.01 (0.01) |             |

Table VIII. Calculated (PBE/BEEF-vdW) and theoretical reference dimer interaction energies of two Mg adatoms adsorbed on (6×3) Mg(1011). All interaction energies are given in eV. For the BEEF-vdW functional, the calculated standard deviation of the dimer interaction energy $E_{\text{int}}$ is given in parenthesis.

| $E_{\text{int}}$ | This work | Other works |
|------------------|------------|-------------|
| Mg(1011)         |            |             |
| 0 ↔ 1            | -0.31      | -0.28 (0.05)| -0.31\textsuperscript{[56]} |
| 0 ↔ 2            | 0.01       | 0.01 (0.02) |             |
| 0 ↔ 3            | -0.01      | 0.00 (0.02) |             |
| 0 ↔ 4*           | -0.35      | -0.29 (0.07)|             |
| 0 ↔ 5            | -0.01      | -0.01 (0.02)|             |

*Since the adsorption site of atom 4 is not stable outside of the dimer configuration, the adsorption energy for this atom was assumed to be equivalent to an fcc position on Mg(0001) to calculate the interaction energy.
As the interaction energy studies (Figure 5, Table IX) have already shown, the diffusion barriers reveal that when two adsorbates meet on Mg(0001), they immediately agglomerate \[ D_{0/2} \rightarrow D_{1/3}, E_a^{for} = 0.00 \text{ eV} \]. We could not detect a barrier below a certain distance. On the contrary, the activation energies for its separation are multiple times higher \[ D_{1/3} \rightarrow D_{0/2}, E_a^{rev} = 0.49/0.46 \text{ eV} \], indicating that one dimer can already be considered a center for further island growth. Also noteworthy is that from the time of dimer formation, the propagation as a dimer on Mg(0001) is higher \[ CD_0 \leftrightarrow CD_1, E_a = 0.07 \text{ eV} \] than that of the monomer still, the dimer is highly mobile. The transition between the observed dimer configurations occurs almost barrierless \[ CD_0 \leftrightarrow CD_2, E_a = 0.01 \text{ eV} \].

On Mg(10\bar{1}1) (Figure 7, Table X), however, there are clearly distinguishable barriers for forward and reverse processes. In the case of two atoms approaching each other within a channel, the forward barrier is about half as large as the reverse barrier \[ d_0 \leftrightarrow d_1, E_a^{for} = 0.25 \text{ eV}, E_a^{rev} = 0.58 \text{ eV} \]. If dimer formation proceeds across the channel along the [10\bar{1}2]-direction, diffusion takes place in a two-step process, but with lower forward barriers in each case \[ d_2 \rightarrow d_3, E_a^{for} = 0.19 \text{ eV}; d_3 \rightarrow d_1, E_a^{for} = 0.15 \text{ eV} \], making this process very likely to occur. The process
across the channel opposite to the [10\(\overline{1}2\)]-direction exhibits both the highest forward and reverse barrier for all investigated dimer formation processes \([d_4 \leftrightarrow d_1, E_a^{for} = 0.37 \text{ eV}, E_a^{rev} = 0.67 \text{ eV}]\). Concerted movement of a dimer on Mg(10\(\overline{1}1\)) is again significantly increased compared to Mg(0001) \([cd_0 \leftrightarrow cd_1, E_a = 0.54 \text{ eV}]\), as already observed with terrace self-diffusion.

![Dimer Merge I](image1) ![Dimer Merge II](image2) ![Dimer Concerted](image3)

Figure 5. Schematic representation of dimer self-diffusion processes on Mg(0001). Green-colored atoms mark the initial, while red-colored atoms mark the final positions.

Table IX. Calculated (PBE) activation energies \(E_a\) for forward and backward dimer and trimer self-diffusion processes on Mg(0001). The values are given in eV.

| Mg(0001) | Path   | Pathway        | \(E_a^{for}\) | \(E_a^{rev}\) |
|----------|--------|----------------|---------------|---------------|
| Dimer    | Merge  | \(D_0 \leftrightarrow D_1\) | 0.00           | 0.49          |
|          |        | \(D_2 \leftrightarrow D_3\) | 0.00           | 0.46          |
|          | Concerted | \(CD_0 \leftrightarrow CD_1\) | 0.07           | 0.07          |
|          |        | \(CD_0 \leftrightarrow CD_2\) | 0.01           | 0.01          |
| Trimer   | Merge  | \(T_0 \leftrightarrow T_1\) | 0.00           | 0.64          |
|          | Concerted | \(CT_0 \leftrightarrow CT_1\) | 0.02           | 0.12          |
|          | Linear | \(TL_0 \leftrightarrow TL_2\) | 0.01           | 0.47          |
|          |        | \(TL_1 \leftrightarrow TL_2\) | 0.02           | 0.46          |
|          | Interchange | \(TL_0 \leftrightarrow TL_1\) | 0.06           | 0.17          |
|          |        | \(TL_0 \leftrightarrow TL_2\) | 0.07           | 0.20          |

If a third atom is approaching, a linear or a triangular trimer is formed, depending on the side of the attack. For Mg(0001), no or only extremely low barriers could be determined \([T_0 \rightarrow T_1, E_a^{for} = 0.00 \text{ eV}; TL_{0/1} \rightarrow TL_{2/3}, E_a^{for} = 0.01/0.02 \text{ eV}]\), as was already the case for the dimer formation. In turn, the linear form can transform itself into the thermodynamically more stable triangular trimer form. However, from a kinetic point of view, the barrier of the interchange to a hcp trimer is slightly lower \([TL_0 \rightarrow TL_1, E_a = 0.06 \text{ eV}]\) than that of the fcc counterpart \([TL_0 \rightarrow TL_2, E_a = 0.07 \text{ eV}]\).
$Tl_2, E_a = 0.07 \text{ eV}$]. Nevertheless, at a later stage, the $hcp$ trimer should clearly switch to the thermodynamically preferred $fcc$ position with a minor barrier [$CD_0 \leftrightarrow CD_1, E_a^{for} = 0.02 \text{ eV}, E_a^{rev} = 0.12 \text{ eV}$].

On the other hand, this contrasts with the $hcp$ packaging series of metallic Mg that should follow the ABABAB-stacking sequence. Two questions arise, first, why are $fcc$ sites favored over $hcp$ sites for smaller islands, and second, at what critical island size does the original packing order become thermodynamically more stable again. Therefore, for islands up to a size of 7 atoms and full monolayers (36 atoms) on (6×6) Mg(0001), the adsorption energies per atom were calculated as shown in SI Figure 5. Additionally, the exact adsorption energies per atom for the islands and for full $hcp$ and $fcc$ monolayers, as well as the stacking fault energies, may be found in SI Table VII. It turns out that starting from a heptamer adsorption is slightly favored on $hcp$ sites, while tetramers, pentamers, and hexamers are indifferent. This finding is consistent with the results of Ortigoza et al. The group confirmed stacking fault up to the trimer but also used only half of the unit cell size ((3×3) vs. (6×6)). They blame Friedel oscillations for inducing an increased charge density at the $fcc$ pocket, which noticeably stabilizes the bond of the adsorbate to its nearest neighbors. At the same time, however, the increased charge density at adjacent $fcc$ positions vanishes, which explains the renewed preference of the $hcp$ position for larger adislands.$^{[67]}$

On the second studied surface Mg(1011), the barriers for trimer formation are generally higher than on Mg(0001). In addition, the linear trimer form is thermodynamically more stable with respect to the triangular trimer form. If an atom encounters a dimer within a channel, the barriers are roughly equivalent to those of the dimer formation [$t_0 \leftrightarrow t_1, E_a^{for} = 0.26 \text{ eV}, E_a^{rev} = 0.58 \text{ eV}$]. Diffusion across the channel proceeds in a two-step process along [$t_2 \rightarrow t_3, E_a^{for} = 0.19 \text{ eV}; t_3 \rightarrow t_4, E_a^{for} = 0.27 \text{ eV}$] and opposite to the [1012]-direction [$t_4 \rightarrow t_5, E_a^{for} = 0.31 \text{ eV}; t_5 \rightarrow t_1, E_a^{for} = 0.24 \text{ eV}$] with the triangle trimer form as intermediate. The barriers are very similar for all investigated processes, making it difficult to draw accurate predictions about the preferred pathway of trimer formation. However, surface growth should most likely proceed in a line along the hollow sites perpendicular to the [1012]-direction. The use of kinetic Monte-Carlo simulations could provide further insights.$^{[69]}$
Figure 6. Schematic representation of trimer self-diffusion processes on Mg(0001). Green-colored atoms mark the initial, while red-colored atoms mark the final positions.

Table X. Calculated (PBE) activation energies $E_a$ for forward and backward dimer and trimer self-diffusion processes on Mg(1011). The values are given in eV.

| Mg(1011) | Path  | Pathway | $E_a^{for}$ | $E_a^{rev}$ |
|----------|-------|---------|-------------|-------------|
| Dimer    | Merge | $d_0 \leftrightarrow d_1$ | 0.25 | 0.58 |
|          |       | $d_2 \leftrightarrow d_3$ | 0.19 | 0.13 |
|          |       | $d_5 \leftrightarrow d_1$ | 0.15 | 0.51 |
|          |       | $d_4 \leftrightarrow d_1$ | 0.37 | 0.67 |
|          | Concerted | $cd_0 \leftrightarrow cd_1$ | 0.54 | 0.54 |
| Trimer   | Merge | $t_0 \leftrightarrow t_1$ | 0.26 | 0.58 |
|          |       | $t_2 \leftrightarrow t_3$ | 0.19 | 0.20 |
|          |       | $t_5 \leftrightarrow t_1$ | 0.27 | 0.54 |
|          |       | $t_4 \leftrightarrow t_5$ | 0.31 | 0.57 |
|          |       | $t_6 \leftrightarrow t_1$ | 0.24 | 0.28 |
Figure 7. Schematic representation of dimer and trimer self-diffusion processes on Mg(10\,\overline{1}1). Green-colored atoms mark the initial, while red-colored atoms mark the final positions.

