

Supplementary Information:

Role of electron localisation in H adsorption and hydride formation in the Mg basal plane under aqueous corrosion: A first-principles study

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1 Electron Localisation Function (ELF) and Charge Density (CD)

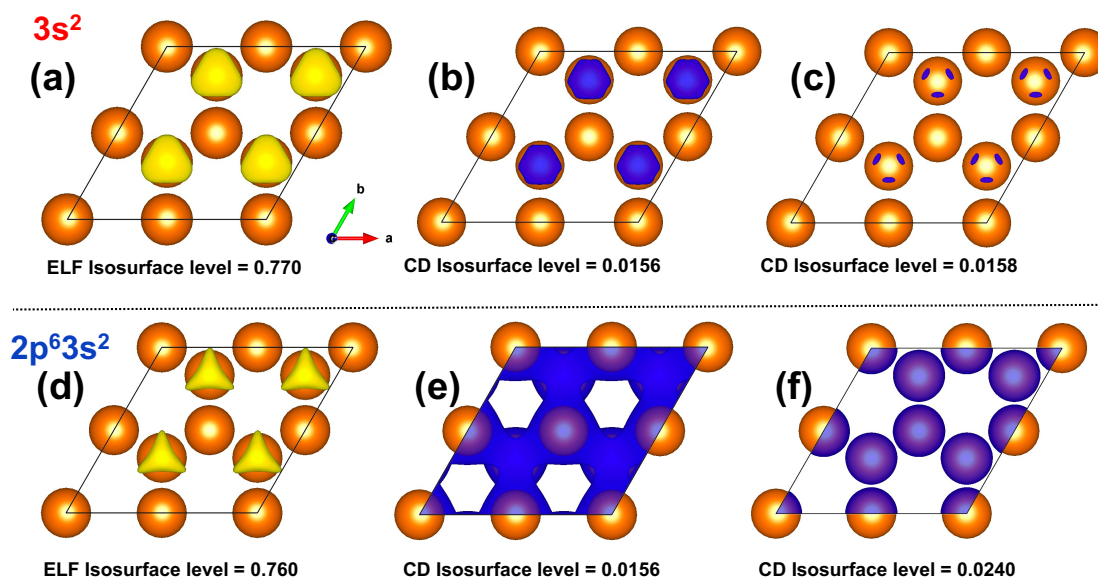


Figure S1: ELF and Charge density (CD) of Mg (0001) surface calculated from DFT calculations with different treatment of the valence electrons for Mg atoms ($3s^2$ and $2p^63s^2$ respectively). (a)-(c) ELF and CD isosurface plots of the Mg (0001) surface (Mg atoms with $3s^2$ as the valence electrons). (d)-(f) ELF and CD isosurface plots of the Mg (0001) surface (Mg atoms with $2p^63s^2$ as the valence electrons). The unit of the ELF isosurface level is 1 and that of the charge density isosurface level is e/Bohr^3 .

The electron localisation function (ELF) reflects the probability of finding an electron near the location of another like-spin electron, thus demonstrating the degrees of localisation of an electron at a point in space.¹ The usual interpretation of a local ELF maximum is that there's likely to be an occupied orbital peaked at the point. One advantage of using the ELF maxima to predict the stable local hydrogen adsorption site of a metal surface is that the ELF depends on the local kinetic energy density that is relatively less prone to

be washed out by the occupation of other orbitals.

As shown in Figure S1 (a) and (d), the ELF plots of the Mg (0001) surface obtained from calculations with different treatments of the Mg valence electrons ($3s^2$ and $2p^63s^2$) both indicate an ELF maximum at the on-surface hcp hollow site, confirming the robustness of the ELF. Although the charge density could also illustrate the electron distribution within a metal surface, the topological shape of the charge density on the other hand, strongly depends on the occupation of not only the interstitial localised orbital but all other orbitals too. As shown in Figure S1 (b), the pseudo charge density calculated using only Mg's 3s electrons looks almost identical to the ELF plot [Figure S1 (a)] with local maxima at the on-surface hcp hollow sites. However, when Mg's 2p electrons are also taken into consideration as valence electrons, the local maxima are washed out by the occupied 2p orbitals [see Figure S1 (e) and (f)]. Therefore, the charge density cannot be used directly to find the potential hydrogen adsorption sites. As a result, for Mg surface, we chose the ELF to determine the position of the hydrogen trap.

