Density functional study of coating on magnesium implants

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Vision

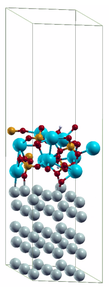
- **Need:** Biocompatible material for orthopedic implants
- **Opportunity:** Magnesium is biocompatible and lightweight but **corrodes quickly**
- **Consequence:** Loss of mechanical strength and early implant failure
- **Approach:** Apply protective coatings magnesium hydroxide **$Mg(OH)_2$** or **HAp** $[Ca_{10}(PO_4)_6(OH)_4]$ to slow corrosion and enhance stability
- Depending on the conditions in which HAp coatings are formed on the surface of magnesium, a layer of $Mg(OH)_2$ may form in between the surface and the coating, preventing the HAp from stabilizing[1]

[1]Tomozawa et al., Surf. & Coat. Techn. **204**, 3243 (2010)

Methods

1) Density functional theory (DFT) calculations of adsorption structure and energies

2) Mg(0001) surface modelled by periodically repeated unit cell of five layers of Mg with vacuum above; the bottom three layers fixed



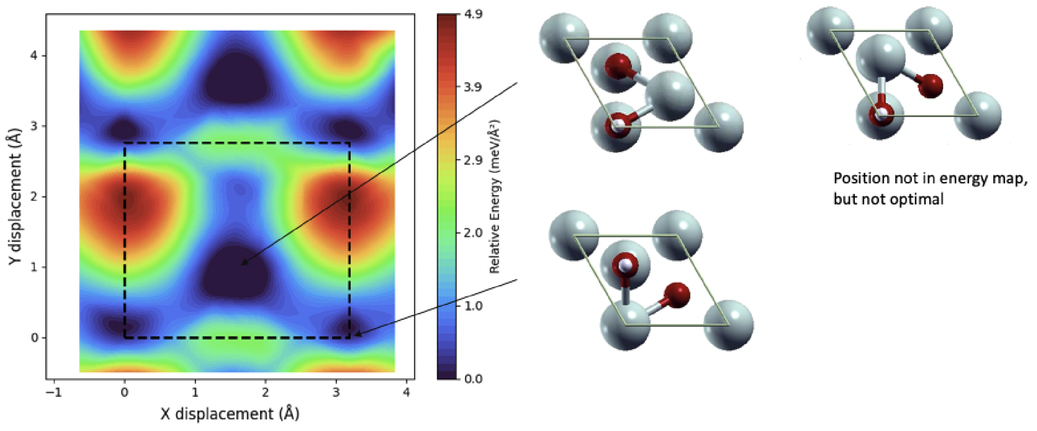
3) Coatings of $Mg(OH)_2$ or HAp added on Mg(0001); testing amino acids adsorbed or Mg(0001) doped

4) The adsorption energy E_{ads} of an overlayer or molecule on the surface is found from

$$E_{ads} = E_{surface+molecule} - E_{surface} - E_{molecule}$$

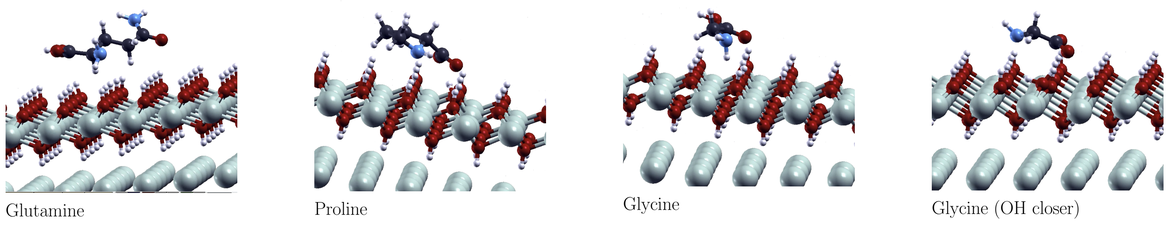
5) $Mg(OH)_2$ and HAp coatings were systematically moved over Mg(0001) at 25 points and $E_{ads}(x, y)$ interpolated; maximal corrugation ΔE_{ads} found from variation in $E_{ads}(x, y)$

$Mg(OH)_2$ on Mg(0001)



- A more beneficial position for the $Mg(OH)_2$ was found than was originally guessed.
- The adsorption energy map shows very small changes across the positions. This means that the layer of $Mg(OH)_2$ easily can slide of (low corrugation).
- Adsorption energy at optimal position $\rightarrow -16.67$ meV/Å^2

$Mg(OH)_2$ with body relevant molecules



Deformation carries a large energy cost when the amino acids are more strongly adsorbed (e.g., Glycine).

meV/molecule	Adsorption energy Molecule on $Mg(OH)_2$	Deformation energy Amino acid	Deformation energy $Mg(OH)_2$
Glutamine	-868	87	205
Glycine	-514	85	108
Proline	-1111	2777*	750
Glycine (OH-closer)	-1050	3051*	1115

*including dissociation of H

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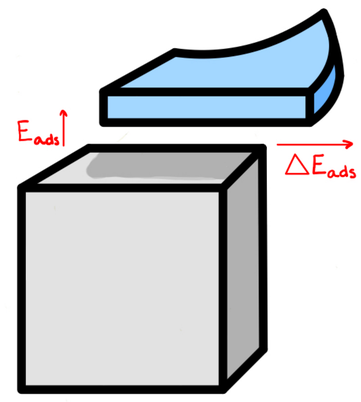
Will coating lift off / slide off?