**Step, kink and corner self-diffusion on Mg(0001) and Mg(10\,\overline{1}1)**

After the formation of initial polyatomic clusters, we would like to discuss further surface growth, especially island formation, by studying additional processes of the terrace-step-kink (TSK) model (step-edge, step-vacancy, kink, inner-corner, and outer-corner).\textsuperscript{[70]} The TSK model describes the diffusion processes taking place during surface growth and discusses several growth mechanisms.\textsuperscript{[71]} As described previously, islands on Mg(0001) are more stable on hcp sites starting from a heptamer. Thus, only processes at hcp steps, kinks, and corners were investigated, which consist of more than 7 atoms. A detailed overview of the processes studied may be found in Table XI, Figure 8, and Figure 10 for Mg(0001) and Table XII, and Figure 9 for Mg(10\,\overline{1}1).

**Table XI. Calculated (PBE) activation energies \(E_a\) for forward and backward step-edge, step-vacancy, kink and corner self-diffusion processes on Mg(0001). The values are given in eV.**

| Mg(0001)     | Path                  | Pathway | \(E_a^{\text{for}}\) | \(E_a^{\text{rev}}\) |
|--------------|-----------------------|---------|-----------------------|-----------------------|
|              | [1\,\overline{1}\,20]-step | S\(_0\leftrightarrow S_1\) | 0.03                 | 0.70                  |
| Step-edge    | [1\,\overline{1}\,20]-step | S\(_1\leftrightarrow S_2\) | 0.22                 | 0.22                  |
|              |                       | S\(_2\leftrightarrow S_3\) | 0.02                 | 0.63                  |
| Step-vacancy | [1\,\overline{1}\,20]-step | SV\(_0\leftrightarrow SV_1\) | 0.03                 | 1.15                  |
|              | [1\,\overline{1}\,20]-step | SV\(_2\leftrightarrow SV_3\) | 0.02                 | 1.23                  |
| Kink         | [1\,\overline{1}\,20]-step | K\(_0\leftrightarrow K_1\) | 0.45                 | 0.17                  |
|              |                       | K\(_0\leftrightarrow K_2\) | 0.91                 | 0.02                  |
|              |                       | K\(_0\leftrightarrow K_3\) | 0.51                 | 0.29                  |
|              | [1\,\overline{1}\,20]-step | K\(_4\leftrightarrow K_5\) | 0.46                 | 0.12                  |
|              |                       | K\(_4\leftrightarrow K_6\) | 0.92                 | 0.01                  |
|              |                       | K\(_4\leftrightarrow K_7\) | 0.56                 | 0.22                  |
| Inner-corner | 60° corner: [1\,\overline{1}\,20]-step | IC\(_0\leftrightarrow IC_1\) | 0.63                 | 0.10                  |
Initially, we want to discuss the process of a free atom approaching the step-edge on Mg(0001). As we have already seen with similar dimer and trimer processes, the forward barrier is negligibly small, but the detachment barrier is many times higher \([S_{0/3} \leftrightarrow S_{1/4}, E_a^{\text{for}} = 0.03/0.02 \text{ eV}, E_a^{\text{rev}} = 0.70/0.63 \text{ eV}]\). This observation becomes even more evident with a defect in the edge. Edge-vacancy formation has the highest barrier of all diffusion processes studied \([SV_{0/2} \leftrightarrow SV_{1/3}, E_a^{\text{rev}} = 1.15/1.23 \text{ eV}]\), indicating an extremely low probability of occurrence. It must be added that all \(fcc\) and \(hcp\) adsorption sites between the initial and the final state of the processes of approaching atoms are unstable and terminate in the initial state during relaxation. Once again, this underlines the high interaction energy on Mg(0001).

On Mg(10\(\bar{1}\)1), it is noticeable that an approaching atom has to overcome higher forward barriers of at least 0.14 up to 0.44 eV, depending on the direction of the step. However, this behavior is expected since the barriers for terrace self-diffusion on Mg(10\(\bar{1}\)1) are already at least 0.30 eV. The ratio between forward and reverse barriers is between 1–4 times, significantly lower than for Mg(0001) (25–40 times).

Step-edge diffusion on Mg(0001) along the [\(\bar{1}\)120] direction \([S_4 \leftrightarrow S_5, E_a = 0.15 \text{ eV}]\) is more probable compared to the [11\(\bar{2}\)0] direction \([S_4 \leftrightarrow S_5, E_a = 0.22 \text{ eV}]\). We explain the difference in energy by considering the structure of the respective transition state (TS). In the TS of the [\(\bar{1}\)120]-directed step, the nearest neighbor atom in the edge row pulls slightly back, leaving a pocket for the diffusing atom to settle in a stabilized \(fcc\)-like position (SI Figure 10). The step-edge diffusion barriers are in agreement with results from Ref. [23], assuming the growth of triangular islands with only \(<\bar{1}\)120>-directed steps due to the preferred diffusion along the [\(\bar{1}\)120] direction. Furthermore, the formation of fractal islands can almost be excluded since the step-edge barriers are easily overcome at room temperature (see section Activation temperature of diffusion processes on Mg(0001) and Mg(10\(\bar{1}\)1)). Fractal islands are formed when an adatom arrives at an edge, but relaxation to a more favorable position is hindered.\(^{[71]}\)

| Outer-corner | 60° corner: [1120]-step | 120° corner | 240° corner | 300° corner: [1120]-step | 300° corner: [1120]-step |
|--------------|-------------------------|-------------|-------------|-------------------------|-------------------------|
|              | \(IC_2 \leftrightarrow IC_3\) | \(IC_4 \leftrightarrow IC_5\) | \(OC_2 \leftrightarrow OC_1\) | \(OC_2 \leftrightarrow OC_3\) \(OC_5 \leftrightarrow OC_4\) | \(OC_6 \leftrightarrow OC_7\) \(OC_6 \leftrightarrow OC_8\) (Ex.) |
|              | 0.62                    | 0.43        | 0.29        | 0.24                    | 0.20                    |
|              |                         |             |             |                         |                         |
|              |                         |             |             |                         | 0.32                    |
|              |                         |             |             |                         |                         |
|              |                         |             |             |                         | 0.16                    |
|              |                         |             |             |                         |                         |

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Looking at the diffusion along the steps on Mg(10\(\overline{1}1\)), it is noticeable that depending on the directions, the barriers are very heterogeneous. On the one hand, there is barrierless diffusion along the \([\overline{1}2\overline{1}0]\)A-directed step \([s_7 \leftrightarrow s_8, E_a = 0.01 \text{ eV}]\), while diffusion along the \([\overline{1}2\overline{1}0]\)A- and \([\overline{1}2\overline{1}0]\)B-directed steps \([s_{1/4} \leftrightarrow s_{2/5}, E_a = 0.13/0.16 \text{ eV}]\) is of the same order of magnitude as for Mg(0001) along \([\overline{1}\overline{1}20]\), and finally, diffusion along \([\overline{1}2\overline{1}0]\)B and \([10\overline{1}2]\) \([s_{10/11} \leftrightarrow s_{13/14}, E_a = 0.40/0.45 \text{ eV}]\) is about 3 times higher compared to diffusion along the \([\overline{1}2\overline{1}0]\)A-directed step. The reason might be due to different coordinations of the diffusing atom in the initial/final sites (hollow vs. fcc-like sites).

![Figure 8. Schematic representation of step-edge and step-vacancy self-diffusion processes on Mg(0001). Green-colored atoms mark the initial, while red-colored atoms mark the final positions.](image)

| Table XII. Calculated (PBE) activation energies \(E_a\) for forward and backward step-edge self-diffusion processes on Mg(10\(\overline{1}1\)). The values are given in eV. |
|---|---|---|---|
| Mg(10\(\overline{1}1\)) | Path | Pathway | \(E_a^{\text{for}}\) | \(E_a^{\text{rev}}\) |
| \([\overline{1}2\overline{1}0]\)A-step | \([s_7 \leftrightarrow s_8]\) | 0.14 | 0.18 |
| \([\overline{1}2\overline{1}0]\)B-step | \([s_6 \leftrightarrow s_7]\) | 0.36 | 0.95 |
| \([\overline{1}0\overline{1}2]\)-step | \([s_{12} \leftrightarrow s_{13}\) | 0.45 | 0.45 |
Figure 9. Schematic representation of step-edge self-diffusion processes on Mg(10\{11\}). Green-colored atoms mark the initial, while red-colored atoms mark the final positions.

Looking at the 240°-outer-corner process \([OC_0 \leftrightarrow OC_1, E_{a}^{for} = 0.29 \text{ eV}, E_{a}^{rev} = 0.22 \text{ eV}]\), we notice a thermodynamically favored OC_0 site, strengthening the hypothesis of growth of triangular islands with only \(<\{11\overline{2}0\}>\)-steps on Mg(0001)\[^{[23]}\]. Alternatively, hexagonal islands with alternating \(<\{1\overline{1}20\}>\) and \(<\{1\overline{1}20\}>\)-steps would be possible at higher temperatures due to vibrational and configurational entropy effects, as assumed for fcc Al(111).\[^{[72]}\] The competing exchange process at the 240°-outer-corner has a higher activation energy and seems unfavorable \([OC_0 \leftrightarrow OC_1 (Ex.), E_{a}^{for} = 0.41 \text{ eV}, E_{a}^{rev} = 0.33 \text{ eV}]\). Equally of interest is the diffusion behavior at the \([1\overline{1}20]\)-directed 300°-corner consisting of three successive hopping steps. First, the adatom jumps from the edge to the tip of the corner \([OC_{2/4} \leftrightarrow OC_{3/5}, E_{a}^{for} = 0.24 \text{ eV}]\), switches sides in a symmetrical process \([OC_3 \leftrightarrow OC_4, E_a = 0.03 \text{ eV}]\) and finally moves barrierless to its final position \([OC_{2/4} \leftrightarrow OC_{3/5}, E_{a}^{rev} = 0.00 \text{ eV}]\). In contrast, at the \([\overline{1}\overline{1}20]\)-directed corner, the exchange process is kinetically preferred with the atom at the tip as exchange partner \([OC_6 \leftrightarrow OC_8 (Ex.), E_a = 0.16 \text{ eV}]\). When looking at the inner corner processes, it becomes clear that in both 60°- and 120°-processes, maximization of the binding partners is associated with lower barriers. In the 120°-processes, the number of binding partners increases from 2 to 3 \([IC_4 \leftrightarrow IC_{5/6}, E_{a}^{for} = 0.43 \text{ eV}, E_{a}^{rev} = 0.18/0.10 \text{ eV}]\), and in the 60°-processes
from 2 to 4 \( [IC_{0/2} \leftrightarrow IC_{1/3}, E_{af}^{\text{for}} = 0.63/0.62 \text{ eV}, E_{rf}^{\text{rev}} = 0.10/0.18 \text{ eV}] \), which is associated with forward/reverse barrier ratios of 2–4 and 6–8, respectively. For completion, the processes at the kink sites were studied. The barriers along the steps are similar to the respective 120°-corner processes \([K_{0/4} \leftrightarrow K_{1/5}, E_{af}^{\text{for}} = 0.45/0.46 \text{ eV}, E_{rf}^{\text{rev}} = 0.17/0.12 \text{ eV}]\). The barriers to leaving the kink position in the direction of the terrace also match the pattern \([K_{0/4} \leftrightarrow K_{2/6}, E_{af}^{\text{for}} = 0.91/0.92 \text{ eV}, E_{rf}^{\text{rev}} = 0.02/0.01 \text{ eV}]\). The barrier height is exactly between the step-edge and edge-vacancy activation energy, accompanied by breaking 2 and 4 bonds, respectively. In addition, the process of forming kink sites is favored over the formation of corners \([K_{0/4} \leftrightarrow K_{3/7}, E_{af}^{\text{for}} = 0.51/0.56 \text{ eV}, E_{rf}^{\text{rev}} = 0.29/0.22 \text{ eV}]\) indicating compact rather than fractal islands.