2 Defect-induced ELF Modification and H adsorption on the Mg (0001) Surface

In this section, we study the ELF of a defective Mg (0001) surface with an atomic vacancy at the top layer and investigate the H adsorption on this defective surface. Removing one Mg atom from the topmost surface layer forces the charge density redistribution, thus leading to a significant change in the onsite electron localisation. As shown in Figure S2 (b), the absence of one Mg atom at the top layer leads to the formation of a new ELF maximum at the on-surface fcc hollow site adjacent to the atomic vacancy (labelled as FCC*). In addition, this atomic vacancy also enhances the electron localisation of the neighbouring hcp hollow site (labelled as HCP* in the figure), which was the previous ELF maximum on the pristine Mg (0001) surface.

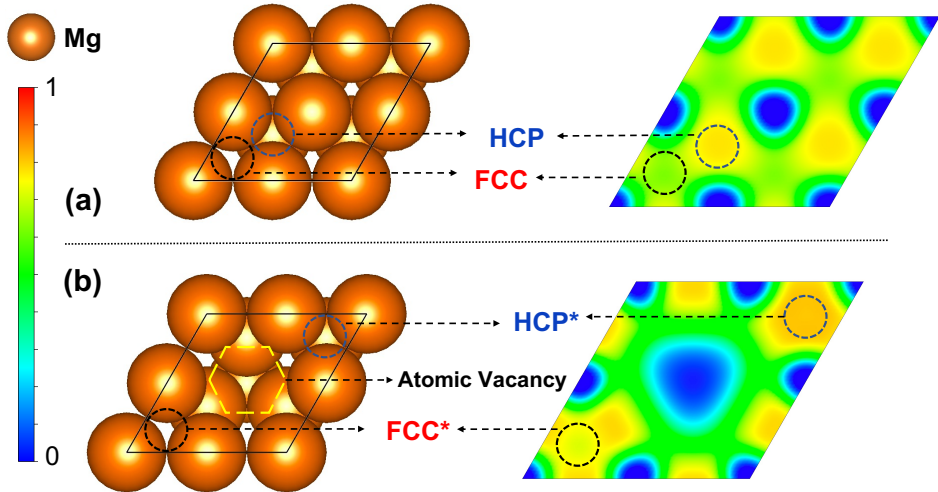


Figure S2: Pristine Mg (0001) surface and defective Mg (0001) surface (with an atomic vacancy) with the corresponding top-view ELF contours. (a) The pristine Mg (0001) surface structure and the ELF contours. The on-surface hcp and fcc sites are also indicated by the circles and labelled as HCP and FCC. (b) The defective Mg (0001) surface structure with a point defect and the ELF contour. The atomic vacancy is demonstrated by the yellow hexagon. HCP* and FCC* indicate the general on-surface hcp and fcc adsorption sites of the defective Mg (0001) surface.

Table S1 shows the ELF value of the on-surface fcc/hcp adsorption sites for the pristine and defective Mg (0001) surface. Consistent with the ELF contours, these ELF values also show that introducing an

Adsorption Site	FCC	HCP	FCC*	HCP*	Atomic Vacancy
On-site ELF	0.666	0.785	0.837	0.860	/
H Adsorption Energy (eV/H)	-0.0167	0.00707	-0.0523	-0.0681	0.0460

Table S1: Onsite ELF value/Hydrogen adsorption energy (eV per H) at the on-surface adsorption sites of the pristine and the defective Mg (0001) surface. The H adsorption energy at the atomic vacancy site (position for the removed Mg atom) is also demonstrated in the table.

atomic vacancy on the Mg (0001) surface increases the onsite ELF value of the hcp and fcc hollow site significantly. The H adsorption energy at the hcp/fcc sites of the imperfect Mg surface becomes more energetically favourable because of the enhanced onsite electron localisation and the improved correlative hydrogen-electron interaction. However, instead of accumulating locally, electrons are less localised at the atomic vacancy of the defective Mg surface according to the ELF contour in Figure S2 (b). Therefore, placing a hydrogen atom at the vacancy is thermodynamically unfavourable due to the lack of localised electrons, with notable positive adsorption energy (see Table S1). Based on the geometry optimisation of the defective Mg (0001) surface with a hydrogen atom at the Mg vacancy, the adsorbed H tends to be adsorbed at the second-layer hcp hollow site (with a higher ELF value compared with the Mg vacancy), rather than staying at the vacancy during the relaxation.

To conclude, the existence of the atomic vacancy on the Mg (0001) surface could modify the electron localisation pattern of the surface. New ELF maxima tend to form at the on-surface hcp/fcc hollow sites in the vicinity of the atomic vacancy rather than at the atomic vacancy, thus contributing to a more robust trap on the surface Mg for hydrogen. As an indicator, the ELF is also able to predict the possible adsorption site for hydrogen on the defective Mg surface. This finding enlightens us that the hydrogen adsorption on the Mg surface during the aqueous corrosion could be impacted by the Mg dissociation reaction (with the point defects forming and the onsite electron localisation changing), which might further influence the sub-surface hydride formation and dissociation.

