Towards a working tight binding model for Ti – water interface

Sasha Lozovoi, Tigany Zarrouk, and Tony Paxton
Department of Physics, King's College London

Outline:

1. What is known about Ti interaction with water?

2. From Ti(d) to Ti(sd)

3. Art of the fitting **[Tigany]**

4. Examples of Ti – water simulations

5. Next steps and conclusions

Corrosion meeting (online), London – Derby, 24 Nov 2021

How much is known about Ti - water interface?

- Surprisingly, not much. Not much at all.

- We know though that Ti surface oxidises in air (standard conditions) and quickly covers itself with a continuous layer of an unspecified Ti oxide 1–2 nm thick.

  For comparison, Al forms a 2–3 nm layer of alumina (amorphous).

  [many thanks to you, Wikipedia!]

- The oxide layer on Ti can grow up to 25 nm in 4 years time.

- A controllable growth of a thicker TiO_2 layer (up to a few μm's) on top of Ti can be done in the procedure called anodising (*e.g.,* wedding rings), but this is a different story. Well, perhaps not entirely.

- Experiment (XPS), $T = 150 - 850$ K:
  O_2 oxidises Ti^0 to Ti^{IV}, Ti^{III}, and Ti^{II}, whereas H_2O only to Ti^{II}.
  Ti^{IV}/Ti^{III} in case of oxygen, and OH group in case of water are mainly detected in the vicinity of the oxide surface, Ti^{II} is found closer to the metal – oxide interface.
  [G. Lu, S.L. Bernasek, J. Schwartz, Surf. Sci. **458**, 80 (2000)]

How much is known about Ti - water interface? (cont.)

- For some reason DFT calculations of water – Ti do not appear hugely popular. So far we've managed to find only two papers (!) with overlapping authors (5-layer Ti slab (27 atoms) + 32 H_2O molecules, VASP) which attempted MD in the presence of electric field using M. Neurock's double reference method [M. Stancheva *et al.*, J. Electrochem. Soc. **161**, E3188 (2014); I. Betova *et al.*, Comp. Mater. Sci. **171**, 109260 (2020)]

- The electrochemical potential (*electromotive force*) for $Ti^{++}(aq)|Ti(s)$ half cell is –1.63 V on the hydrogen scale. For comparison, those for $Pt^{++}(aq)|Pt(s)$, $Al^{+++}(aq)|Al(s)$, and $Mg^{++}(aq)|Mg(s)$ are +1.2 V, –1.66 V, and –2.37 V, respectively [Tony's notes, ver.15, pp. 37–38].

- To summarise:

  - Presumably, as soon as water molecules come in contact with Ti surface, a few of them dissociate and the 'liberated' O atoms are utilised for building some kind of oxide layer.

  - What then happens to H atoms is not entirely clear. They might either (i) dissolve into Ti bulk as H^-; (ii) take part in the oxide structure; (iii) dissolve into electrolyte as H^+; or (iv) form neutral H_2 molecules and depart.

Historical overview

The chain of TB models:

1. It all started with Tony's JCP paper on the orthogonal TB model for water [JCP (2011)]

2. The model was further developed and extended to TiO_2 + water + small organic molecules in 2014 ['three papers', JCP (2014)] which was essentially an effort of the whole Tony's group. Ti in this model had only d electrons

3. A couple of years ago Tigany created a new model for pure Ti (bulk phases, phonons, defects, stalking faults, etc.) which was also orthogonal and d-only