![Figure 10](https://example.com/f10.png)  
**Figure 10.** Schematic representation of kink, inner- and outer-corner self-diffusion processes on Mg(0001). Green-colored atoms mark the initial, while red-colored atoms mark the final positions.

**Ehrlich-Schwoebel-barrier and upper step self-diffusion on Mg(0001) and Mg(10\( \overline{1} \)1)**

So far, we have only considered 2-dimensional processes. However, to get a complete picture of surface growth, 3-dimensional processes such as upper-step diffusion followed by its descent are particularly important. The activation energies of the respective processes (step-down, step-down (dimer), upper-step) as well as the calculated Ehrlich–Schwoebel barriers for Mg(0001) and Mg(10\( \overline{1} \)1) are summarized in Table XIII and Table XIV. The schematic illustrations of the processes are given in Figure 11 and Figure 12.
Exactly as we have already seen for the terrace self-diffusion on Mg(0001), the upper-step diffusion onwards the step-edge occurs almost barrierless for both facets. Nevertheless, there are small differences from a kinetic and thermodynamic perspective. For example, on $[\bar{1}\bar{1}20]$-[US$_{\bar{4}/\bar{5}}$ ↔ US$_{\bar{5}/\bar{6}}$, $E^{\text{for}}_a = 0.00$ eV, $E^{\text{rev}}_a = 0.03/0.02$ eV] as opposed to $[\bar{1}\bar{1}20]$-steps [US$_0$ ↔ US$_1$, $E^{\text{for}}_a = 0.02$ eV, $E^{\text{rev}}_a = 0.01$ eV; US$_1$ ↔ US$_2$, $E^{\text{for}}_a = 0.01$ eV, $E^{\text{rev}}_a = 0.03$ eV], both forward barriers of the two step-process are lower than the reverse barriers. Moreover, from a thermodynamic point of view, the energy difference between the US$_2$ and US$_0$ sites is much smaller (7 meV) than between US$_6$ and US$_4$ sites (40 meV), indicating that diffusion occurs preferentially toward the [$\bar{1}\bar{1}20$]-directed step-edges, followed by the subsequent descent. Likewise, upper-step diffusion could only be studied along the step-edge at $[\bar{1}\bar{1}20]$-steps [US$_2$ ↔ US$_3$, $E_d = 0.02$ eV], while at $[\bar{1}\bar{1}20]$-steps [US$_6$ ↔ US$_7$] the diffusing atom immediately descends to the lower level (drops down to $E_2$ site). In general, the descent takes place via the exchange process $[E_{2/3} ↔ E_{1/3} \text{(Ex.)}, E^{\text{for}}_a = 0.01/0.02$ eV, $E^{\text{rev}}_a = 0.69/0.56$ eV]. In both cases, this has a significantly reduced barrier compared to the corresponding hopping processes $[E_{0/2} ↔ E_{1/3} \text{, } E^{\text{for}}_a = 0.09/0.16$ eV, $E^{\text{rev}}_a = 0.75/0.70$ eV]. In addition, the exchange processes show negative Ehrlich–Schwoebel barriers indicating a uniform and smooth growth due to a high rate of interlayer mass transport.$^{[71]}$ Likewise, the descent is clearly preferred to the ascent following the observed increase in coordination partners. All step-down barriers are in agreement with the literature.$^{[23,62]}$

Going one step further, we wanted to investigate the influence of a second adatom on the step-down barriers. It becomes immediately apparent that the barriers to descent for hopping $[ED_{0/2} ↔ ED_{1/3}, E^{\text{for}}_a = 0.58/0.67$ eV, $E^{\text{rev}}_a = 0.74/0.68$ eV] as well as exchange processes $[ED_{0/2} ↔ ED_{1/3} \text{ (Ex.)}, E^{\text{for}}_a = 0.21/0.11$ eV, $E^{\text{rev}}_a = 0.38/0.15$ eV] increase significantly. It can be assumed that the larger the cluster, the stronger the effect. For smooth surface growth, the adatom must reach the step-edge faster than it reaches another adatom. Thus, the higher the deposition rate, the more likely new islands aggregate on top of existing islands before the bottom layer is fully complete.$^{[71]}$ A further interesting case is the exchange process at the [$\bar{1}\bar{1}20$]-step. In this process, the barriers for ascent and descent are very close together. However, it is important to note that the second atom follows the diffusing atom into the fcc position above the exchange atom during descent. This arrangement maintains the dimer conformation until beyond the TS (SI Figure 11) and lowers the activation energy of the process to half of the corresponding exchange process at the $[11\bar{2}0]$-step.
Table XIII. Calculated (PBE) activation energies $E_a$ for forward and backward step-down, step-down (dimer) and upper-step self-diffusion processes on Mg(1011). The values are given in eV.

| Mg(0001) | Path | Pathway | $E_{a\text{for}}$ | $E_{a\text{rev}}$ | $E_{ES}$ |
|----------|------|---------|-------------------|-------------------|---------|
| Step-down | [1120]-step | $E_0 \leftrightarrow E_1$ | 0.09 | 0.75 | 0.07 |
| | | $E_0 \leftrightarrow E_1$ (Ex.) | 0.01 | 0.67 | -0.02 |
| | [1120]-step | $E_2 \leftrightarrow E_3$ | 0.16 | 0.70 | 0.14 |
| | | $E_2 \leftrightarrow E_3$ (Ex.) | 0.02 | 0.56 | -0.01 |
| Step-down (dimer) | [1120]-step | $E_{D0} \leftrightarrow E_{D1}$ | 0.58 | 0.74 | |
| | | $E_{D0} \leftrightarrow E_{D1}$ (Ex.) | 0.21 | 0.38 | |
| | [1120]-step | $E_{D2} \leftrightarrow E_{D3}$ | 0.67 | 0.68 | |
| | | $E_{D2} \leftrightarrow E_{D3}$ (Ex.) | 0.11 | 0.15 | |
| Upper-step | [1120]-step | $U_{S0} \leftrightarrow U_{S1}$ | 0.02 | 0.01 | |
| | | $U_{S1} \leftrightarrow U_{S2}$ | 0.01 | 0.03 | |
| | | $U_{S2} \leftrightarrow U_{S3}$ | 0.02 | 0.02 | |
| | [1120]-step | $U_{S4} \leftrightarrow U_{S5}$ | 0.00 | 0.03 | |
| | | $U_{S5} \leftrightarrow U_{S6}$ | 0.00 | 0.02 | |

Figure 11. Schematic representation of step-down, step-down (dimer) and upper-step self-diffusion processes on Mg(0001). Green-colored atoms mark the initial, while red-colored atoms mark the final positions.

On Mg(10\bar{1} 1), in almost all cases (except [1\bar{2} 10]A-step), the exchange process has the lowest barrier on the descent. The smallest step-down barrier is found at the [1\bar{2} 10]B-step [$e_8 \leftrightarrow e_9$}
(Ex.), $E_{\text{for}}^{0} = 0.07 \text{ eV}$], whereas the lowest ascent barrier is found at the \(1\bar{2}10\)A-step \(e_0 \leftrightarrow e_2\) (Ex.), $E_{\text{for}}^{0} = 0.34 \text{ eV}$. The most frequent descent route is likely to be along the \(10\bar{1}2\)-step \(e_{11} \leftrightarrow e_{12}\) (Ex.), $E_{\text{for}}^{0} = 0.20 \text{ eV}$. Here an adatom can diffuse within a channel to the edge, and subsequently descend via the exchange process.

Table XIV. Calculated (PBE) activation energies $E_a$ for forward and backward Step-down self-diffusion processes on Mg(1011). The values are given in eV.

| Mg(10\bar{1}1) | Path | Pathway | $E_{\text{for}}^{a}$ | $E_{\text{rev}}^{a}$ | $E_{\text{ES}}$ |
|-----------------|------|---------|---------------------|---------------------|---------------|
| Step-down       | [1210]A-step | $e_0 \leftrightarrow e_1$ | 0.44                | 0.67                | 0.14          |
|                 |       | $e_0 \leftrightarrow e_2$ (Ex.) | 0.11                | 0.34                | -0.19         |
|                 | [1210]B-step | $e_3 \leftrightarrow e_4$ (Ex.) | 0.26                | 0.58                | -0.04         |
|                 |       | $e_5 \leftrightarrow e_6$ (Ex.) | 0.29                | 0.53                | 0.17          |
|                 | [1210]A-step | $e_5 \leftrightarrow e_7$ (Ex.) | 0.47                | 0.96                | 0.14          |
|                 | [1210]B-step | $e_8 \leftrightarrow e_9$ (Ex.) | 0.44                | 0.59                | -0.23         |
|                 |       | $e_{11} \leftrightarrow e_{12}$ (Ex.) | 0.38                | 0.89                | 0.08          |

Figure 12. Schematic representation of ESB self-diffusion processes on Mg(1011). Green-colored atoms mark the initial, while red-colored atoms mark the final positions.
e. Activation temperature of diffusion processes on Mg(0001) and Mg(10\(\overline{1}1\))

In addition to the diffusion barriers, the pre-exponential factors of the Arrhenius equations were calculated via the Einstein approximation to determine the activation temperatures of the processes studied on Mg(0001) and Mg(10\(\overline{1}1\)). The obtained activation temperatures at which the respective diffusion processes start to contribute to surface growth are shown in Figure 13 and Figure 14.

