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Florida Laboratory for Advanced Materials Engineering Simulation

Applications of Charge Optimized Many Body (COMB) Potentials in Multicomponent Systems

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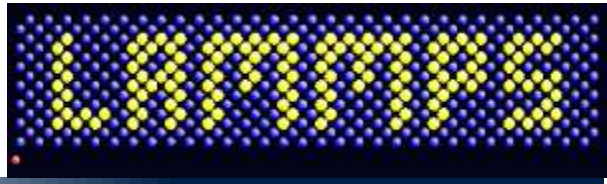
Aug 6, 2015

August 2015 LAMMPS Users' Workshop and Symposium,
August 5-6, 2015 at Albuquerque, NM



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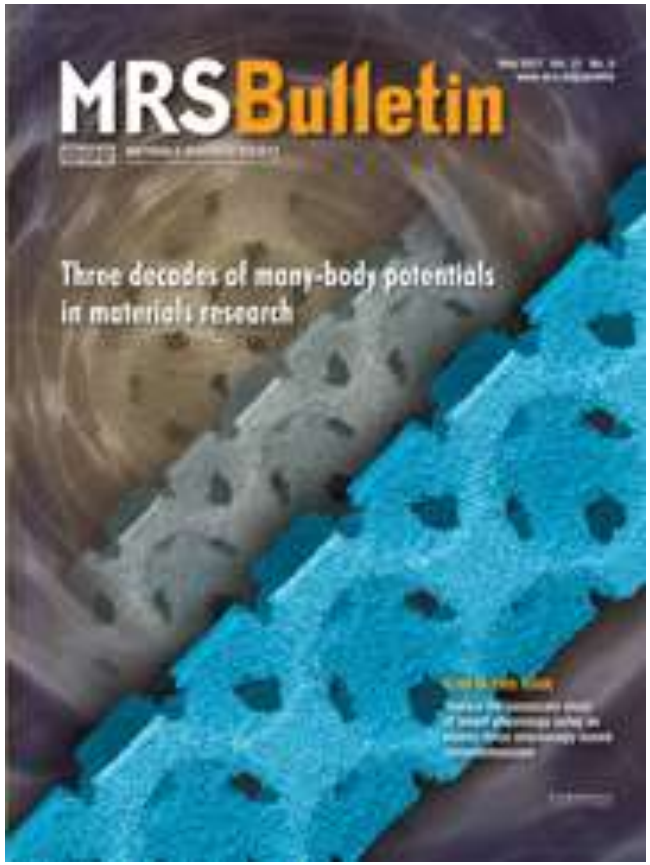
Current COMB3 on LAMMPS is out dated
Contact me (TUL17@psu.edu) for updates

Reactive many-body empirical potentials to model materials



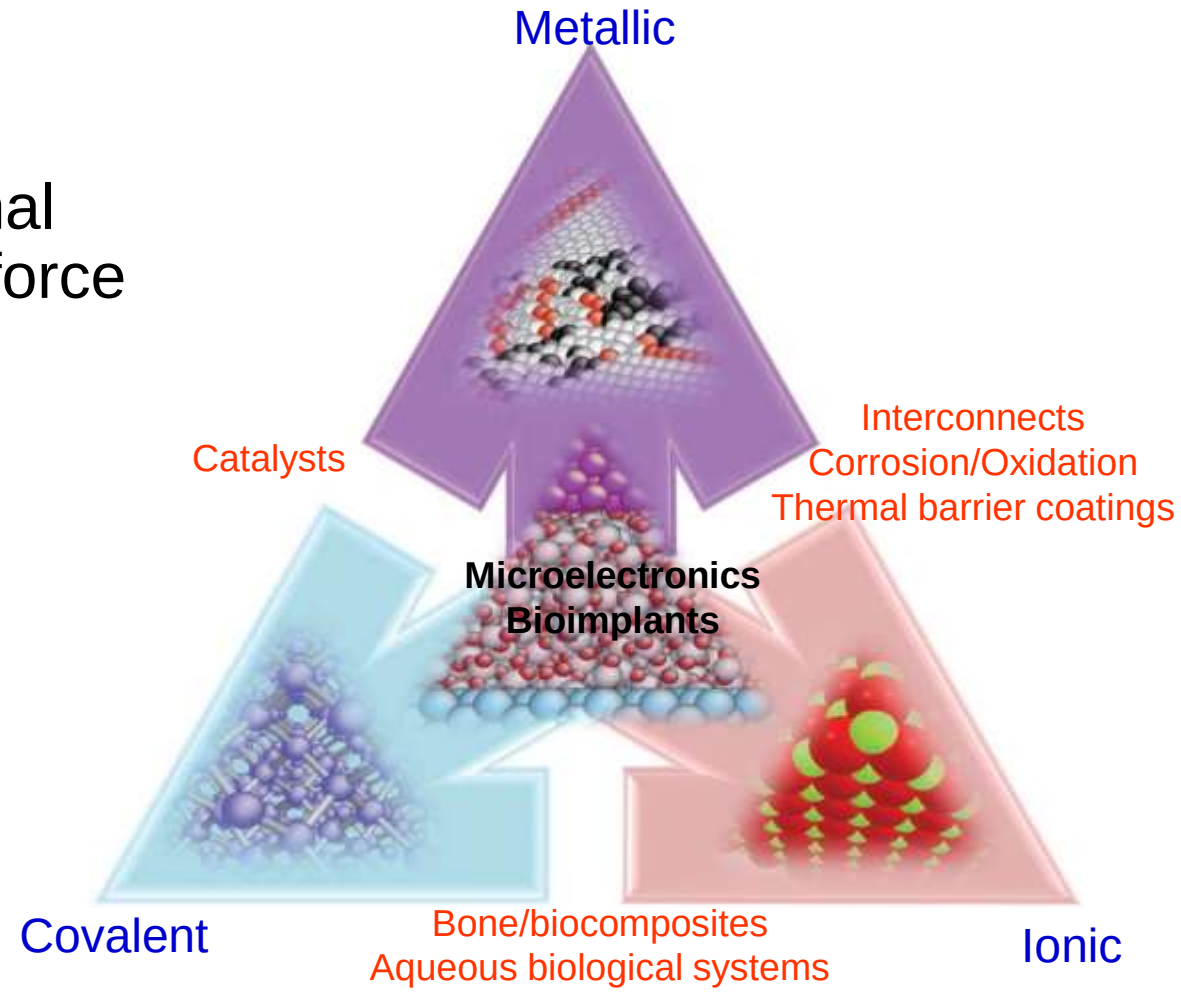
May 2012 issue

Historically developed for materials with specific types of chemical bonds

- SW and Tersoff potentials for Si
  - Brenner or REBO potential for C,H + O,F,S,….
  - AIREBO
- EAM potentials for metals
  - MEAM for metals and oxides
  - EAM+ES for metals and oxides
- Buckingham potentials for ionically bound materials

Modeling Multicomponets Systems

- Inherent to many applications
- Challenge for traditional empirical potentials (force fields)
- This need spurred the development of *next generation potentials*: charge optimized many body (COMB), ReaxFF, EAM+ES and a few others



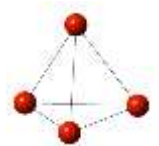
S.R. Phillpot and S.B. Sinnott, Science (2009)

Functional form of COMB3 potential

$$E_T = \sum_i \left\{ E_i^{Self}(q_i) + \frac{1}{2}\sum_{j\neq i}\left[V_{ij}^{short}(r_{ij}, q_i, q_j) + V_{ij}^{Coul}(r_{ij}, q_i, q_j)\right] + B_i(q_i) + C_i(r_{ij}, \theta_{ijk}) + E^{polar}(q_i, r_{ij}) + E^{vdW}(r_{ij}) \right\}$$

- **Self energy**: ionization energies and electron affinities; includes penalty function to capture change in self-energy due to the field from the ionic lattice
- **Short-range interactions**: reactive bond-order potential
- **Coulomb interactions**: Coulomb integral over the charge densities
- **Charge and angular correction terms**
- **Polarization**: Atomic polarizabililty for organic systems
- **van der Waals energy**

S.R. Phillpot and S.B. Sinnott, Science (2009)
T. Liang et al., Materials Science and Engineering R (2013)