4. The ambition was to combine models (2) and (3) above so that one could study Ti – water interface.

5. Alas, it didn't work. At least not straight away.

Titania bands

DFT
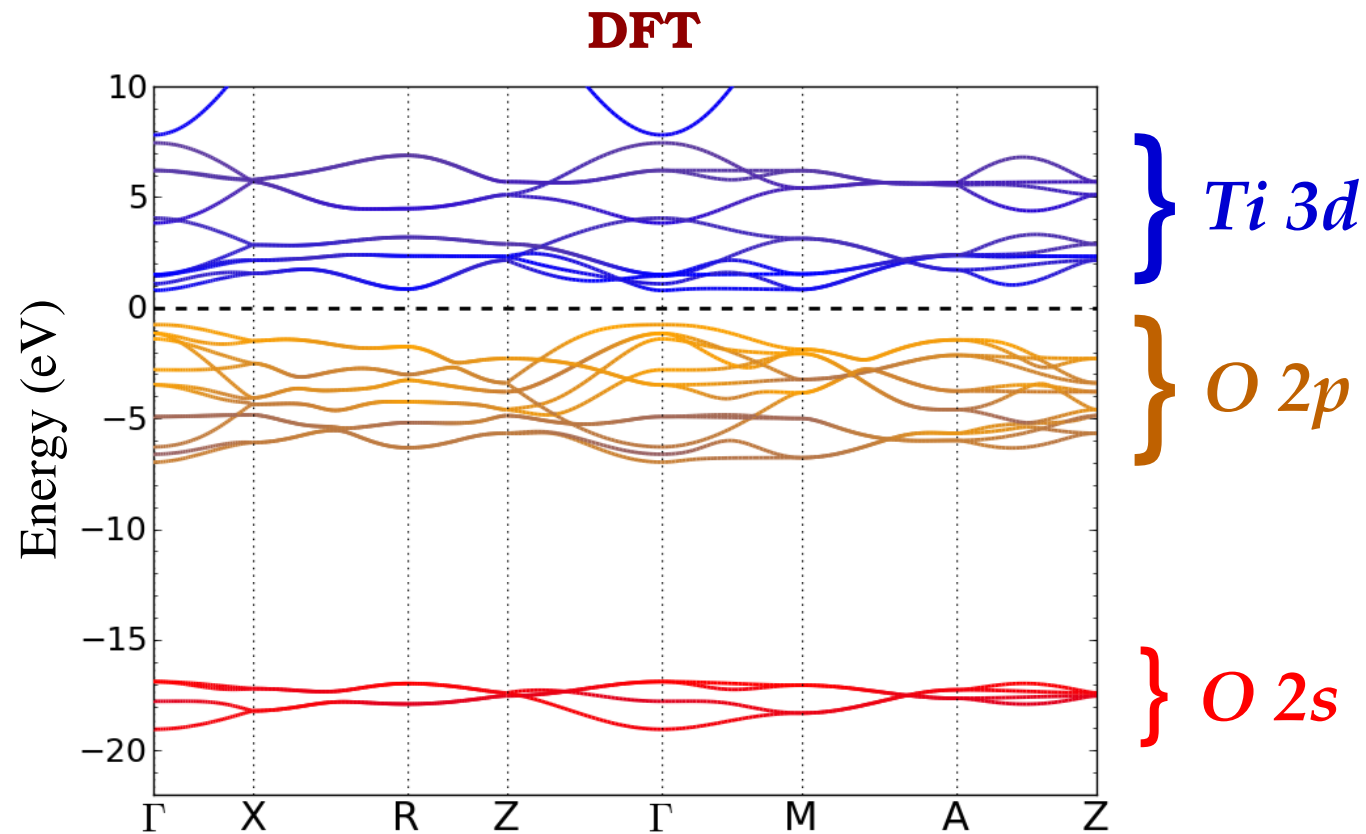
TiO$_2$ (rutile) band structure at experimental lattice constants, LDA

The problem with Ti d–only models in a nut shell

The problem appears to originate from having only d electrons for Ti

pure Ti: DOS of pure Ti is a typical DOS of a transition sd metal: a sharp d–band on the background of a broad extended s–band. E_F of course falls inside this d–band so most properties are defined by d–electrons. It is therefore admissible to ignore s–states altogether and delegate their contribution to d–electrons. Furthermore, according to Tony's experience, d–only TB models are often superior to sd models.
d–model: s–orbitals absent; $N_s(\text{Ti}) = 0$

titania: TiO_2 (rutile or anatase) is an insulator with the valence band made of oxygen s and p states. States originated from Ti constitute the conduction band $\simeq 3$ eV above. Ti–s states in particular are unoccupied and can be omitted with no impact on the ground state properties of TiO_2. Ti s–electrons are essential as they are used to fill up the O bands
d–model: s–orbitals absent; $N_s(\text{Ti}) = 2$

intermediate compositions: Hence, although the neglect of Ti s–states seems justified in both limiting cases, pure Ti and TiO_2, it's not clear what one should do in intermediate cases where $0 < \text{O:Ti} < 2$ and what $N_s(\text{Ti})$ should be there? Include Ti s–orbitals, perhaps?
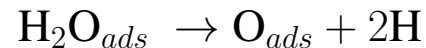**sd–model:** s–orbitals present; $N_s(\text{Ti}) = 2$