On Mg(0001), processes such as terrace self-diffusion, the formation of dimers and trimers, and the step-down process do not have significant barriers and are already activated at temperatures below 25 K. It must be noted that dimer and trimer formation is highly favored compared to the respective separation processes due to a very high interaction energy. At this point, we would like to address the hypothesis that lower terrace self-diffusion and step-down barriers on Mg(0001) vs. Li(100) are responsible for reduced dendrite formation.\(^{[23]}\) We were able to confirm lower barriers for Mg(0001). However, the corresponding processes for metallic lithium become activated at 16 and 43 K, respectively.\(^{[24]}\) At room temperature, these processes should run almost equally and have no significant influence on dendrite formation. We believe that to adequately explain dendrite growth, a holistic and more exhaustive model needs to be developed that considers the influence of the SEI interface, the stability of different surface terminations, the diffusion barriers on the respective surfaces, the applied potential, the deposition conditions, and the electrolyte used. It remains an open question to what extent this is already possible with the current theoretical tools. However, the data presented in this work could serve as a reference for future studies where these additional effects are successively accounted for.

At a temperature below 100 K on Mg(0001), a variety of further diffusion processes become active such as dimer and trimer propagation, diffusion along an edge, the formation of 60° and 120° corners, switching sides at 240° and 300° corners and kink incorporation. Especially the activated corner-crossing barriers contribute to the growth of compact rather than fractal islands.\(^{[71]}\) Interestingly, both the dimer step-down and step-up processes become possible in this temperature range, contrary to uniform and smooth surface growth.

On Mg(10\(\overline{1}1\)), we found that the activation temperatures for diffusion processes are generally higher. Below 100 K, it is only possible for an adatom to step-down, form a dimer, or diffuse towards an edge. Terrace diffusion within and across a channel and diffusion along an edge on Mg(10\(\overline{1}1\)) becomes possible at elevated temperatures above 100 K.

In the same temperature range, processes in which the coordination number of the diffusing atom is reduced become available on Mg(0001), such as in the 120° corner and kink breaking processes. Above 200 K, the dimer and trimer separation processes, edge evaporation, and
60° corner separation are also enabled, as well as the step-up process. Despite that, the statement still applies that bond breakages are extremely unlikely for magnesium and that the increase of the coordination number always proceeds preferentially. For example, kink evaporation and the formation of a step-vacancy are not possible at room temperature for Mg(0001). Nevertheless, activated evaporation and separation processes are necessary for island ripening (redistribution of mass).[71] We assume many small islands form in the low-temperature range, and new adsorbates join existing ones. At higher temperatures, island ripening should begin, and smaller islands dissolve at the expense of larger islands.

On Mg(10\,\bar{1}\,1), all processes studied can occur at ambient conditions. In the temperature range between 200 and 300 K, dimer and trimer separation, edge evaporation, and the exchange step-up process are activated. In addition, concerted dimer propagation proceeds at about 200 K.

Figure 13. Activation temperatures of diffusion processes to impact surface growth on Mg(0001).
Figure 14. Activation temperatures of diffusion processes to impact surface growth on Mg(10\overline{1}1).

At this point, we would like to refer to the Supporting Information, which summarizes all calculated data. SI Table V and SI Table VI show the pre-exponential factors, activation energies, room-temperature rate constants, and activation temperatures for the terrace self-diffusion processes for the PBE and BEEF-vdW functionals, respectively. Corresponding schematic representations and energy profiles are provided in SI Figure 4. In addition, overviews of all investigated diffusion processes on Mg(0001) are available in SI Figure 6 and on Mg(10\overline{1}1) in SI Figure 8. The corresponding pre-exponential factors, activation energies, room temperature rate constants, activation temperatures, and energy profiles may be found in SI Table VIII, SI Figure 7, SI Table IX, and SI Figure 9.
4. CONCLUSION

This work aimed to determine and summarize the atomistic properties of magnesium and discuss the initial stages of surface growth in a possible magnesium-ion battery. Therefore, bulk, surface, adsorption, and diffusion properties of magnesium were calculated at the level of density functional theory. We are aware that in a real battery environment, the operation conditions, the potential, the electrolyte, charge- and discharge products, and especially the SEI environment might have a tremendous impact on the atomistic properties of magnesium. Nevertheless, we still believe that our studies already provide informative insights into the actual processes taking place.

First, the present calculations confirm the preference of magnesium to crystallize in a hcp crystalline structure at ambient conditions, with surface terminations Mg(0001), Mg(10\bar{1}0)A, and Mg(10\bar{1}1) being, in this order, most stable. Interestingly, the surface proportions in a nanocrystal are quite different. According to the Wulff construction, Mg(10\bar{1}1) has the largest share of the surface with a surface fraction of about 50%, while the remaining area is distributed evenly between Mg(0001) and Mg(10\bar{1}0)A, as shown in Figure 1. The Wulff construction clearly illustrates that diffusion properties must be discussed for all three surfaces collectively and cannot be limited to the thermodynamically most stable surface Mg(0001), as done in previous studies.

Furthermore, we found the highest adsorption energies for an Mg atom on the occurring surfaces for the hollow site on Mg(10\bar{1}1) and the ontop-bottom site on Mg(10\bar{1}0)A. Adsorption energies on Mg(0001) are about 40% lower, indicating primary adsorption to take place on Mg(10\bar{1}0)A and Mg(10\bar{1}1). Preferred adsorption on Mg(0001) occurs on the fcc site, which is valid for a trimer, too. Adsorption on hcp sites is energetically favored starting from heptamers. The reason for the stacking fault might be Friedel oscillations causing an increased charge density pocket at the fcc site for smaller magnesium clusters.\(^{[67]}\)

Terrace self-diffusion of single atoms runs almost barrier-free on Mg(0001) but with higher activation energies on Mg(10\bar{1}1). When adsorbates collide on the surfaces, initial dimer, trimer, and cluster structures are formed, which is highly favored due to high attractive interactions between the adsorbates. The small cluster structures can be seen as seeds for further island growth, which shape on Mg(0001) could be either triangular with only \(<\bar{1}20>\)-steps as proposed by Jäckle et al.\(^{[23]}\) or hexagonal with alternating \(<11\bar{2}0>\) and \(<\bar{1}20>\)-steps at elevated temperatures\(^{[72]}\). However, the island pattern should be compact rather than fractal due to low step-edge and corner crossing barriers.\(^{[71]}\) On Mg(10\bar{1}1), the diffusion barriers are in general higher compared to Mg(0001), but the ratios for bond formation and breakage are
closer together. All processes studied on Mg(10\bar{1}1) can occur at ambient conditions, while on Mg(0001) kink evaporation and the formation of a step-vacancy are not activated at room temperature. Surface growth on Mg(10\bar{1}1) could proceed in a line along the hollow sites perpendicular to the [10\bar{1}2]-direction.

The three-dimensional diffusion studies reveal negative Ehrlich–Schwoebel barriers for all investigated exchange descend processes on Mg(0001) and Mg(10\bar{1}1) (except [1\bar{2}10]A-step), indicating a uniform and smooth surface growth due to a high rate of interlayer mass transport at low deposition rates.\[71] However, a second adatom significantly increases the descent barriers for hopping and exchange processes, fostering the aggregation of new islands on top of existing islands if the adatom meets another adatom faster than it reaches the step-edge.

All generated data will be used in a future work as a training set for parameterizing the reactive force field ReaxFF. ReaxFF allows a more realistic investigation of the battery system by including the electrolyte, and at the same time, lowers the computational cost but with similar accuracy.\[27,28,73] Furthermore, the calculated rate constants may be used in kinetic Monte-Carlo simulations to investigate and visualize the kinetic effects of surface growth.\[69]

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SUPPORTING INFORMATION

First-principles studies on the atomistic properties of metallic magnesium as anode material in magnesium-based batteries

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SI Figure 1. Convergence studies of the cutoff energy (\textsuperscript{E}NCUT Tag) and grid density of the \textit{k}-points (\textsuperscript{\textalpha}KSPACING Tag).

SI Table I. Number of layers used for the calculation of surface energies.

| Surface       | Layers | Surface       | Layers |
|---------------|--------|---------------|--------|
| Mg(0001)      | 7      | Mg(1122)      | 24     |
| Mg(10\overline{1}0)\textit{A}/ Mg(10\overline{1}0)\textit{B} | 12     | Mg(1120)      | 20     |
| Mg(10\overline{1}1) | 14     | Mg(2131)      | 32     |
| Mg(10\overline{1}2)\textit{A}/ Mg(10\overline{1}2)\textit{B} | 18     | Mg(2241)      | 40     |
| Mg(21\overline{3}0)\textit{A}/ Mg(21\overline{3}0)\textit{B} | 30     | Mg(1121)      | 22     |
| Mg(2132)      | 32     | Mg(2021)      | 24     |
SI Table II. Surface directions, number of layers and supercell used for the calculation of adsorption, dimer interaction, diffusion, and frequency properties. One layer consists of 2 Mg atoms for Mg(0001). The asterisk * indicates the use of vicinal slabs.

| Surface | Property/Process | Direction | Layers | Supercell |
|---------|------------------|-----------|--------|-----------|
| Mg(0001) | Adsorption, Dimer interaction | [0001] | 3 | 6×6 |
| | Terrace, Dimer, Trimer | | | |
| | Kink, Inner-corner, Outer-corner ([1120]-step) | [1016]* | 20 | 6×1 |
| | Kink, Inner-corner, Outer-corner ([1120]-step) | [1016]* | 20 | 6×1 |
| | Step-edge, Step-vacancy, Step-down, Step-down (dimer), Upper-step ([1120]-step) | [1018]* | 26 | 4×1 |
| | Step-edge, Step-vacancy, Step-down, Step-down (dimer), Upper-step ([1120]-step) | [1018]* | 26 | 4×1 |
| Mg(1010) | Adsorption, Dimer interaction | [1010] | 6 | 6×3 |
| | Terrace | | | |
| Mg(1011) | Adsorption, Dimer interaction | [1011] | 6 | 6×3 |
| | Terrace, Dimer, Trimer | | | |
| | Step-edge, Step-down ([1210]A/B-step) | [3032]* | 18 | 5×1 |
| | Step-edge, Step-down ([1210]A/B-step) | [3034]* | 21 | 5×1 |
| | Step-edge, Step-down ([1012]-step) | [5165]* | 34 | 3×1 |