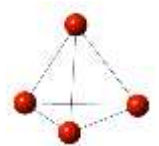


Current status of COMB3

- **Semiconductors**
  - Si
- **Metals**
  - Cu, Zn, Al, Zr, Ti, U, Pt, Ni, Au
- **Compounds**
  - Cu_2O, ZnO, UO_2, NO_X, NH_3, Al_2O_3, TiO_2, NiO
  - Ni_3Al, ZnCu
  - TiN, AlN,TiC,TiH_2,TiC

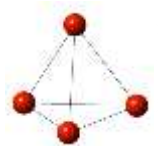
- Carbon based systems
  - CHO systems
  - H_2O and O_2
  - C/H/Cu/O/Zn
  - C/H/O/Ti
  - CN
  - CHON/Ti

T. Liang et al., Materials Science and Engineering R (2013)
T. Liang et al., J. Physical Chemistry A (2011)
Yu-Ting Cheng et al., Surface Science (2013)
Yangzhong Li et al., J. Physics: Condense Matter (2012)
Mark J. Noordhoek et al., J. Nuclear Materials (2013)

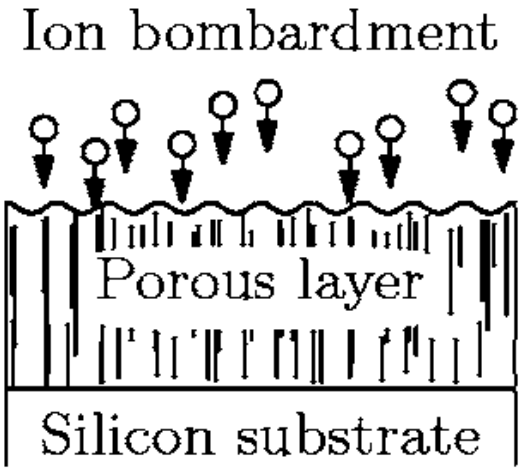


- O_2 densification of porous titanium tetra-isopropoxide (TTIP) on TiO_2 surfaces

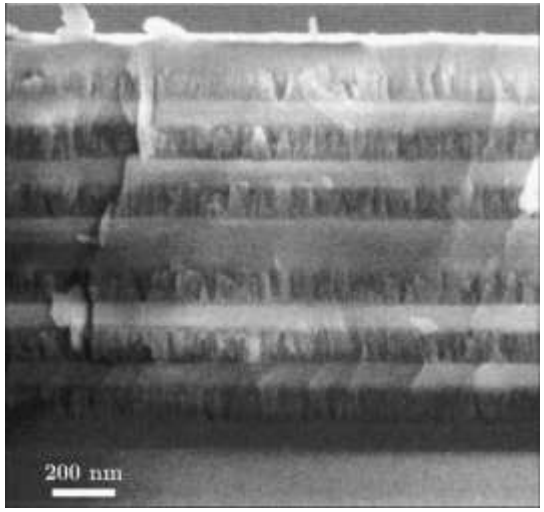
- Applications in electrochemical systems



Motivation



densification



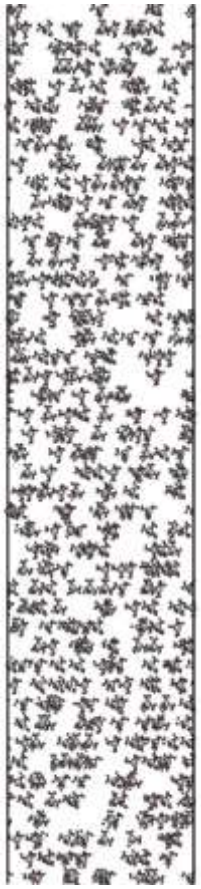
Cross section of the treated SiN_x:H filter film

- Plasma Enhanced Chemical vapor deposition (PECVD): surface treatment, thin film growth, ion densification …
- Ti-$(OC_3H_7)_4$/TiO_2 commonly used in optical devices
- Details of thin film growth mechanisms not well understood

Vernhes and et al, JAP, 99 (2006)

Building Porous TTIP Layer on TiO_2 Support

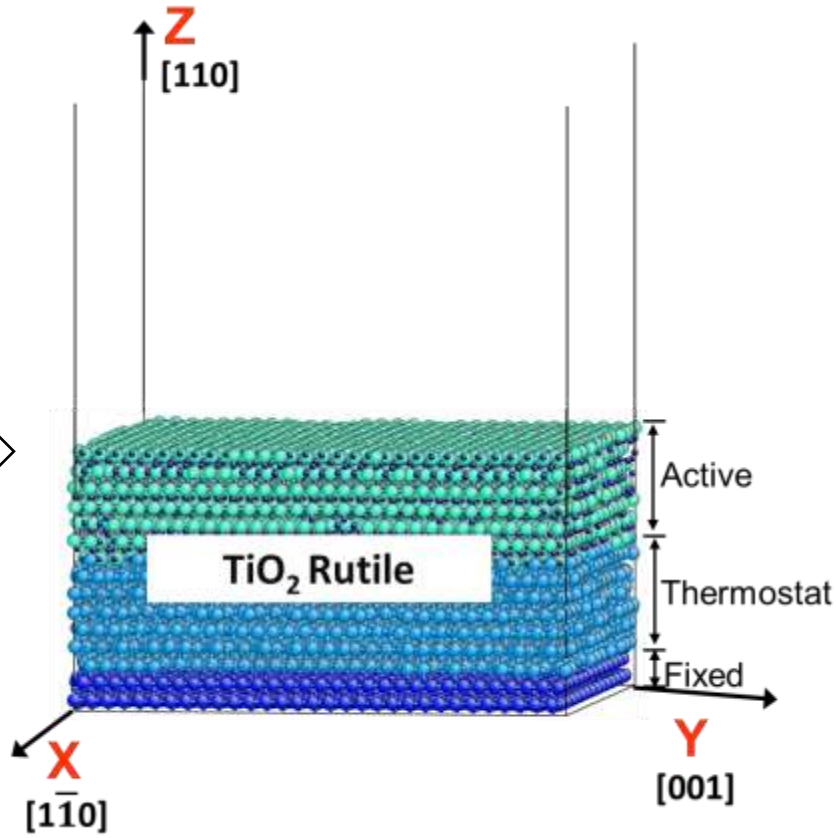
TTIP



500 TTIPs

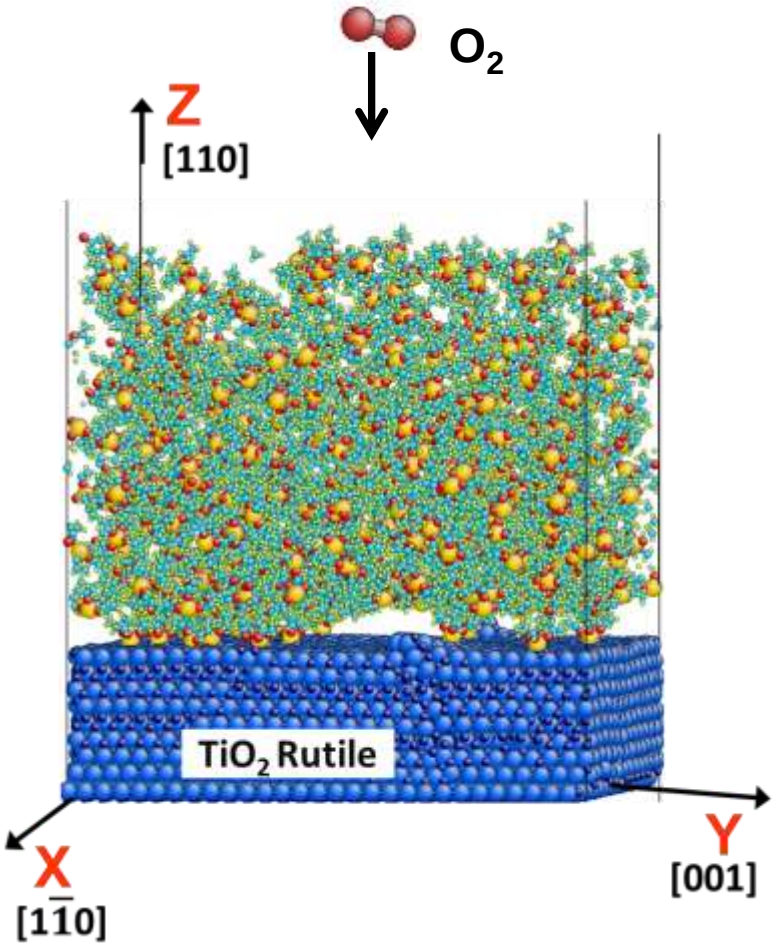
Depositing on TiO_2 support

5 eV/mole



TiO_2 support (9x9x5 nm)
TiO- or O-terminated TiO_2 (110)

