Surface Chemistry, Retention and Sputtering of Solid Li, Li-O and C-Li-O surfaces, irradiated by D and D₂

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Princeton Plasma Physics Laboratory (PPPL)

Current Spotlight

U.S.-China collaboration makes excellent start in optimizing <u>lithium to control fusion plasmas</u>Plasma that fuels fusion must stay stable and hot. Lithium can be effective for both, researchers find.





Our thanks to John Hogan (FED, ORNL)

Many thanks to PMI close collaborators in the past:

Theory:

CMD



PWDFT 🗸

Mat

ORNL

CMD 🔰



TBDFT modeling



Carlos Reinhold PD, ORNL

- **Steve Stuart** Clemson U.
- Paul Kent Alain Allouche CNRS, Fr

Yong Wu, IAPCM, China K. Morokuma, J. Jakowski, NICS, ORNL Kyoto U., Jp

H. Witek, Taiwan

Experiment:



Fred Meyer Eric Hollmann D. Stotler Chase Taylor (PD, ORNL) (UCSD) PPPL (Purdue, INL) beam and plasma beam plasma Jeff Harris, Rick Goulding, FED, ORNL

Past Students in PMI



lae	lonny	Chris
(ORISE)	(UTK)	(MTSU)
PhD	PhD	PhD

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Present collaborators in PMI: Many thanks!



F. Bedoya UIUC (PD)



J.P. Allain UIUC



R. Kaita, PPPL



C. Skinner PPPL



EXPE





S. Irle, ORNL 13-15 March, 2019 L. Han, IACS



J. Dominguez, IACS



Y. Zhang, EMNL,SBU



R. Harrison IACS Т

J. Wells

ORNL

THEO

Guiding principles:

6

If Edison had a needle to find in a haystack, he would proceed at once with the diligence of the bee to examine straw after straw until he found the object of his search... I was a sorry witness of such doings, knowing that a little theory and calculation would have saved him 90% of his labor. –Nikola Tesla, New York Times, October 19, 1931

"You do not really understand something unless you can explain it to your grandmother." Albert Einstein



The traditional trial-and-error approach to PMI for future fusion devices by successively refitting the walls of toroidal plasma devices with different materials and component designs is becoming prohibitively slow and costly

Need bottom-up approach arising from the fundamental atomistic and nano science with the primary goal to understand the phenomenology of PMI for fusion

LAYOUT (Why, How, What?):

- Why to study PMI for nuclear fusion?
- Methods of simulation; preparation of a target CMD: REAXFF QCMD: SCC-DFTB
- Results: Main Accomplishments LICO:D, BCO:D, LiBCO:D, LiO:D systems retention, sputtering

WHY are we DOING IT?

Challenges at the Plasma-Material INTERFACE

This is not the material science! Science of the interface has many fundamental processes & synergies



Application of SCC-DFTB: Lithium wall conditioning improves confinement! Why?

• From in-situ experiments labs, and more than 7 different tokamak machines (TFTR, CDX-U, FTU, DIII-D, TJ-II, EAST, and NSTX): Graphite with thin lithium coatings have a "significant" effect on plasma behavior: Reduced hydrogen recycling, erosion and ELMs, improved energy confinement time



• Initially the experimentalists conjecture was that there was some "functionality" that governed the behavior of the Li-C-O-H system observed indirectly by analyzing the O(1s) and C(1s) peaks.

Working assumption was that the main generator was Li-H chemistry

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Lithium dynamics: Difficult to study theoretically by usual classical MD because of Li polarizing features when interacting with other elements

Electronegativity is chemical property of an element defining its tendency to attract electrons: Li has it exceptionally low in comparison to H , C, O, Mo, W.



Quantum-Classical MD based on Self-Consistent-Charge Density-Functional Tight-Binding (SCC-DFTB) method (developed by Bremen Center for Computational Mat. Science, Germany) a possible answer for qualitative phenomenology is our choice Li-C-O-H parameterization came form K. Morokuma and S. Maeda, Kyoto U.

"State of the Art" Plasma Simulation Codes Use Rudimentary PMI Models

- SOLPS = B2 (2-D fluid plasma transport) + EIRENE (3-D kinetic neutral transport) used to simulate JET, design ITER, etc.
- UEDGE (2-D fluid plasma transport) & XGC (kinetic plasma turbulence & transport) use specified recycling coefficients,
 - Can be coupled to DEGAS 2 kinetic neutral transport to use TRIM reflection data.
- PMI do not evolve in response to plasma ⇒ no consistent solution to plasma-material system.
- Replace with dynamic, first principles, atomistic, multi-scale model:
 - Consistent treatment of D retention & recycling,
 - Surface morphology evolution through erosion & redeposition,
 - Kinetic characterization of impurity sources,
- Etc. 13-15 March, 2019

Multiscale nature of the physical processes at interface How does PMI see a flux of 10²⁵ particles/m²s mean (ITER)?