SI Table III. Calculated (PBE/BEEF-vdW) and literature physical constants of the hcp bulk phase of magnesium. The lattice constants $a_0$ and $c_0$ are given in Å, bulk moduli $B_0$ in GPa and the cohesive energy $E_{coh}$ in eV·atom$^{-1}$.

| Code | $a_0$ | $c_0$ | $B_0$ | $E_{coh}$ |
|------|-------|-------|-------|----------|
| This work | PBE | 3.18  | 5.21  | 36.5 | 1.50 | VASP |
| | BEEF-vdW | 3.19  | 5.21  | 37.1 | 1.33 | VASP |
| Other works | PBE | 3.19  | 5.18  | - | 1.51 | VASP |
| | PW91 [66] | 3.21  | 5.16  | 35.5 | 1.45 | Quantum Espresso |
| | PW91 [75] | 3.20  | 5.20  | - | 1.50 | VASP |
| | PW91 [58] | 3.19  | 5.14  | 35.5 | 1.50 | fhi98md |
| | PBE | 3.19  | 5.18  | - | - | VASP |
| | LDA | 3.12  | 5.08  | - | - | VASP |
| | PBE | 3.19  | 5.22  | - | - | VASP |
| | PW91 | 3.19  | 5.20  | - | - | VASP |
| | PBE | 3.19  | 5.18  | - | - | VASP |
| | Experiment [54] | 3.21  | 5.21  | 35.6 | 1.51 | |
SI Figure 2. Representation of the surface terminations A and B of surface Mg(10\bar{1}0). The respective structures are shown in a side- and a bird’s eye-view.

SI Table IV. Calculated (PBE/BEEF-vdW) and literature surface energies \( \gamma \) for low- and high-index surfaces of magnesium. The surface energy \( \gamma \) is given in meVÅ\(^{-2}\). For the BEEF-vdW functional the calculated standard deviation of the surface energy is given in parenthesis.

| \( \gamma \)          | This work | Other works |
|-----------------------|-----------|-------------|
|                       | PBE       | BEEF-vdW    | PBE | PBEsol | EAM | Experiment |
| Mg(0001)              | 33.9      | 38.7 (9)    | 34.6\(^{[56]}\), 32.9\(^{[23]}\), 32.5\(^{[74]}\), 33.0\(^{[68]}\), 31.8\(^{[67]}\) | 39.0\(^{[56]}\), 35.0\(^{[88]}\) | 31.0\(^{[60]}\) | 51.0\(^{[61]}\) |
| Mg(10\bar{1}0)A       | 40.2      | 44.9 (9)    | 39.9\(^{[56]}\), 40.1\(^{[88]}\), 37.4\(^{[57]}\) | 45.9\(^{[60]}\), 51.2\(^{[88]}\) | 31.1\(^{[60]}\) |
| Mg(1011)              | 40.9      | 45.8 (8)    | 40.9\(^{[56]}\), 46.4\(^{[58]}\), 39.3\(^{[57]}\) | 45.9\(^{[60]}\), 51.2\(^{[88]}\) | 31.1\(^{[60]}\) |
| Mg(1012)A             | 44.9      | 49.6 (10)   | 38.4\(^{[58]}\), 43.7\(^{[57]}\) | 45.9\(^{[60]}\), 51.2\(^{[88]}\) | 31.1\(^{[60]}\) |
| Mg(2130)A             | 45.9      | 50.6 (10)   | 46.6\(^{[58]}\), 43.7\(^{[57]}\) | 45.9\(^{[60]}\), 51.2\(^{[88]}\) | 31.1\(^{[60]}\) |
| Mg(1012)B             | 46.1      | 50.9 (10)   | | | |
| Mg(2132)              | 46.7      | 51.3 (10)   | 46.2\(^{[57]}\) | | |
| Mg(1122)              | 46.8      | 51.3 (10)   | 48.4\(^{[88]}\), 46.2\(^{[57]}\) | | |
| Mg(1120)              | 47.1      | 51.7 (10)   | 45.7\(^{[56]}\), 44.9\(^{[57]}\), 51.4\(^{[59]}\), 34.3\(^{[68]}\) | | |
| Mg(2131)              | 47.1      | 51.7 (10)   | 45.6\(^{[57]}\) | | |
| Mg(2241)              | 47.9      | 52.5 (10)   | 46.8\(^{[57]}\) | | |
| Mg(1121)              | 48.7      | 53.0 (10)   | 48.1\(^{[56]}\), 47.7\(^{[58]}\), 47.4\(^{[57]}\) | | |
| Mg(2021)              | 48.8      | 53.4 (10)   | 48.1\(^{[57]}\) | | |
| Mg(2130)B             | 52.0      | 56.3 (11)   | | 56.1\(^{[59]}\) | | |
| Mg(1010)B             | 55.5      | 59.4 (11)   | 53.7\(^{[74]}\), 60.6\(^{[60]}\), 38.5\(^{[68]}\) | | |
SI Figure 3. Schematic representation of the adsorption sites on Mg(0001), on the two surface terminations A and B of Mg(10\overline{1}0) and on Mg(10\overline{1}1).
SI Table V. Pre-exponential factors $\nu$, activation energies $E_a$, rate constants $k_{\text{RT}}$, and activation temperatures $T_a$ for forward and backward terrace self-diffusion processes from PBE calculations. The values are given in $10^{12}$ Hertz, eV, Hz, and K, respectively.

| Terrace   | Pathway          | $\nu^{\text{for}}$ | $E_a^{\text{for}}$ | $k_{\text{RT}}^{\text{for}}$ | $T_a^{\text{for}}$ | $\nu^{\text{rev}}$ | $E_a^{\text{rev}}$ | $k_{\text{RT}}^{\text{rev}}$ | $T_a^{\text{rev}}$ |
|-----------|------------------|---------------------|---------------------|--------------------------|-----------------|------------------|---------------------|--------------------------|-----------------|
| Mg(0001)  | fcc$\leftrightarrow$hcp$_1$ | 0.6                 | 0.02                | 2.7E+11                | 9               | 1.3             | 0.01                | 1.0E+12                | 2               |
| Mg(0001)  | fcc$\leftrightarrow$hcp$_2$ (Ex.) | 3.0                 | 0.74                | 6.0E-01                | 298             | 4.1             | 0.72                | 1.6E+00                | 289             |
| Mg(1010)  | ob$_0$$\leftrightarrow$ob$_1$ | 1.2                 | 0.02                | 4.6E+11                | 10              | 1.2             | 0.02                | 4.6E+11                | 10              |
| Mg(1010)  | ob$_0$$\leftrightarrow$ob$_2$ | 1.2                 | 0.42                | 6.8E+04                | 176             | 1.2             | 0.42                | 6.8E+04                | 176             |
| Mg(1010)  | ob$_0$$\leftrightarrow$ob$_2$ (Ex.) | 0.7                 | 0.46                | 7.3E+03                | 198             | 0.7             | 0.46                | 7.3E+03                | 198             |
| Mg(1011)  | h$_0$$\leftrightarrow$h$_1$ | 7.2                 | 0.30                | 5.2E+07                | 117             | 7.2             | 0.30                | 5.2E+07                | 117             |
| Mg(1011)  | h$_0$$\leftrightarrow$h$_1$ (Ex.) | 4.7                 | 0.59                | 3.0E+02                | 236             | 4.7             | 0.59                | 3.0E+02                | 236             |
| Mg(1011)  | h$_0$$\leftrightarrow$h$_2$ | 4.5                 | 0.42                | 2.5E+05                | 168             | 7.8             | 0.42                | 4.3E+05                | 165             |

SI Table VI. Pre-exponential factors $\nu$, activation energies $E_a$, rate constants $k_{\text{RT}}$, and activation temperatures $T_a$ for forward and backward terrace self-diffusion processes from BEEF-vdW calculations. The values are given in $10^{12}$ Hertz, eV, Hz, and K, respectively.

| Terrace   | Pathway          | $\nu^{\text{for}}$ | $E_a^{\text{for}}$ | $k_{\text{RT}}^{\text{for}}$ | $T_a^{\text{for}}$ | $\nu^{\text{rev}}$ | $E_a^{\text{rev}}$ | $k_{\text{RT}}^{\text{rev}}$ | $T_a^{\text{rev}}$ |
|-----------|------------------|---------------------|---------------------|--------------------------|-----------------|------------------|---------------------|--------------------------|-----------------|
| Mg(0001)  | fcc$\leftrightarrow$hcp$_1$ | 3.5                 | 0.02 (0.02)         | 1.5E+12                | 8               | 3.4             | 0.01 (0.01)        | 2.6E+12                | 4               |
| Mg(0001)  | fcc$\leftrightarrow$hcp$_2$ (Ex.) | 5.8                 | 0.79 (0.23)         | 1.7E-01                | 312             | 9.6             | 0.77 (0.23)        | 5.3E-01                | 299             |
| Mg(1010)  | ob$_0$$\leftrightarrow$ob$_1$ | 8.1                 | 0.02 (0.04)         | 3.8E+12                | 8               | 8.1             | 0.02 (0.04)        | 3.8E+12                | 8               |
| Mg(1010)  | ob$_0$$\leftrightarrow$ob$_2$ | 6.2                 | 0.35 (0.15)         | 6.7E+06                | 138             | 6.2             | 0.35 (0.15)        | 6.7E+06                | 138             |
| Mg(1010)  | ob$_0$$\leftrightarrow$ob$_2$ (Ex.) | 4.8                 | 0.47 (0.14)         | 3.7E+04                | 187             | 4.8             | 0.47 (0.14)        | 3.7E+04                | 187             |
| Mg(1011)  | h$_0$$\leftrightarrow$h$_1$ | 5.8                 | 0.27 (0.06)         | 1.2E+08                | 107             | 5.8             | 0.27 (0.06)        | 1.2E+08                | 107             |
| Mg(1011)  | h$_0$$\leftrightarrow$h$_1$ (Ex.) | 1.7                 | 0.62 (0.16)         | 3.4E+01                | 255             | 1.7             | 0.62 (0.16)        | 3.4E+01                | 255             |
| Mg(1011)  | h$_0$$\leftrightarrow$h$_2$ | 5.4                 | 0.38 (0.08)         | 1.8E+06                | 150             | 4.7             | 0.38 (0.08)        | 1.6E+06                | 151             |
SI Figure 4. Schematic representation, energy profile and PBE activation energies $E_a$ of terrace self-diffusion processes on Mg(0001), Mg(1010), and Mg(1011). Green-colored atoms mark the initial, while red-colored atoms mark the final positions. The values are given in eV.
SI Figure 5. Adsorption energies per atom for islands of different sizes adsorbed in fcc and hcp positions on 6x6 Mg(0001). From a heptamer onwards, islands in hcp positions are more stable. Trimers, pentamers, and hexamers may form different conformations, with the most thermodynamically stable conformation used for the plot. 36 atoms correspond to a full monolayer.