System Configuration for Densification with O_2



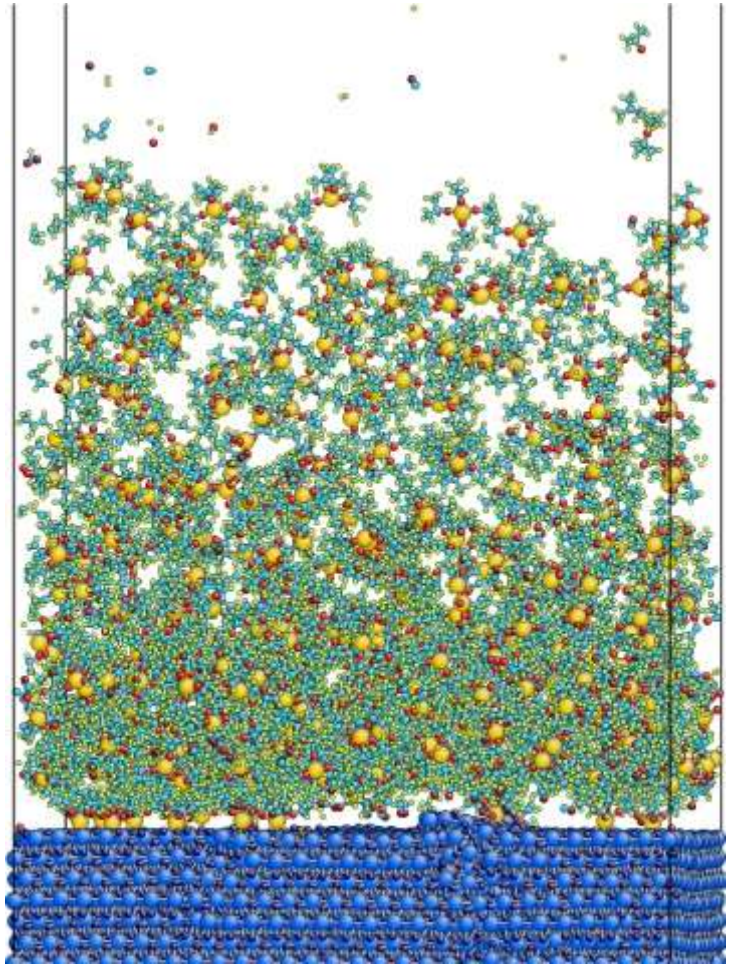
Densification settings:

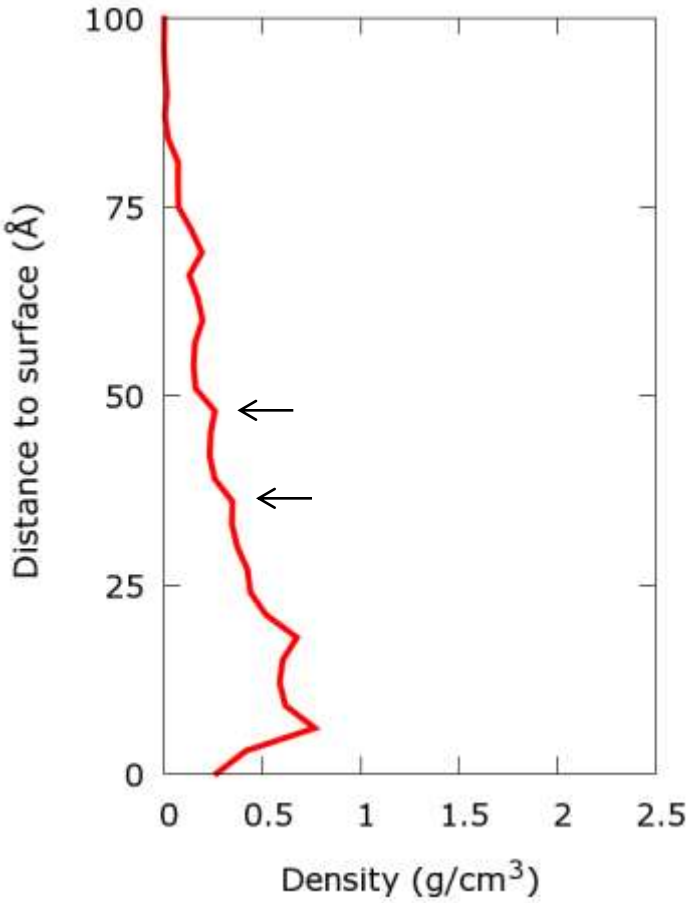
- Incident energy 100 eV/O_2
- Every round has 400 O_2 molecules
- Performed 5 rounds of bombardment
- Ion/TTIP ratio: 4

- Thermostat at 300 K
- Relaxation time between incident beams 0.5 ps
- Time step 0.2 fs

Porous TTIP layer with TiO_2 support

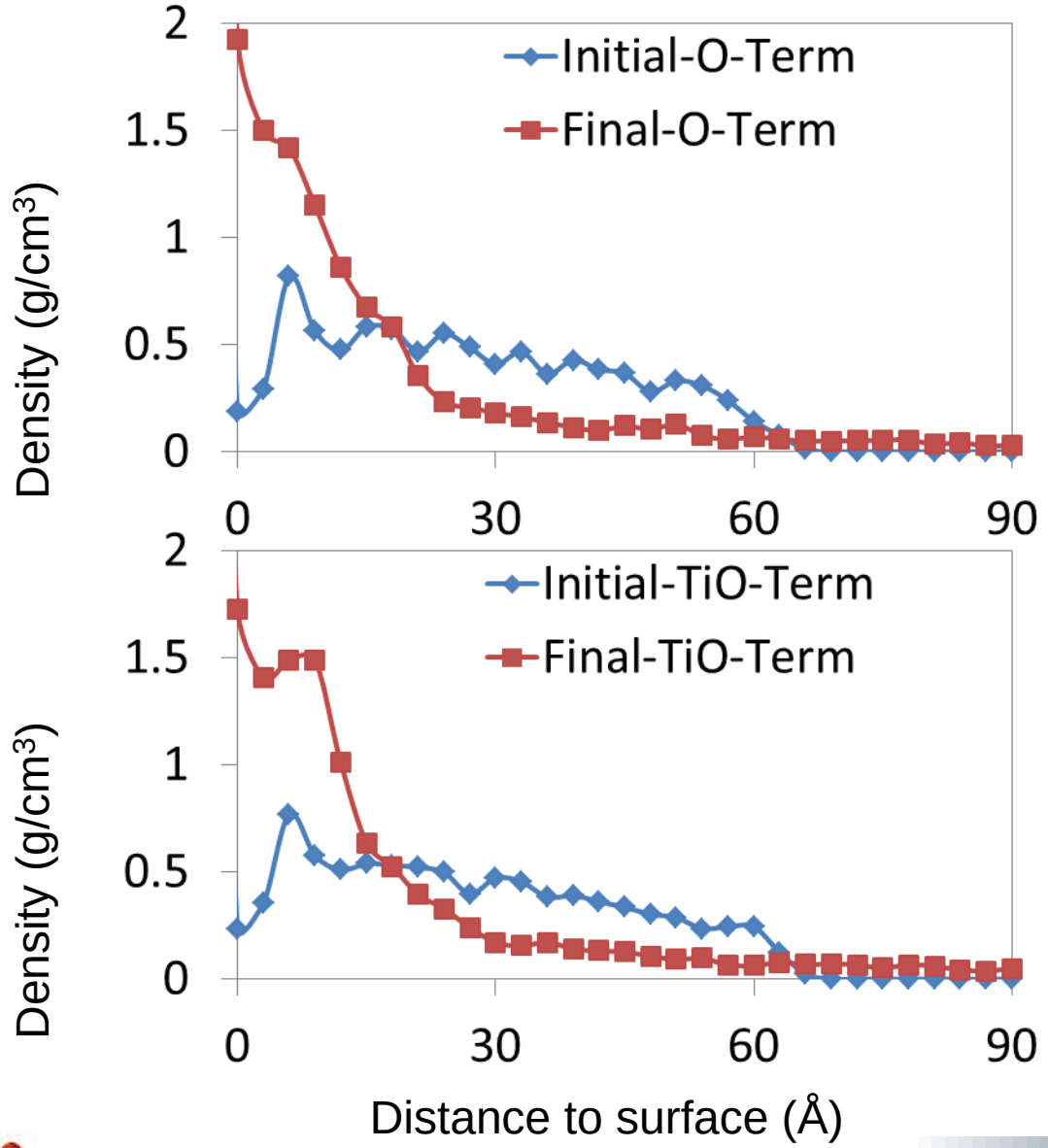
TTIP Desorption





At early stage

Densification



- Density increases more than two times near the surface region
- Densification only happens around 1.5 nm above the surface
- No TTIP stay as TTIP
- Wide range of molecular segments formed
- More than 200 water molecule form