The flux is 0.01 particle/nm²ns, i.e. 1 particle each 10 ns at 10 nm²



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Interface is dynamic, changing on nanoscale!!! A typical evolution of deuterium impact at 100 eV even with chemical sputtering in carbon takes no more than 50 ps, and penetration no more than 2 nm; in tungsten events even faster

Each particle will functionalize the material, change the surface for the subsequent impact! Processes essentially discrete Atomistic Happening at nanoscale in both time and space, scales determined by impact plasma particle energy

The traditional trial-and-error approach to PMI for future fusion devices by successively refitting the walls of toroidal plasma devices with different materials and component designs is becoming prohibitively slow and costly

Need bottom-up approach arising from the fundamental atomistic and nano science IAEA CRP: Atomic Data for Vapor Shielding in Fusion Devices, RCM#1, Vienna

Building from bottom-up



How uncertainty propagates through scales?

As these computational codes have limits, so do the experimental and metrology tools. The key is to fill the gaps in knowledge from both approaches and recognize regions of validation in combination with the data uncertainty and more importantly *identify appropriate and strategic problems to solve*

HOW WE BUILD PMI THEORY?

Uncertainty Quantification Quantifying uncertainty in computer simulations

Sensitivity Analysis (which parameters are most important?) Variability Analysis (intrinsic variation associated with physical system) Uncertainty Analysis (degree of confidence in data and models)

Uncertainty quantification in computer simulations is an active&recent research area: *A key for credible predictions*

Currently Applied in: Meteorology, Geology, Engineering (FEM-codes) Military Research (Accelerated Strategic Computing Initiative (ASCI (2000)).

Recent international workshop at Stony Brook U. brought together physicists in plasma,

materials and atomic physics and UQ mathematicians to help developing UQ in fusion related sciences: Adequate algorithms exist, need to be adapted by joined effort, http://www.iacs.stonybrook.edu/uq/pages/workshop

METHODS: Use all tools available and reasonable

Classical Molecular Dynamics (CMD) with REAXFF method and potentials

What is CMD?

In generic sense method which solves Newton equations of motion of all atoms in a sample.

Atoms mutually interact with forces which are determined by gradient of the potential, which is given in advance. Classical potential for a given mixture of atoms is a fit of many parameters, fit functions define various potentials (BOP, EAM,....) +parameters calculated by QM (usually DFT)+ Empirical (exp.) parameters. **CMD is as good as the potential used is good.** *Why do we chose REAXFF potential*? It is BOP, i.e. simulate chemistry within accuracy, has showed good in other applications. **LAMMPS with REAXFF** is capable to re-calculate charges at the atoms after each step or number of steps, **using EEM**, EEM: semi-empirical, semi-quantum method. CMD cannot calculate anything with electron cloud. *Why do we need EEM*? Our atoms have different electronegativities. Thus, LI has 0.94, B has ~2, C and H have ~2.5, O has 3.4. This means atoms could mutually charge and long range Coulomb forces will influence dynamics.

Quantum Classical Molecular Dynamics (QCMD) with SCC-DFTB quantum component

What is QCMD?

Each time step (fraction of fs) freeze all atoms and solve QM problem for all electrons. From this it follows QM potential and its gradient gives forces, to move atoms between the steps by CMD with QM "frozen". *Why we chose SCC-DFTB*? It is a good approximation to DFT, the QM method, which is about 1000 times faster than DFT. QCMD is still 1000 slower than CMD, but about 100 times slower than REAXFF-CMD (because of EEM). QM component of QCMD calculates all charges and forces dynamically, no need for potential defined in advance, or EEM to treat charging.

Because QCMD is here 100 slower than CMD, we do CMD but verify the results occasionally by QCMD.

Classical MD is only as good as the interatomic potential model used

Most advanced: hydro-carbon potential developed for chemistry

- Brenner, 1990, 2002 : REBO, short range, 0.2nm
- more sophisticated AIREBO (Stuart, 2000, 2004, 1.1 nm)
- > 400 semi-empirical parameters, "bond order", chemistry

Adaptive Intermolecular Reactive Bond Order (AIREBO) potential : torsion, dispersion, Van der Waals,

EX: MD calc. of reflection coeff.

- Significant sensitivity to changes in potential model for some processes
- Experimental validation essential to establish credible MD simulation.
- Interatomic potentials for W, Be, C exist (talk of Nordlund)
- Experimental validation?