Art of fitting: over to Tigany

Water dissociation on Ti

- There have been created quite a few sd models already, thanks to Tigany. But in all of them water on Ti(0001) dissociates immediately and fully:

$$H_2O_{ads} \rightarrow O_{ads} + 2H$$

- The current model in particular leaves the oxygen atom near the Ti – Ti bridge site and two hydrogen atoms embedded into the Ti surface layer.
  Atomic charges are $Q(O) = -0.940 \, |e|$ and $Q(H) = -0.989 \, |e|$, taken mainly from the top Ti layer in which $Q(Ti) = 0.612 \div 0.786 \, |e|$.

- **Movie I**
  System: Ti(hcp) 2x2 six layer slab (24 at.) with two adsorbed H_2O molecules, one on each side
  Mode: Static relaxation
  Symmetry: none
  Constraints: Ti atoms are frozen, H and O allowed to relax

- For comparison, in our LDA DFT calculation H_2O stays non-dissociated during the relaxation (preferred site: Ti – Ti bridge site), but when dissociated 'by hand' into either O + 2H (double dissociation) or OH + H (single dissociation), the total energy decreases.

Ti - water interface

- Next we move to a larger simulation, our first attempt to emulate the interface between bulk Ti and bulk water. There is no vacuum gap in the cell.

- **Movies II and III**
  System: 6 layer Ti slab (24 atoms) and 32 water molecules
  Mode: Static relaxation
  Symmetry: none
  Constraints: H and O can relax, substrate Ti atoms are initially frozen, but then released layer-by-layer

- What is the rôle of the dissolved H atoms?

- It appears we can control the extent of the oxidation by just freezing/unfreezing Ti atoms!

- Hopefully, this nice feature does not go away during MD simulations.
  For instance, the next in our plans are NVT runs of a longer cell with all Ti atoms frozen in order to have a good view of the double layer structure.

Next steps

- A new version of the model is on its way, thanks to Tigany who works hard on it.

- The most annoying 'fly' in the current model is an instability wrt a transition to some ionic structure with lower energy, as is occasionally observed during MD.

- Large scale simulation: MD, double layer

  - A thicker water layer in order to look at the structure of the double layer with all Ti atoms frozen.

  - Also need to establish the cell with the correct density of water.

  - Extraction of Ti into water solution: let us give it a try.

- Electric field created by TB 'pseudo' ions, such as Ab atom (an analog of chlorine atom except there is no interaction with other atoms apart from the electrostatic one [Sebastian Budd])