- O_2 densification of porous titanium tetra-isopropoxide (TTIP) on TiO_2 surfaces

- Applications in electrochemical systems
  - Recent change in O_2
  - Reactive water potential with the variable charge
  - Proton transfer
  - Applying voltage in the variable charge potentials

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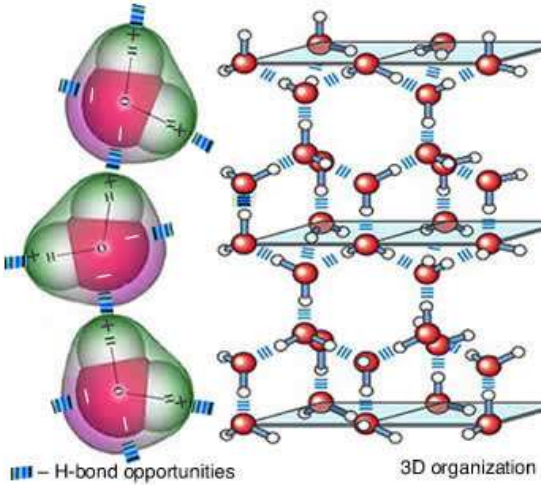
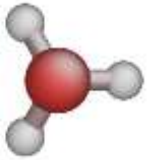
Water Properties (within training database)

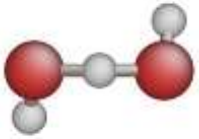


Properties	TIP4P	SPC/E	Exp.	COMB
H_2O				
ΔH_f (eV/mole.)			-2.50	-2.41
Charge on O, q_O (e)	-1.04	-0.82		-0.71
Dipole moment (eÅ)	0.62	0.49	0.39	0.42
Ice I_h				
a (Å)			4.52[a]	4.55
c (Å)			7.36[a]	7.39
O-O distance (Å)			2.76[b]	2.78
ΔH_f (eV/mole.)			-3.02[c]	-3.16
Charge on O, q_O (e)	-1.04	-0.82		-0.87
Dipole moment (eÅ)	0.62	0.49	0.52[d], 0.64[e]	0.53

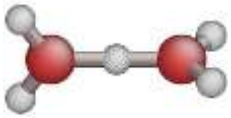
H_2O



H_3O

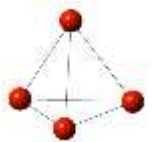


H_3O_2



H_5O_2

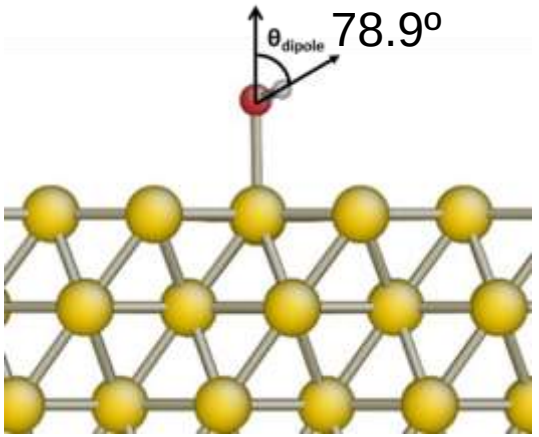
Structures	Exp. or DFT	COMB
H_2O	-2.41	-2.41
HO	0.38	0.31
H_2O_2	-1.34	-1.72
H_3O	1.25	1.25
H_3O_2 ($HO\text{-}H_2O$)	-1.80	-1.80
H_5O_2 (H bridge 2 H_2O)	-1.45	3.40

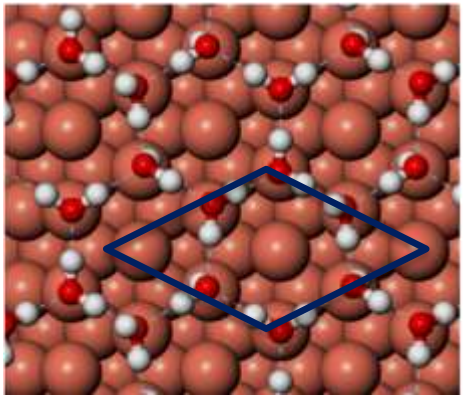


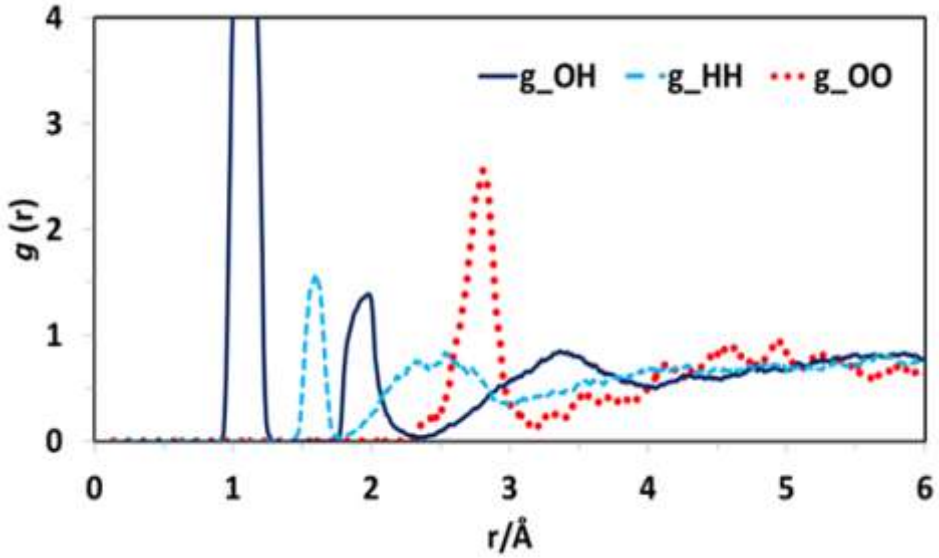
Predicted water properties

Selected properties of water

	TIP4P	SPC/E	Exp	COMB
ΔH_f (eV/unit)			-2.96	-2.81
ΔH^{sol} (eV/unit)			-0.46	-0.40
Density (g/cm^3)	0.99	1.02	1.00	1.00
Dipole (eÅ)	0.45	0.49	0.6	0.45
Diffusion Coeff. (10^{-5} cm^2/s)	3.9	2.52	2.30	0.96