SI Table VII. Adsorption energies per atoms for islands of different sizes absorbed in fcc and hcp positions on 6x6 Mg(0001). The last column shows the stacking fault energy $\Delta E_{ad} = E_{ad, fcc} - E_{ad, hcp}$. Units are given in eV·atom$^{-1}$.

| Island size | $E_{ad}$ per atom | $E_{ad}$ per atom | $\Delta E_{ad}$ |
|-------------|-------------------|-------------------|-----------------|
| 1           | -0.58             | -0.56             | -0.02           |
| 2           | -0.83*            | -0.84**           | 0.01            |
| 3           | -0.96, -0.93      | -0.95, -0.93      | 0.01            |
| 4           | -1.05             | -1.05             | 0.00            |
| 5           | -1.09, -1.07      | -1.09, -1.07      | 0.00            |
| 6           | -1.12, -1.10, -1.08 | -1.12, -1.10, -1.09 | 0.00           |
| 7           | -1.15             | -1.16             | 0.01            |
| 36 (Full monolayer) | -1.48          | -1.49             | 0.01            |

* Both adsorbates are in bridge-like positions as shown in Figure 4a.

** Adsorbates are in a fcc and a hcp position, respectively as shown in Figure 4b.
SI Table VIII. Pre-exponential factors $\nu$, activation energies $E_a$, rate constants $k_{@RT}$, and activation temperatures $T_a$ for forward and backward various self-diffusion processes from PBE calculations on Mg(0001). The values are given in $10^{12}$ Hz, eV, Hz, and K respectively.

| System | Pathway | Path | $\nu$ | $E_a$ | $k_{@RT}$ | $T_a$ | $\nu$ | $E_a$ | $k_{@RT}$ | $T_a$ |
|--------|---------|------|------|------|-----------|------|------|------|-----------|------|
| Dimer  | Merge   | $D_0 \leftrightarrow D_1$ | -    | 0.00 | -         | 0    | -    | 0.49 | -         | 194  |
|        |         | $D_2 \leftrightarrow D_3$ | -    | 0.00 | -         | 2    | -    | 0.46 | -         | 183  |
|        | Concerted | $CD_1 \leftrightarrow CD_1$ | 0.7  | 0.07 | 1.3E+11   | 30   | 2.2  | 0.07 | 4.1E+10   | 29   |
|        |         | $CD_1 \leftrightarrow CD_2$ | 0.4  | 0.01 | 5.4E+11   | 6    | 0.9  | 0.01 | 2.2E+11   | 5    |
|        | Merge   | $T_0 \leftrightarrow T_1$ | -    | 0.00 | -         | 1    | -    | 0.64 | -         | 254  |
|        | Concerted | $CT_0 \leftrightarrow CT_1$ | 9.2  | 0.02 | 3.8E+10   | 7    | 3.8  | 0.12 | 4.5E+12   | 46   |
| Trimer | Linear  | $TL_0 \leftrightarrow TL_2$ | 2.3  | 0.01 | 1.1E+05   | 6    | 10.4 | 0.47 | 1.3E+12   | 180  |
|        |         | $TL_1 \leftrightarrow TL_2$ | 1.5  | 0.02 | 3.3E+04   | 7    | 2.3  | 0.46 | 7.3E+11   | 186  |
|        |         | $TL_3 \leftrightarrow TL_5$ | 1.5  | 0.00 | 5.3E+03   | 1    | 0.6  | 0.47 | 1.3E+12   | 201  |
|        |         | $TL_4 \leftrightarrow TL_5$ | 1.2  | 0.01 | 6.9E+03   | 3    | 0.6  | 0.46 | 9.1E+11   | 198  |
|        |         | $TL_5 \leftrightarrow TL_8$ | 0.7  | 0.01 | 1.8E+04   | 3    | 4.3  | 0.49 | 5.8E+11   | 194  |
|        | Interchange | $Tb \leftrightarrow Tb_1$ | 2.6  | 0.06 | 5.2E+10   | 24   | 24   | 0.17 | 2.5E+11   | 62   |
|        |         | $Tb_2 \leftrightarrow Tb_1$ | 0.4  | 0.07 | 1.3E+09   | 30   | 3.8  | 0.20 | 2.3E+10   | 81   |
| Step-edge | Step-vacancy | $SV_0 \leftrightarrow SV_1$ | 0.6  | 0.03 | 2.8E-07   | 12   | 19.4 | 1.15 | 2.0E+11   | 438  |
|        | [1120]-step | $SV_2 \leftrightarrow SV_3$ | 0.4  | 0.02 | 3.9E-08   | 10   | 54.1 | 1.23 | 1.7E+11   | 451  |
| Step-edge | Step-vacancy | [1120]-step | $SV_2 \leftrightarrow SV_3$ | 0.4  | 0.02 | 3.9E-08   | 10   | 54.1 | 1.23 | 1.7E+11   | 451  |
| Kink   | [1120]-step | $K_3 \leftrightarrow K_1$ | 9.4  | 0.45 | 1.8E+05   | 178  | 2.8  | 0.17 | 2.9E+09   | 70   |
|        |         | $K_0 \leftrightarrow K_2$ | 21.4 | 0.91 | 4.1E-03   | 346  | 1.5  | 0.02 | 7.4E+11   | 7    |
|        |         | $K_0 \leftrightarrow K_3$ | 4.9  | 0.51 | 8.7E+03   | 202  | 3.4  | 0.29 | 3.5E+07   | 117  |
|        | [1120]-step | $K_4 \leftrightarrow K_5$ | 8.3  | 0.46 | 8.7E+04   | 181  | 3.0  | 0.12 | 2.8E+10   | 48   |
|        |         | $K_4 \leftrightarrow K_6$ | 17.9 | 0.92 | 2.6E-03   | 350  | 0.4  | 0.01 | 3.2E+11   | 3    |
|        |         | $K_4 \leftrightarrow K_7$ | 5.4  | 0.56 | 1.1E+03   | 223  | 2.2  | 0.22 | 3.1E+08   | 92   |
| Inner-corner | 60° corner: [1120]-step | $IC_0 \leftrightarrow IC_1$ | 11.2 | 0.63 | 1.5E+02   | 244  | 4.7  | 0.10 | 9.7E+10   | 39   |
|        |         | $IC_2 \leftrightarrow IC_3$ | 13.9 | 0.62 | 3.4E+02   | 237  | 4.1  | 0.08 | 2.0E+11   | 30   |
|        | 120° corner | $IC_4 \leftrightarrow IC_5$ | 6.8  | 0.43 | 3.1E+05   | 168  | 5.2  | 0.18 | 3.8E+09   | 72   |
|        |         | $IC_4 \leftrightarrow IC_6$ | 5.6  | 0.43 | 2.1E+05   | 171  | 2.4  | 0.10 | 4.1E+10   | 42   |
| Outer-corner | 240° corner | $OC_0 \leftrightarrow OC_1$ | 0.7  | 0.29 | 1.2E+08   | 125  | 2.6  | 0.22 | 1.5E+12   | 88   |
|        |         | $OC_0 \leftrightarrow OC_1$ (Ex.) | 8.6  | 0.41 | 9.3E+05   | 158  | 9.1  | 0.33 | 2.1E+07   | 128  |
|        | 300° corner: [1120]-step | $OC_2 \leftrightarrow OC_3$ | 1.0  | 0.24 | 9.5E+07   | 99   | 4.0  | 0.00 | 3.5E+12   | 1    |
|        |         | $OC_2 \leftrightarrow OC_4$ | 1.3  | 0.03 | 3.4E+11   | 14   | 1.6  | 0.03 | 4.2E+11   | 14   |
|        |         | $OC_2 \leftrightarrow OC_5$ (Ex.) | 8.0  | 0.32 | 3.1E+07   | 123  | 7.8  | 0.32 | 3.0E+07   | 123  |
| 300° corner: [1120]-step | OC₁ ↔ OC₂ | 0.2 | 0.20 | 7.2E+07 | 89 | 2.0 | 0.03 | 7.4E+11 | 10 |
| OC₂ ↔ OC₃ | 1.5 | 0.16 | 2.7E+09 | 66 | 2.2 | 0.16 | 4.0E+09 | 65 |
| (Ex.) | | | | | | | | | |
| Step-down | [1120]-step | E₀ ↔ E₁ | 2.0 | 0.09 | 1.5E+00 | 38 | 13.6 | 0.75 | 5.2E+10 | 289 |
| E₂ ↔ E₁ (Ex.) | 2.4 | 0.01 | 7.0E+01 | 2 | 21.5 | 0.67 | 1.9E+12 | 253 |
| [1120]-step | E₂ ↔ E₃ | 0.8 | 0.16 | 7.5E+00 | 67 | 8.5 | 0.70 | 1.6E+09 | 273 |
| E₃ ↔ E₃ (Ex.) | - | 0.02 | - | 6 | - | 0.56 | - | 222 |
| Step-down (dimer) | [1120]-step | ED₀ ↔ ED₁ | 6.9 | 0.58 | 2.1E+00 | 226 | 10.1 | 0.74 | 8.9E+02 | 286 |
| ED₀ ↔ ED₁ (Ex.) | 4.4 | 0.21 | 2.7E+06 | 85 | 7.6 | 0.38 | 9.9E+06 | 147 |
| [1120]-step | ED₂ ↔ ED₃ | 15.1 | 0.67 | 4.7E+00 | 256 | 2.6 | 0.68 | 4.6E+01 | 277 |
| ED₂ ↔ ED₃ (Ex.) | 3.0 | 0.11 | 8.2E+09 | 44 | 3.2 | 0.15 | 4.1E+10 | 61 |
| Upper-step | [1120]-step | US₀ ↔ US₁ | 1.7 | 0.02 | 3.1E+11 | 6 | 1.7 | 0.01 | 1.2E+12 | 2 |
| US₁ ↔ US₂ | 1.7 | 0.01 | 1.2E+12 | 4 | 0.8 | 0.03 | 3.1E+11 | 11 |
| US₂ ↔ US₃ | 0.9 | 0.02 | 4.9E+11 | 6 | 1.3 | 0.02 | 7.2E+11 | 6 |
| [1120]-step | US₄ ↔ US₅ | 0.8 | 0.00 | 2.9E+11 | 1 | 2.9 | 0.03 | 2.1E+12 | 12 |
| US₅ ↔ US₆ | 2.2 | 0.00 | 2.1E+12 | 0 | 0.6 | 0.02 | 2.9E+11 | 7 |
SI Figure 6. Schematic representation of all investigated diffusion pathways on Mg(0001).
Dimer: Merge 1