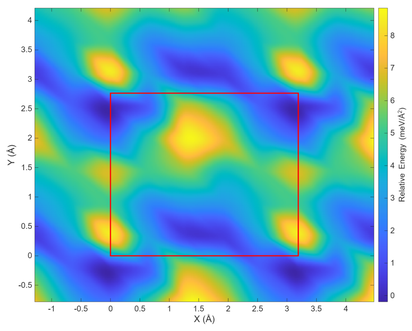
Protection of the Mg surface depends on the stability of the coating:

- If adsorption energy E_{ads} is small, coating may lift off
- If the difference in adsorption energy ΔE_{ads} in positions across the surface is small (small corrugation), coating can readily slide off
- Results suggest both lifting and sliding off is possible

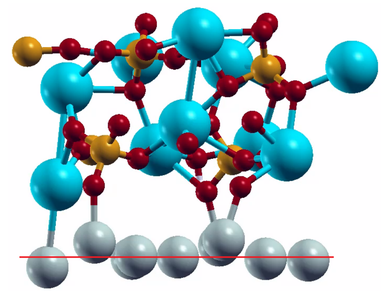


meV/Å^2	E_{ads}	ΔE_{ads}
Graphene on graphite	-25.3	3.7
$Mg(OH)_2$ on magnesium	-15.8	4.9
HAp on magnesium	-12.5	8.6

Hydroxyapatite (HAp) on Mg(0001)



*Map **interpolated** from 25 calculated positions. Areas outside the red square are periodic repetitions*



HAp over Mg(0001) surface. Red line: original position of Mg atoms.

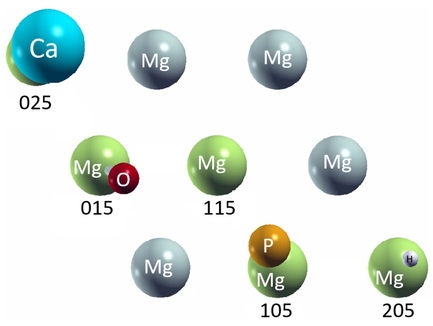
- HAp likely has a **favored adsorption site**
- **Small adsorption energy differences** across the cell $\rightarrow$ lateral sliding is easy.
- **Adsorption energy** at optimal position (lowest energy) $\rightarrow -12.5$ meV/Å^2

HAp on Zn/Ca doped Mg(0001) surface

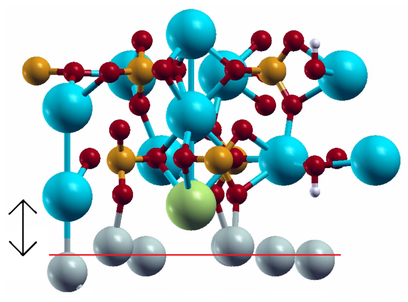
E_{ads} for HAp on Mg(0001) with/without doping (meV/Å^2).

Position	015	025	105	115	205
HAp-Mg	-12.5	-12.5	-12.5	-12.5	-12.5
HAp-Mg-Zn	-19.4	-17.2	-12.3	-13.3	-14.3
HAp-Mg-Ca	-17.4	-4.50	-18.0	-18.4	-11.0

Position of substituted atom affects
$\rightarrow$ Adsorption energy
$\rightarrow$ Distance between HAp and surface.

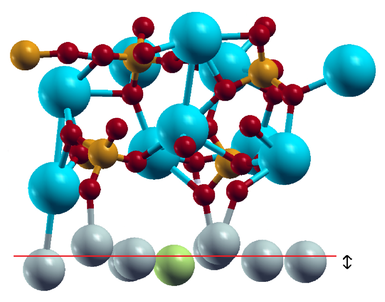


Positions of substituted atoms relative lowest HAp atoms.



Green atom: Ca substituted. Red line: original position

- Repositioning of Ca after optimization $\rightarrow +1.94$ Å in z-direction

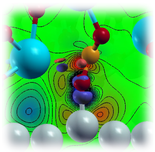


Green atom: Zn substituted. Red line: original position

- Repositioning of Zn after optimization $\rightarrow -0.25$ Å in z-direction.

Future Work

- Map the **electron density changes** to better understand bonding at the interface
- Examine **other doping elements** to further determine influence of such substitutions
- Add environments such as **water** for a more accurate modeling of implant in the body
- How do **atoms/ions from the environment** affect the coating stability?
- If $Mg(OH)_2$ forms underneath HAp, how is the **stability** affected?
- How does **doping of Mg(0001)** affect the interaction with **$Mg(OH)_2$**?



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