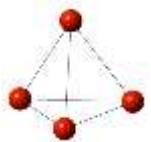




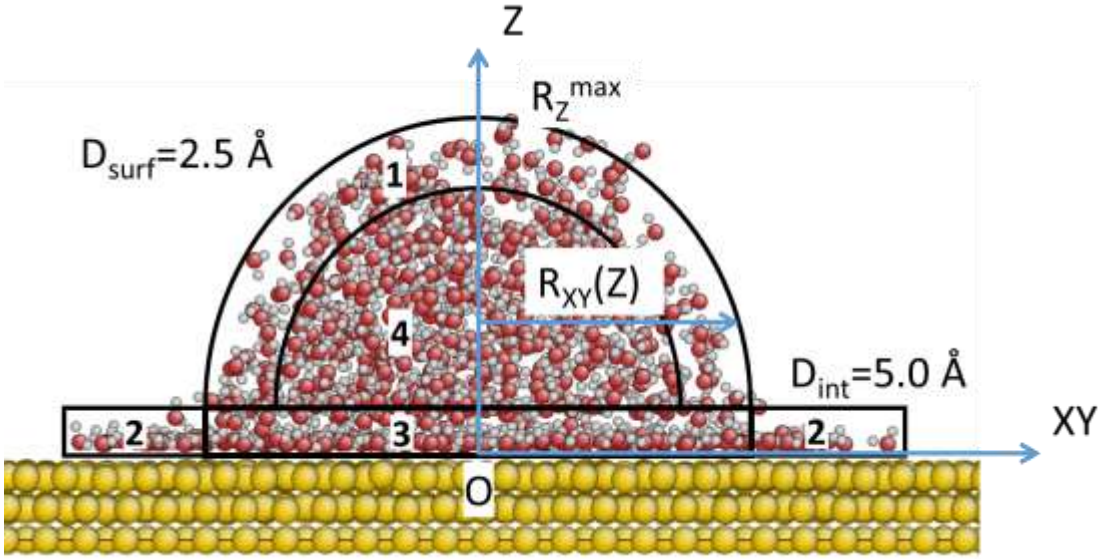


Pair distribution of water

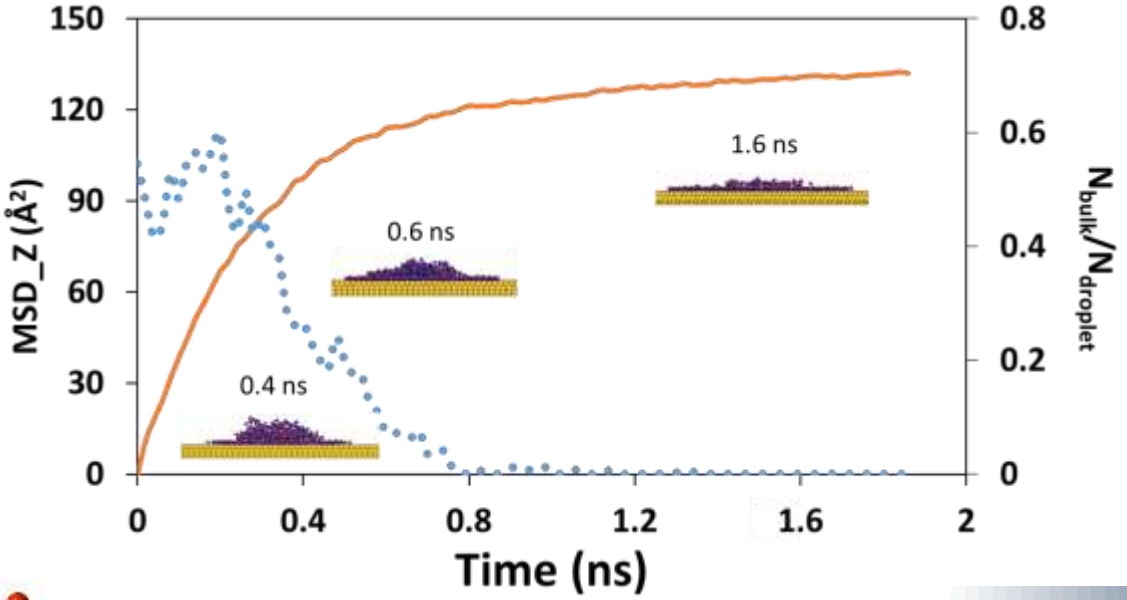
	DFT+vdW	COMB3
H_2O_{atop}	-0.40	-0.49
$H_2O_{fcc/hcp}$	-0.28	-0.54
H_2O_{dimer}	-0.55	-0.59
$H_2O_{hexamer}$	-0.73	-0.91