Pathway $E_\text{for}$ $E_\text{rev}$
$D_0 \leftrightarrow D_1$ 0.00 0.49

Dimer: Merge 2

Pathway $E_\text{for}$ $E_\text{rev}$
$D_2 \leftrightarrow D_3$ 0.00 0.46

Dimer: Concerted

Pathway $E_\text{for}$ $E_\text{rev}$
$CD_0 \leftrightarrow CD_1$ 0.07 0.07
$CD_0 \leftrightarrow CD_2$ 0.01 0.01

Trimer: Merge

Pathway $E_\text{for}$ $E_\text{rev}$
$T_0 \leftrightarrow T_1$ 0.00 0.64
Trimer: Concerted

Pathway $E^{for}_{a}$ $E^{rev}_{a}$

$CT_0 \leftrightarrow CT_1$ 0.02 0.12

Trimer: Linear 1

Pathway $E^{for}_{a}$ $E^{rev}_{a}$

$TL_0 \leftrightarrow TL_2$ 0.01 0.47

$TL_1 \leftrightarrow TL_2$ 0.02 0.46

Trimer: Linear 2

Pathway $E^{for}_{a}$ $E^{rev}_{a}$

$TL_3 \leftrightarrow TL_5$ 0.00 0.47

$TL_4 \leftrightarrow TL_5$ 0.01 0.46

Trimer: Linear 3

Pathway $E^{for}_{a}$ $E^{rev}_{a}$

$TL_6 \leftrightarrow TL_8$ 0.01 0.49

$TL_7 \leftrightarrow TL_8$ 0.02 0.49
Trimer: Interchange 1

Pathway | $E_{\text{for}}$ | $E_{\text{rev}}$
--- | --- | ---
$T_0 \leftrightarrow T_1$ | 0.06 | 0.17

Trimer: Interchange 2

Pathway | $E_{\text{for}}$ | $E_{\text{rev}}$
--- | --- | ---
$T_0 \leftrightarrow T_2$ | 0.07 | 0.20
Step-edge: [11\bar{2}]\text{-}step

Pathway \quad \begin{array}{|c|c|}
\hline
\text{Pathway} & E_{\text{i}} & E_{\text{f}} \\
\hline
S_0 \leftrightarrow S_1 & 0.03 & 0.70 \\
S_1 \leftrightarrow S_2 & 0.22 & 0.22 \\
\hline
\end{array}

Step-edge: [\bar{1}1\bar{2}]\text{-}step

Pathway \quad \begin{array}{|c|c|}
\hline
\text{Pathway} & E_{\text{i}} & E_{\text{f}} \\
\hline
S_3 \leftrightarrow S_4 & 0.02 & 0.63 \\
S_4 \leftrightarrow S_5 & 0.15 & 0.15 \\
\hline
\end{array}

Step-vacancy: [11\bar{2}]\text{-}step

Pathway \quad \begin{array}{|c|c|}
\hline
\text{Pathway} & E_{\text{i}} & E_{\text{f}} \\
\hline
SV_0 \leftrightarrow SV_1 & 0.03 & 1.15 \\
\hline
\end{array}

Step-vacancy: [\bar{1}1\bar{2}]\text{-}step

Pathway \quad \begin{array}{|c|c|}
\hline
\text{Pathway} & E_{\text{i}} & E_{\text{f}} \\
\hline
SV_2 \leftrightarrow SV_3 & 0.02 & 1.23 \\
\hline
\end{array}
Kink: [11\bar{2}0]-step

Pathway \( E_{\text{FOR}} \) \( E_{\text{REV}} \)
\( K_0 \leftrightarrow K_1 \) 0.45 0.17
\( K_0 \leftrightarrow K_2 \) 0.91 0.02
\( K_0 \leftrightarrow K_3 \) 0.51 0.29

Kink: [\bar{1}1\bar{2}0]-step

Pathway \( E_{\text{FOR}} \) \( E_{\text{REV}} \)
\( K_4 \leftrightarrow K_5 \) 0.46 0.12
\( K_4 \leftrightarrow K_6 \) 0.92 0.01
\( K_4 \leftrightarrow K_7 \) 0.56 0.22

Inner-corner: 60° corner: [11\bar{2}0]-step

Pathway \( E_{\text{FOR}} \) \( E_{\text{REV}} \)
\( I_{C_0} \leftrightarrow I_{C_1} \) 0.63 0.10

Inner-corner: 60° corner: [\bar{1}1\bar{2}0]-step

Pathway \( E_{\text{FOR}} \) \( E_{\text{REV}} \)
\( I_{C_2} \leftrightarrow I_{C_3} \) 0.62 0.08
**Inner-corner: 120° corner**

Pathway \( E_{\text{for}} \) \( E_{\text{rev}} \)

\( IC_4 \leftrightarrow IC_5 \) 0.43 0.18

\( IC_4 \leftrightarrow IC_6 \) 0.43 0.10

**Outer-corner: 240° corner**

Pathway \( E_{\text{for}} \) \( E_{\text{rev}} \)

\( OC_0 \leftrightarrow OC_1 \) 0.29 0.22

\( OC_0 \leftrightarrow OC_1 \text{ (Ex.)} \) 0.41 0.33

**Outer-corner: 300° corner: [1120]-step**

Pathway \( E_{\text{for}} \) \( E_{\text{rev}} \)

\( OC_2 \leftrightarrow OC_3 \) 0.24 0.00

\( OC_3 \leftrightarrow OC_4 \) 0.03 0.03

\( OC_3 \leftrightarrow OC_4 \text{ (Ex.)} \) 0.32 0.32

**Outer-corner: 300° corner: [\bar{1}120]-step**

Pathway \( E_{\text{for}} \) \( E_{\text{rev}} \)

\( OC_6 \leftrightarrow OC_7 \) 0.20 0.03

\( OC_6 \leftrightarrow OC_7 \text{ (Ex.)} \) 0.16 0.16
Step-down: [1120]-step

Pathway $E_{a}^{\text{for}}$ $E_{a}^{\text{rev}}$
$E_{0} \leftrightarrow E_{1}$ 0.09 0.75
$E_{0} \leftrightarrow E_{1} \text{(Ex.)}$ 0.01 0.67

Step-down: [1120]-step

Pathway $E_{a}^{\text{for}}$ $E_{a}^{\text{rev}}$
$E_{2} \leftrightarrow E_{3}$ 0.16 0.70
$E_{2} \leftrightarrow E_{3} \text{(Ex.)}$ 0.02 0.56

Step-down (dimer): [1120]-step

Pathway $E_{a}^{\text{for}}$ $E_{a}^{\text{rev}}$
$ED_{0} \leftrightarrow ED_{1}$ 0.58 0.74
$ED_{0} \leftrightarrow ED_{1} \text{(Ex.)}$ 0.21 0.38

Step-down (dimer): [1120]-step

Pathway $E_{a}^{\text{for}}$ $E_{a}^{\text{rev}}$
$ED_{2} \leftrightarrow ED_{3}$ 0.67 0.68
$ED_{2} \leftrightarrow ED_{3} \text{(Ex.)}$ 0.11 0.15
SI Figure 7. Schematic representation, energy profile and PBE activation energies $E_a$ of self-diffusion processes studied on Mg(0001). Green-colored atoms mark the initial, while red-colored atoms mark the final positions. The values are given in eV.
SI Table IX. Pre-exponential factors $\nu$, activation energies $E_a$, rate constants $k_{\text{RT}}$, and activation temperatures $T_a$ for forward and backward various self-diffusion processes from PBE calculations on Mg(1011). The values are given in $10^{12}$ Hertz, eV, Hz, and K, respectively.