3 Influence of the Solvent Effect

To investigate the influence of the solvent effect on the surface adsorption of the Mg (0001) surface during aqueous corrosion, we employ the implicit solvent method with VASPsol²⁻⁴ to calculate the adsorption energy of atomic H, O and OH radical in aqueous conditions. As illustrated in Figure S3, the adsorption energy of H, O and OH on the Mg basal plane in an implicit water environment becomes more negative compared to the adsorption energy in the vacuum. This suggests that the solvent effect could stabilize the adsorbed species on the Mg (0001) surface. Nevertheless, including the solvent effect in the calculation does not change the adsorption patterns in all adsorption cases (i.e. the order of the adsorption energy for H/OH/O at different adsorption sites for all coverage resist change by the solvent). As we are interested in the most stable adsorption structure, we conclude that it is rational to use the adsorption energy in the vacuum to determine the most stable adsorption phase in our calculations.

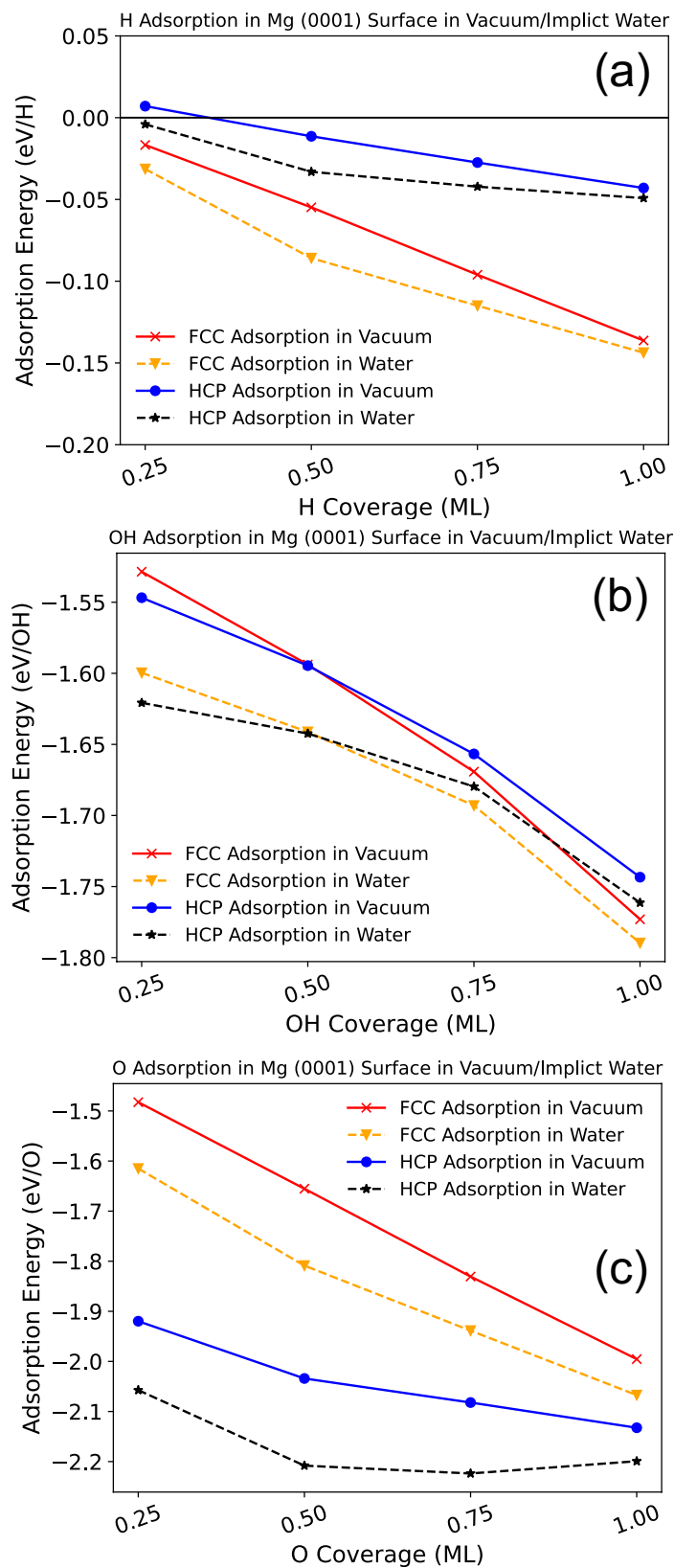


Figure S3: H/OH/O adsorption energy (eV per adsorbate) at different on-surface adsorption sites (hcp and fcc) of the Mg (0001) surface in the vacuum/implicit water.

References

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