Wetting Mechanism

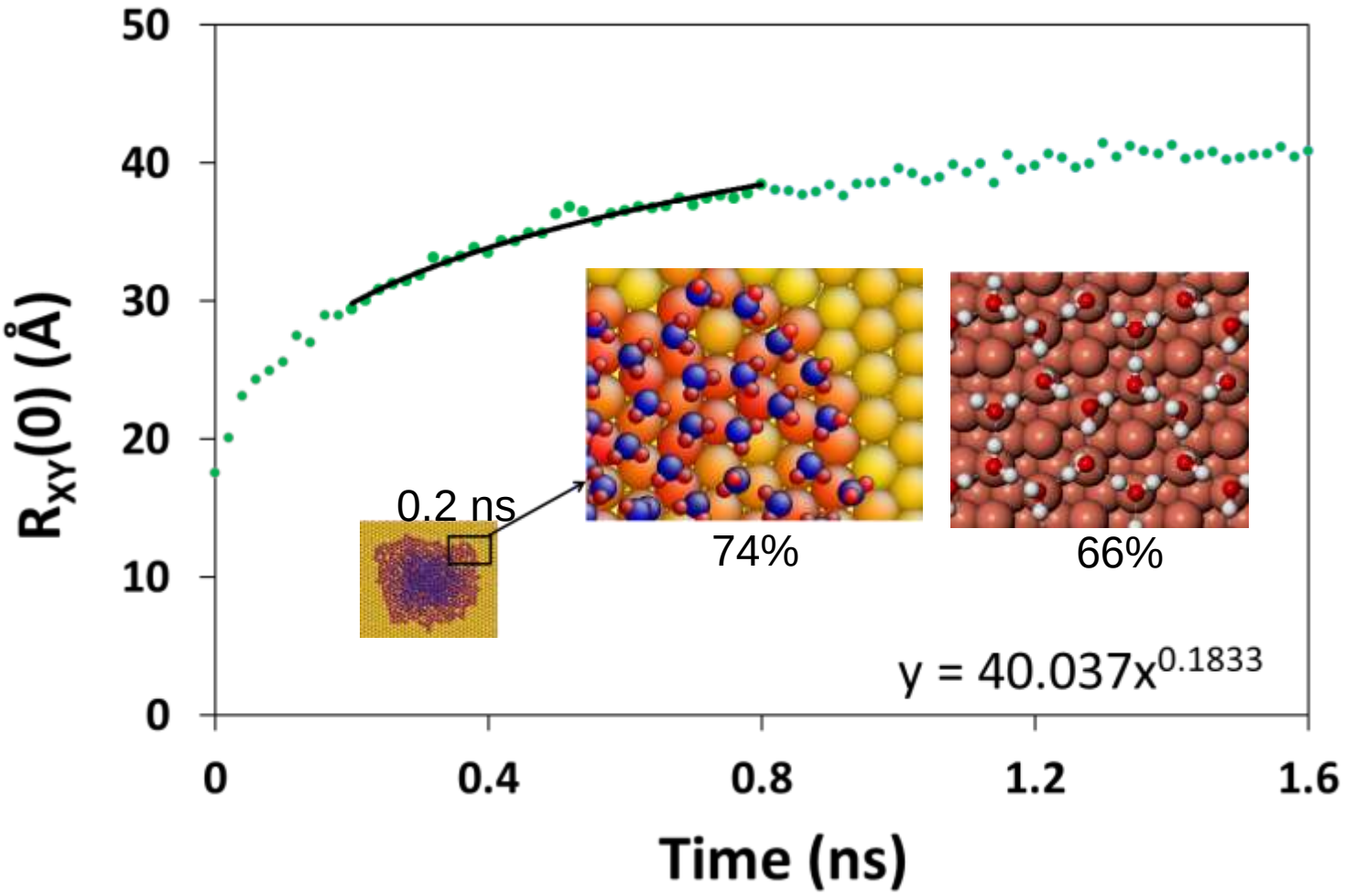


1. Surface water
2. Precursor water
3. Interfacial water
4. Bulk water



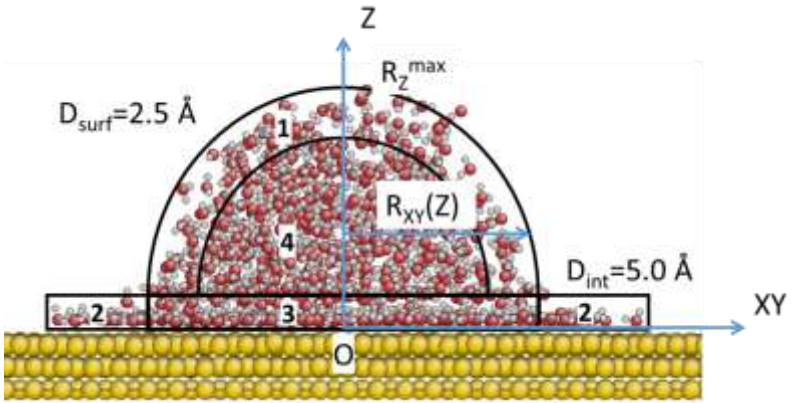
No bulk water after 0.8 ns

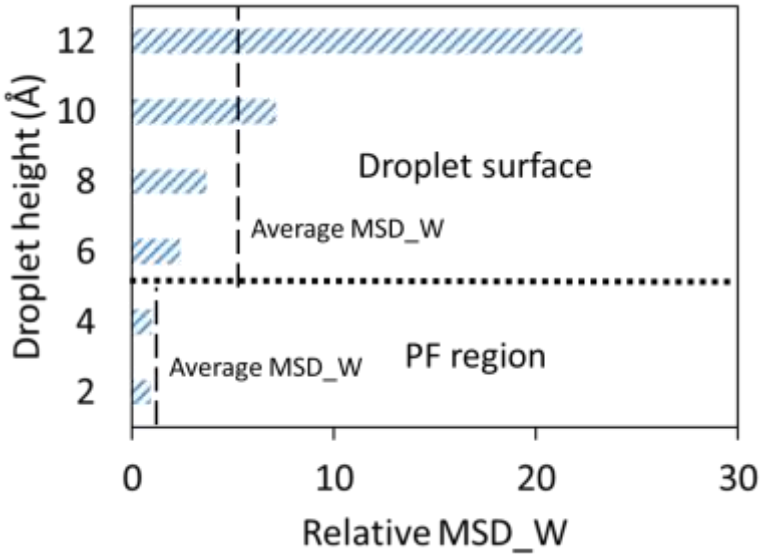
Wetting Mechanism

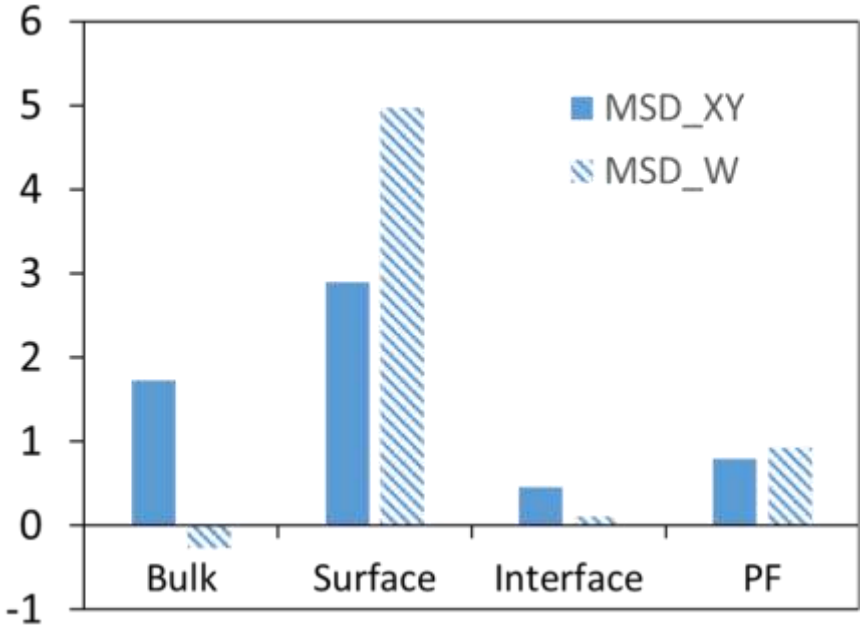


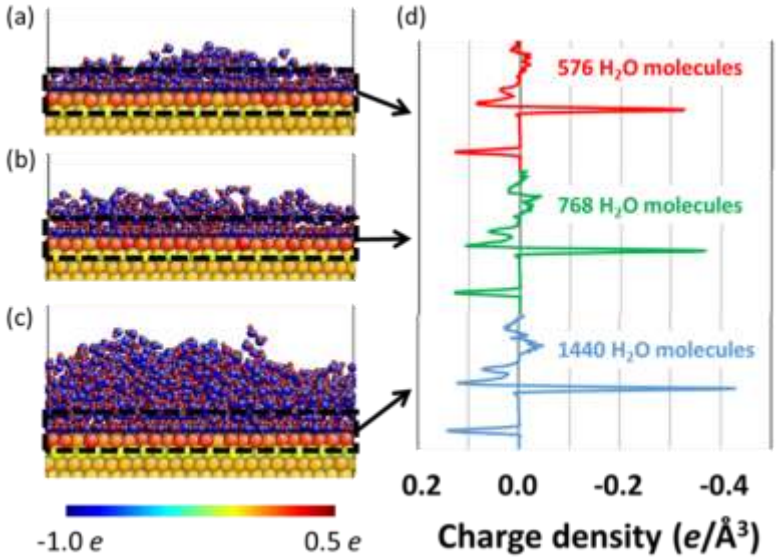
$R \sim t^{0.15}$

Wetting Mechanism

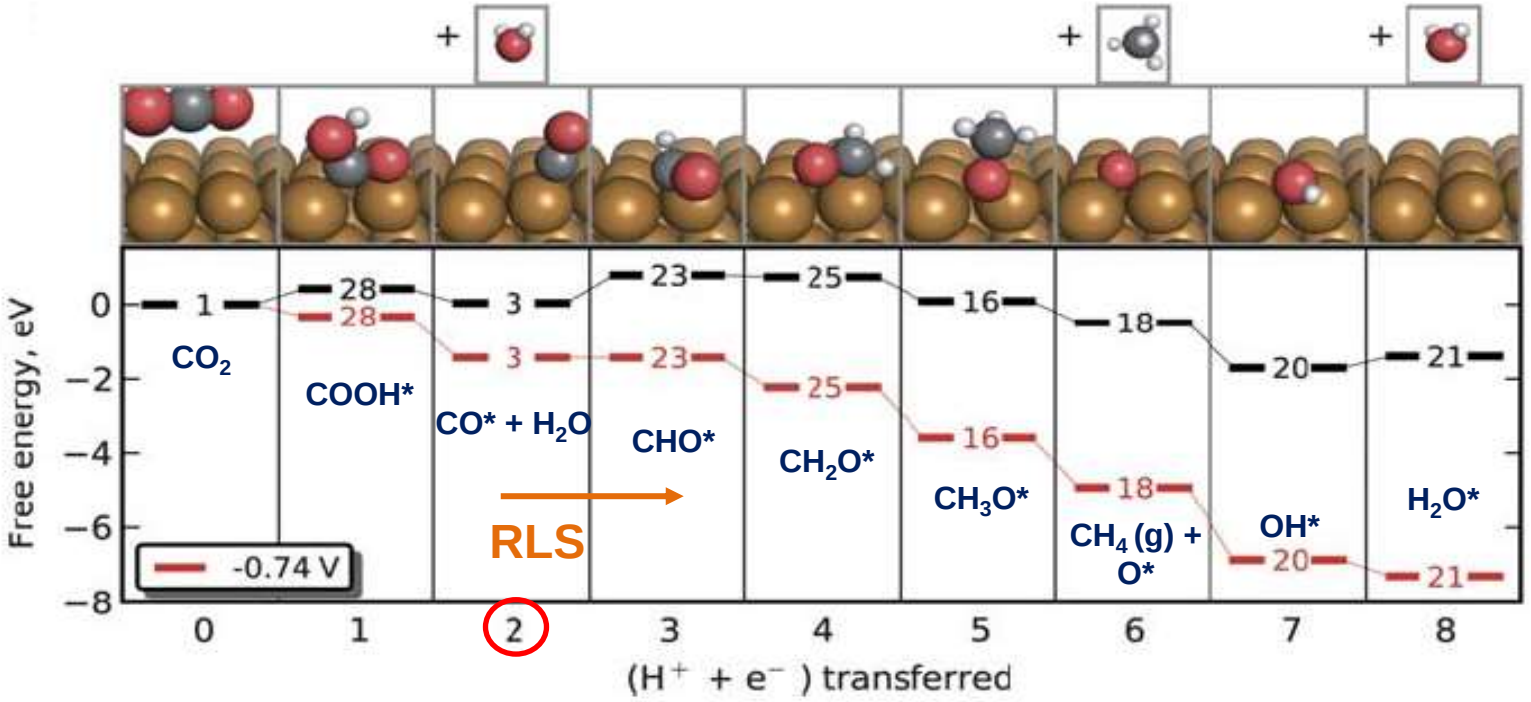








Reaction Energies ΔG of Steps in Electrochemical Reactions



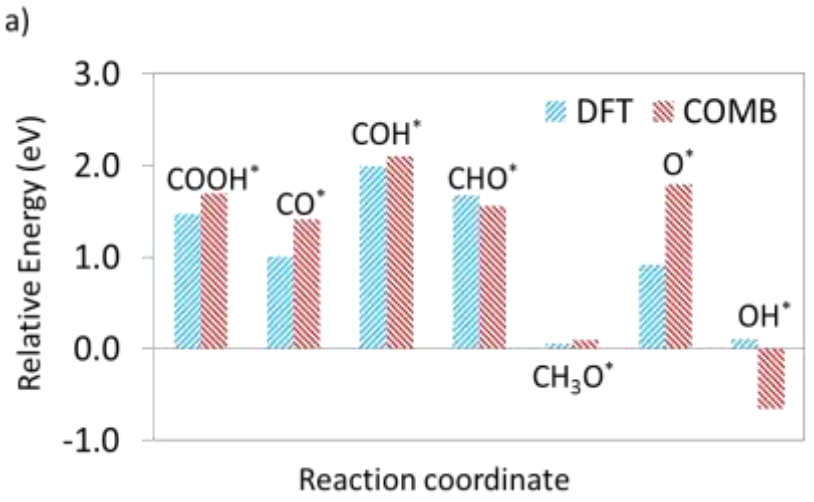
$$CO_2 + 2\,H^+_{(aq)} + 2\,e^- \rightarrow CO^* + H_2O$$

$$\Delta G_{CO^*}(U) = G_{CO^*} - G_* - G_{CO2(g)} + G_{H2O(aq)} - G_{H2(g)} + 2\,eU$$

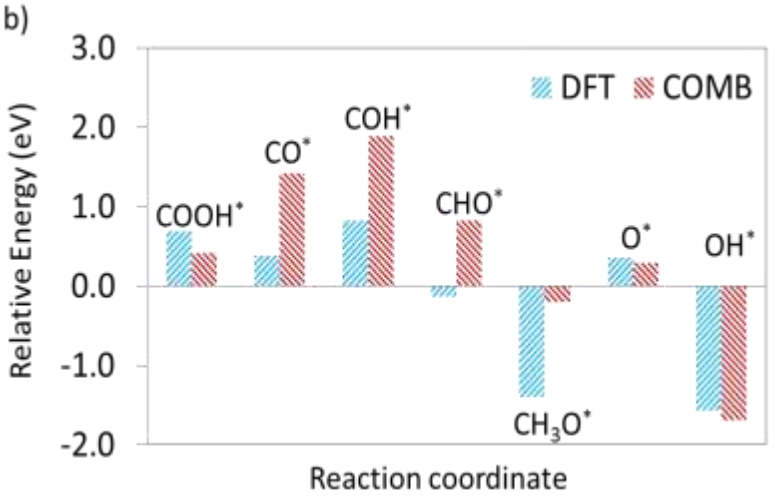
Kinetics dictate the activity and selectivity with the CO_2 ER pathway

Peterson, Andrew A., et al. *Energy Environ. Sci.* 3.9 (2010): 1311-1315

CO_2 Reduction on Cu and 1ML Cu/ZnO



Cu (111)



1 ML Cu/ZnO