| System | Pathway | Path | $\nu_{\text{for}}$ | $E_{a_{\text{for}}}$ | $k_{\text{for}_{\text{RT}}}$ | $T_{a_{\text{for}}}$ | $\nu_{\text{rev}}$ | $E_{a_{\text{rev}}}$ | $k_{\text{rev}_{\text{RT}}}$ | $T_{a_{\text{rev}}}$ |
|--------|---------|------|--------------------|----------------------|-------------------|----------------|--------------------|----------------------|-------------------|----------------|
| Dimer  | Merge   | $d_0 \leftrightarrow d_1$ | 11.6 | 0.25 | 5.0E+08 | 98 | 23.6 | 0.58 | 2.6E+03 | 218 |
|        |         | $d_2 \leftrightarrow d_2$ | 4.8 | 0.19 | 2.8E+09 | 75 | 2.6 | 0.13 | 1.5E+10 | 53  |
|        |         | $d_3 \leftrightarrow d_1$ | 2.4 | 0.15 | 6.0E+09 | 61 | 10.6 | 0.51 | 2.0E+04 | 197 |
|        |         | $d_4 \leftrightarrow d_1$ | 10.2 | 0.37 | 5.2E+06 | 142 | 11.9 | 0.67 | 3.2E+01 | 259 |
| Concerted | $c_{d_0} \leftrightarrow c_{d_1}$ | 19.0 | 0.54 | 1.0E+04 | 205 | 18.9 | 0.54 | 1.0E+04 | 205 |
| Trimer | Merge   | $t_2 \leftrightarrow t_1$ | 5.6 | 0.26 | 2.3E+08 | 103 | 13.1 | 0.58 | 1.2E+03 | 223 |
|        |         | $t_2 \leftrightarrow t_5$ | 7.8 | 0.19 | 4.6E+09 | 73 | 4.1 | 0.20 | 1.3E+09 | 82  |
|        |         | $t_5 \leftrightarrow t_3$ | 3.3 | 0.27 | 7.6E+07 | 109 | 11.0 | 0.54 | 5.7E+03 | 209 |
|        |         | $t_6 \leftrightarrow t_5$ | 8.1 | 0.31 | 3.5E+07 | 122 | 6.3 | 0.57 | 9.3E+02 | 225 |
|        |         | $t_5 \leftrightarrow t_1$ | 1.6 | 0.24 | 1.4E+08 | 98 | 4.9 | 0.28 | 8.4E+07 | 110 |
| Step-edge | [1210]A-step | $s_0 \leftrightarrow s_1$ | 9.6 | 0.35 | 1.1E+07 | 134 | 9.9 | 0.59 | 6.8E+02 | 229 |
|        |         | $s_1 \leftrightarrow s_2$ | 2.7 | 0.13 | 1.8E+10 | 51 | 4.1 | 0.13 | 2.8E+10 | 50  |
|        | [1210]B-step | $s_2 \leftrightarrow s_4$ | 9.3 | 0.44 | 2.6E+05 | 171 | 6.8 | 0.73 | 2.3E+00 | 285 |
|        |         | $s_4 \leftrightarrow s_5$ | 3.7 | 0.16 | 8.0E+09 | 62 | 3.4 | 0.16 | 7.3E+09 | 62  |
|        | [1210]A-step | $s_6 \leftrightarrow s_7$ | 6.8 | 0.14 | 2.5E+10 | 56 | 0.1 | 0.18 | 1.1E+08 | 81  |
|        |         | $s_7 \leftrightarrow s_8$ | 1.0 | 0.01 | 6.3E+11 | 5  | 0.6 | 0.06 | 4.1E+11 | 5   |
|        | [1210]B-step | $s_9 \leftrightarrow s_{10}$ | 4.5 | 0.36 | 2.7E+06 | 144 | 15.6 | 0.95 | 7.5E-04 | 363 |
|        |         | $s_{10} \leftrightarrow s_{11}$ | 10.2 | 0.40 | 1.2E+06 | 156 | 11.3 | 0.40 | 1.3E+06 | 156 |
|        | [1012]-step | $s_{12} \leftrightarrow s_{13}$ | 18.5 | 0.18 | 1.5E+10 | 68 | 46.2 | 0.71 | 3.4E+01 | 260 |
|        |         | $s_{13} \leftrightarrow s_{14}$ | 6.8 | 0.45 | 1.3E+05 | 177 | 7.4 | 0.45 | 1.3E+05 | 176 |
| Step-down | [1210]A-step | $e_0 \leftrightarrow e_1$ | 10.2 | 0.44 | 3.1E+05 | 169 | 10.3 | 0.67 | 3.8E+01 | 258 |
|        |         | $e_0 \leftrightarrow e_2$ (Ex.) | 4.1 | 0.11 | 5.5E+10 | 44 | 3.9 | 0.34 | 6.0E+06 | 135 |
|        | [1210]B-step | $e_3 \leftrightarrow e_4$ | 8.3 | 0.43 | 3.3E+05 | 168 | 13.7 | 0.75 | 1.7E+00 | 288 |
|        |         | $e_5 \leftrightarrow e_6$ (Ex.) | 5.4 | 0.26 | 1.8E+08 | 103 | 7.2 | 0.58 | 7.1E+02 | 228 |
|        | [1210]A-step | $e_6 \leftrightarrow e_6$ | 6.0 | 0.29 | 7.3E+07 | 113 | 2.4 | 0.04 | 4.9E+11 | 16  |
|        |         | $e_6 \leftrightarrow e_7$ | 3.5 | 0.12 | 3.3E+10 | 47 | 1.3 | 0.42 | 7.8E+04 | 175 |
|        |         | $e_6 \leftrightarrow e_7$ (Ex.) | 9.9 | 0.47 | 8.6E+04 | 182 | 1.6 | 0.53 | 1.5E+03 | 217 |
|        | [1210]B-step | $e_8 \leftrightarrow e_9$ | 6.9 | 0.44 | 1.7E+05 | 174 | 11.0 | 0.96 | 3.6E-04 | 371 |
|        |         | $e_8 \leftrightarrow e_{10}$ (Ex.) | 3.3 | 0.07 | 1.9E+11 | 29 | 8.4 | 0.59 | 6.5E+02 | 229 |
|        | [1012]-step | $e_{11} \leftrightarrow e_{12}$ | 18.7 | 0.38 | 5.5E+06 | 144 | 21.6 | 0.89 | 1.2E-02 | 336 |
|        |         | $e_{11} \leftrightarrow e_{12}$ (Ex.) | 6.8 | 0.20 | 2.8E+09 | 77 | 12.5 | 0.71 | 9.4E+00 | 271 |
SI Figure 8. Schematic representation of all investigated diffusion pathways on Mg(1011).
Dimer: Merge

Pathway | $E^\text{for}_a$ | $E^\text{rev}_a$
---|---|---
$d_2 \leftrightarrow d_1$ | 0.25 | 0.58
$d_2 \leftrightarrow d_3$ | 0.19 | 0.13
$d_3 \leftrightarrow d_1$ | 0.15 | 0.51
$d_4 \leftrightarrow d_1$ | 0.37 | 0.67

Dimer: Concerted

Pathway | $E^\text{for}_a$ | $E^\text{rev}_a$
---|---|---
$cd_2 \leftrightarrow cd_1$ | 0.54 | 0.54

Trimer: Merge

Pathway | $E^\text{for}_a$ | $E^\text{rev}_a$
---|---|---
$t_0 \leftrightarrow t_1$ | 0.26 | 0.58
$t_2 \leftrightarrow t_1$ | 0.19 | 0.20
$t_3 \leftrightarrow t_1$ | 0.27 | 0.54
$t_4 \leftrightarrow t_1$ | 0.31 | 0.57
$t_5 \leftrightarrow t_1$ | 0.24 | 0.28
Step-edge: [1210]A-step

\[
\begin{align*}
\text{Pathway} & \quad \Delta E_{\text{for}} \quad \Delta E_{\text{rev}} \\
S_0 \leftrightarrow S_1 & \quad 0.35 \quad 0.59 \\
S_1 \leftrightarrow S_2 & \quad 0.13 \quad 0.13
\end{align*}
\]

Step-edge: [1210]B-step

\[
\begin{align*}
\text{Pathway} & \quad \Delta E_{\text{for}} \quad \Delta E_{\text{rev}} \\
S_3 \leftrightarrow S_4 & \quad 0.44 \quad 0.73 \\
S_4 \leftrightarrow S_5 & \quad 0.16 \quad 0.16
\end{align*}
\]

Step-edge: [1210]A-step

\[
\begin{align*}
\text{Pathway} & \quad \Delta E_{\text{for}} \quad \Delta E_{\text{rev}} \\
S_6 \leftrightarrow S_7 & \quad 0.14 \quad 0.18 \\
S_7 \leftrightarrow S_8 & \quad 0.01 \quad 0.01
\end{align*}
\]

Step-edge: [1210]B-step

\[
\begin{align*}
\text{Pathway} & \quad \Delta E_{\text{for}} \quad \Delta E_{\text{rev}} \\
S_9 \leftrightarrow S_{10} & \quad 0.36 \quad 0.95 \\
S_{10} \leftrightarrow S_{11} & \quad 0.40 \quad 0.40
\end{align*}
\]
**Step-edge: [1012]-step**

Pathway | $E_{a}^{for}$ | $E_{a}^{rev}$
---|---|---
$S_{12} \leftrightarrow S_{13}$ | 0.18 | 0.71
$S_{13} \leftrightarrow S_{14}$ | 0.45 | 0.45

**Step-down: [1210]A-step**

Pathway | $E_{a}^{for}$ | $E_{a}^{rev}$
---|---|---
$e_{0} \leftrightarrow e_{1}$ | 0.44 | 0.67
$e_{0} \leftrightarrow e_{2}$ (Ex.) | 0.11 | 0.34

**Step-down: [1210]B-step**

Pathway | $E_{a}^{for}$ | $E_{a}^{rev}$
---|---|---
$e_{3} \leftrightarrow e_{4}$ | 0.43 | 0.75
$e_{3} \leftrightarrow e_{4}$ (Ex.) | 0.26 | 0.58

**Step-down: [1210]A-step**

Pathway | $E_{a}^{for}$ | $E_{a}^{rev}$
---|---|---
$e_{5} \leftrightarrow e_{6}$ | 0.29 | 0.04
$e_{6} \leftrightarrow e_{7}$ | 0.12 | 0.42
$e_{5} \leftrightarrow e_{7}$ (Ex.) | 0.47 | 0.53
SI Figure 9. Schematic representation, energy profile and PBE activation energies $E_a$ of self-diffusion processes studied on Mg(1011). Green-colored atoms mark the initial, while red-colored atoms mark the final positions. The values are given in eV.

| Pathway | $E_a^{for}$ | $E_a^{rev}$ |
|---------|-------------|-------------|
| $\theta_8 \leftrightarrow \theta_9$ | 0.44 | 0.96 |
| $\theta_8 \leftrightarrow \theta_{10}$ (Ex.) | 0.07 | 0.59 |

SI Figure 10. Transition states of step-edge diffusion pathways along [1$\bar{2}$0]- and [11$\bar{2}$0]-steps steps. In the TS of the [1$\bar{2}$0]-step, the nearest neighbor atom in the edge row pulls slightly back, leaving a pocket for the diffusing atom (green) to settle in a stabilized fcc-like position.
SI Figure 11. Transition state of step-down (dimer) diffusion pathway along the [1120]-step. The second atom (gray) follows the diffusing atom (green) into the fcc position above the exchange atom. This maintains the dimer conformation until beyond the TS and lowers the activation energy of the process.