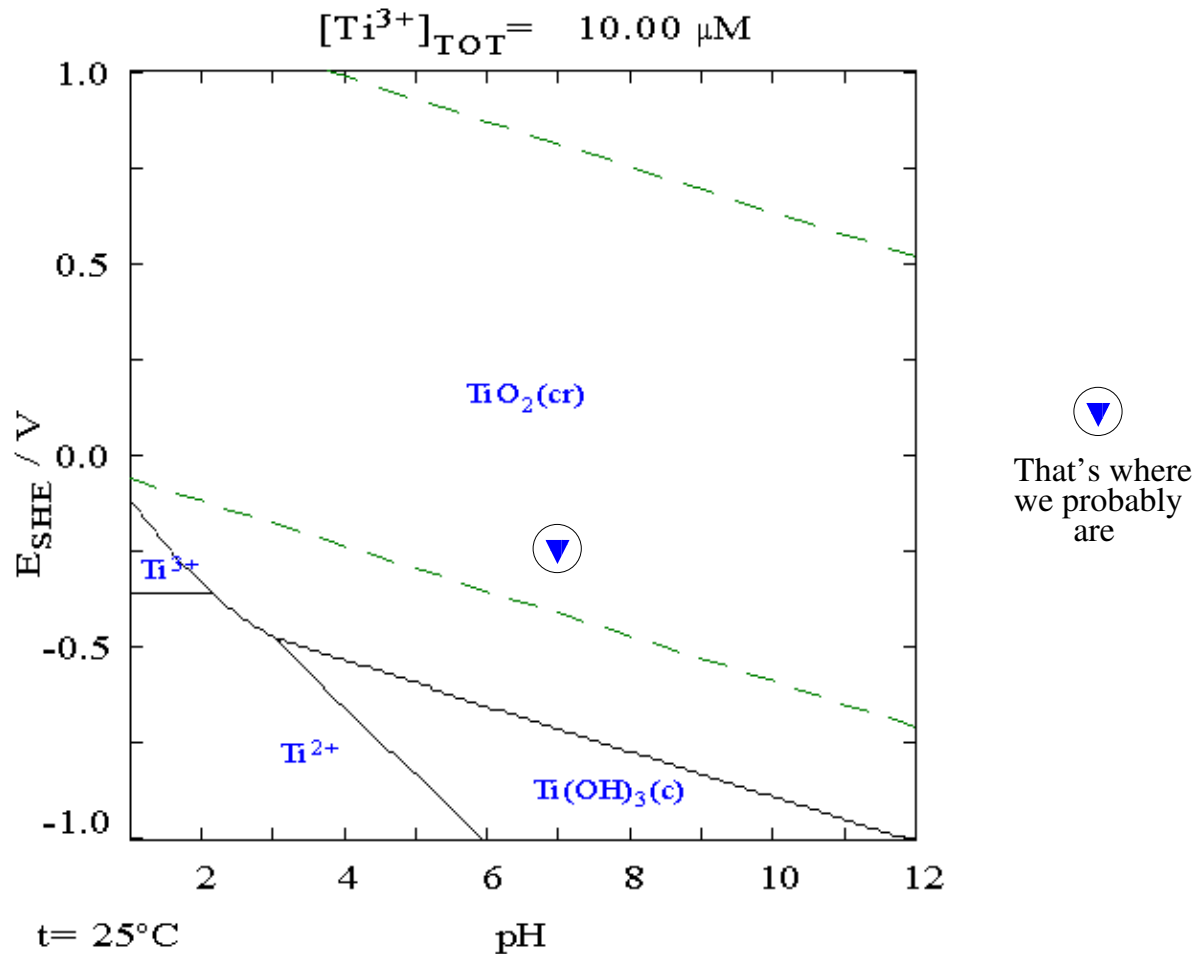- Hairy probe, of course. Margherita experience will be priceless!

Conclusions

1. A reasonably decent (in our opinion) TB model to investigate Ti - water interface has been developed.

2. The breakthrough was due to the switching from Ti(d–only) to Ti(sd) description.

3. Instability in the bulk Ti(hcp) MD simulations with impurity (O or H) is occasionally observed. Currently we are trying to fix this.

4. The static relaxation of 24 Ti + 32 H_2O system shows a strong tendency for water molecules near Ti surface to fully dissociate.

5. Released O atoms then try to build a precursor of an oxide layer, whereas the released H atoms either diffuse inside Ti or combine into H_2 molecules and stay near the surface.

6. The growth of the oxide can be controlled in the simulation by freezing Ti atoms.

Appendix

- Below is the Pourbaix diagram for Ti in water.

- An approximate position of our TB simulations on it is shown with a blue triangle.

$[Ti^{3+}]_{TOT} = 10.00 \ \mu M$

$TiO_2(cr)$

Ti^{3+}

Ti^{2+}

$Ti(OH)_3(c)$

E_{SHE} / V

pH

t= 25°C

That's where we probably are

Ref: Puigdomenech, Ignasi (2004) Hydra/Medusa Chemical Equilibrium Database and Plotting Software, KTH Royal Institute of Technology.