The calculated reaction energies with added entropic terms at 0V vs. RHE

Reaction	Surface	DFT (eV)	COMB (eV)
$CO^* + H^+ + e^- \rightarrow COH^*$	Cu (111)	1.31	1.02
	1ML Cu/ZnO	0.83	0.85
$CO^* + H^+ + e^- \rightarrow CHO^*$	Cu (111)	0.96	0.44
	1ML Cu/ZnO	-0.14	-0.22

T. Liang and etal, CAT. Comm., 52 (2014)

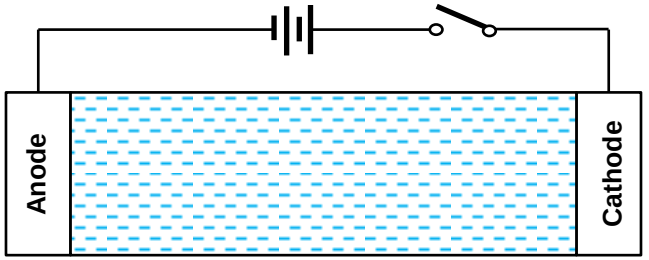
Applying Potential in COMB3

At ES equilibrium:

- Electronegativity ($\partial U/\partial q$) is equal at all sites

$$\chi_i = \frac{\partial U}{\partial q_i}$$

$$\bar{\chi} = \frac{1}{N}\sum_i \chi_i$$

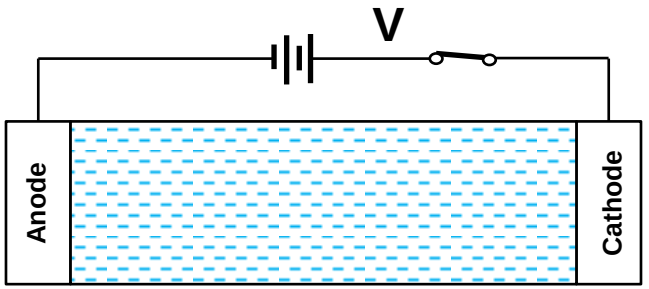


EOM $m_q \ddot{q}_i = \bar{\chi} - \chi_i + \upsilon \dot{q}_i$

At ES non-equilibrium:

- Electronegativity is biased by V

$$\frac{\partial U_{cathode}}{\partial q_i} - \frac{\partial U_{anode}}{\partial q_i} = V$$

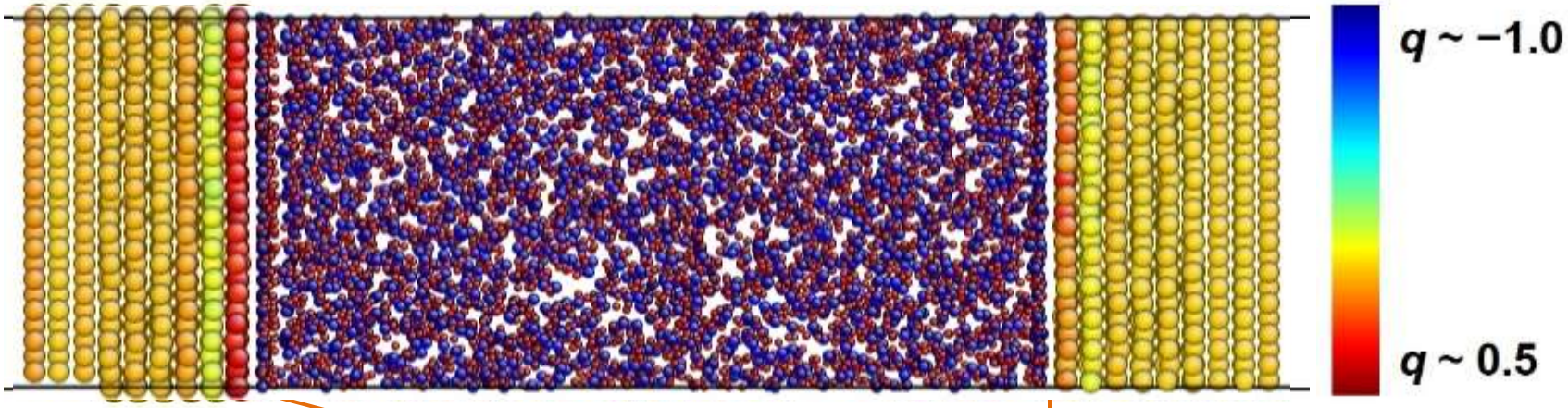


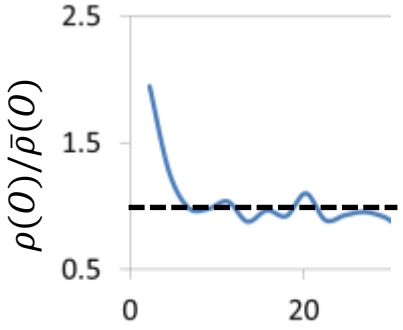
E: $m_q \ddot{q}_i = \bar{\chi} - \chi_i + \upsilon \dot{q}_i$

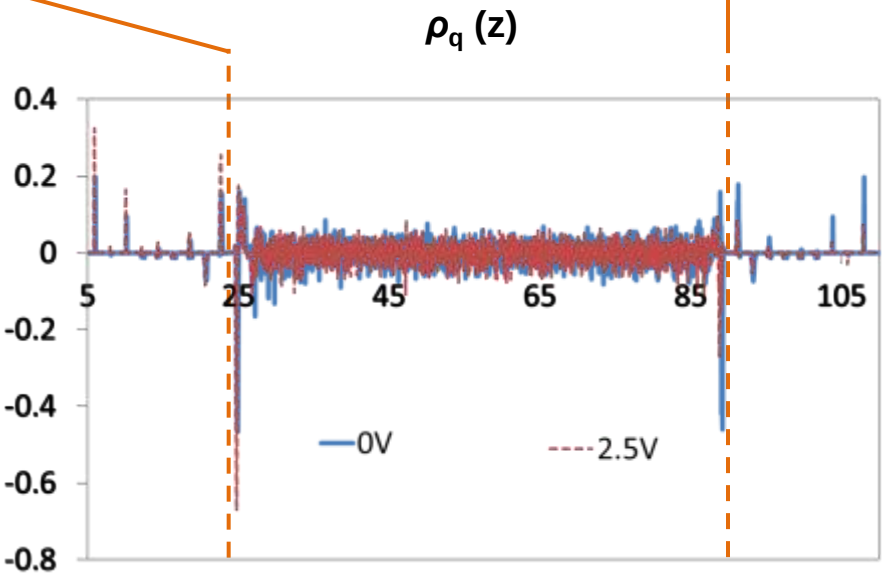
C: $m_q \ddot{q}_i = \bar{\chi} + \frac{N_C}{N_A + N_C} V - \chi_i + \upsilon \dot{q}_i$

A: $m_q \ddot{q}_i = \bar{\chi} - \frac{N_A}{N_A + N_C} V - \chi_i + \upsilon \dot{q}_i$

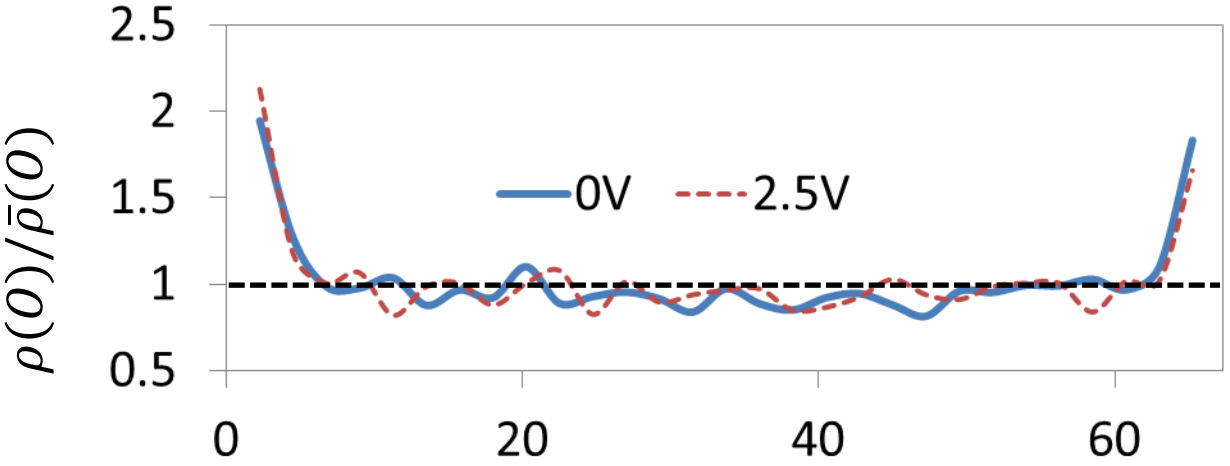
E-COMB Results

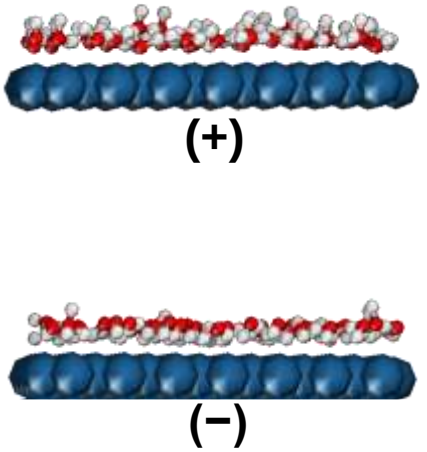


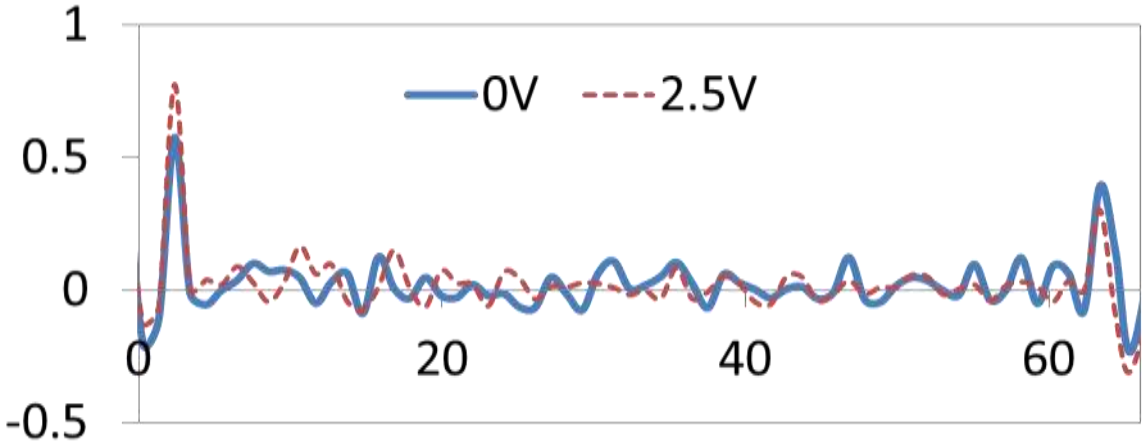




E-COMB Results



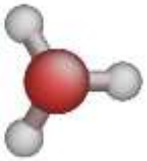




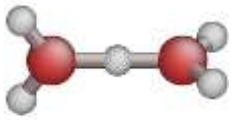
$$P(z) = \langle \frac{1}{N(z)} \sum_{i=1}^{N} \frac{\left(3\hat{\mu}_{z,l}^2 - 1\right)}{2} \rangle$$

Order parameter

Proton transfer

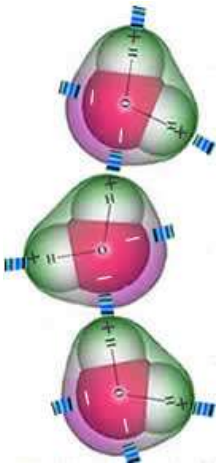


H_3O

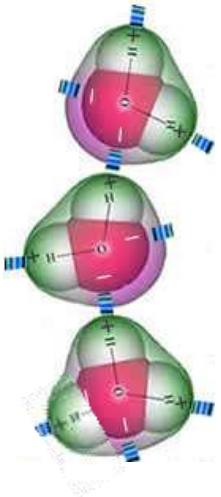


H_5O_2

OH distance = 1.2 Å



OH distance = 0.96 Å
Hydrogen bond = 1.78 Å



Proton transfer

Barrier ~ 0.2 eV
COMB ~ 1.5 eV

Ongoing applications

- CDC materials
- Electrochemical simulations with applied potentials
- TiC_2, Ti_2C_3 2D MXene materials
- Proton transfer in electrochemical systems and MXene materials