Improvements to CH potentials done (Kent et al, 2010) New Li-C-H-O potentials being developed (Dadras et al,

Even for hydrocarbons problems visible



Examples of verification of CMD/REAXFF vs. QCMD







In BCOD with 20% O and 20% of B, bonding of D to O suppressed by B?

Both methods give this effects qualitatively, numbers somewhat different

Filled symbols is CMD/REAXFF

How efficient are various constituents of a surface in bonding D?

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More examples of validation with experiment

Exposure to plasma Days after boronization Partial cleaning each day 100 B-O-D O-C O-B COC-OC-C -<mark>O-</mark>DB-C Experiment: MAPP in NSTX-U B-O B-D B-B 80 60 40 20 (b) B1s 01s C1s (a) Boronization B(CD3)3 OC 100 OB 12 **Atomic Percentage (%)** 00 00 09 00 00 00 OBD 100 Carbon Bonds (%) 00 00 07 00 08 (b) CC Intensity CO CB CD 12 -2 10 Time after last boronization (Days) 100 D O- (BD) BC Calculation (-->) done for 20% of ²⁹⁰ ²⁸⁵ ²⁸⁰ Binding energy (eV) 534 528 198 192 540 186 BO B and O and 60% of C following exp (above) 40⁄ XPS at days of BD 20 OBD Approx. conc. 13-15 March, 2019 as left BOC 12% D 24% D 38% D IAEA CRP: Atomic Data for Vapor Shielding in Fusion Devices, (Krstic et al, Nucl. Fusion 57 086050, 2017 RCM#1, Vienna Surface configuration

Preparation of a target surface: learned from experiment

1) Populate amorphous carbon cell with desired % of Li, B, O atoms randomly distributed. Size of the cell depends on the desired impact energy.

- 2) Heat, anneal it until all atoms sit "comfortably" in their potential chairs
- 3) **Thermalize** the sample to desired T (usually 300K-most of the experiments).
- 4) If study hydrogenated sample at a given impact energy, **bombard the sample with H (D)** and register the implanted % (after each impact stabilizes thermalize the sample, relax).

10

0

z (Angstrom)

b)

—5 eV

- · 10 eV

-- 20 eV 30 eV

-10

 $3x10^{3}$

Time (ps)

5) The 2D **periodicity in the** surface direction is applied in all steps: Surface boundary -5 eV



BCO cell bombarded by 5 eV D (yellow) 13-15 March, 2019

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 5×10^{3}

6x10³

Implanted D (in Li-C-O)



Element/E nergy	5 eV	10 eV	20 eV	30 eV
D _{acc} (%)	10.18	11.52	13.02	14.18
C (%)	54.26	53.65	52.79	52.09
Li (%)	17.54	17.18	16.98	16.51
O (%)	18.02	17.65	17.21	17.22

Method of calculation for any variable

- 1)Take the **target cell, prepared** for a particular energy, temperature,..., with a desired % of accumulated D
- 2) **Vary** a position of the **impact particle randomly** over the surface, defining impact trajectories
- 3)**Repeat the impact** of each of these trajectories and do full computation (typically 5,000 trajectories)
- 4)Calculate the desired results for each trajectory, and **do statistics** over all trajectories (ME, SD, SE,...).
- Repeat the procedure of preparation and MC bombardment for each set of input parameters (impact energy and angle, T, surface mixture,...

Do not apply thermostat during the collision cascade!!!

• Verify and validate, present results (ME +SE)

Examples of the successes of the atomistic aproachs to PMI processes



Remarkable agreement of theory & beam exp't when simulation prepare the sample at the level of nanoscale (fluence) to mimic exp't. No fitting parameters! CARBON

Chemical sputtering of carbon Meyer et al, PS T128, 50 (2007).

LITHIUM

Krstic et al, Phys. Rev. Lett. 110, 105001 (2013)



Presence of Li requires QM approach on nm scale, resulted in answer:

If there is a SIGNIFICANT amount of oxygen on surface with lithium present in the graphite matrix, OXYGEN becomes the main player in retentionerosion chemistry; NOT LITHIUM!!!

Main challenges and opportunities in the new phenomenologies lay by far in the lithium based divertor!!!

RESULTS

1) D retention in Li-C-O (2013, 2017)

Krstic et al, Phys. Rev. Letters **110**, 105001 (2013) Dominguez et al, Nucl. Mater. Energy 12, 334 (2017)

2) Chemical sputtering by D impacts of Li-C-O (2018) Dominguez et al, J. of Nucl. Mat. **492**, 56 (2017) Dominguez et al, Nucl. Mater. Energy **12**, 334 (2017)

3) D retention in Li and oxidized Li as function of T (90-650K) (2018) Buzi et al, J. Nucl. Mat. 502, 161 (2018).

4) D retention and reflection, sputtering of solid Li by D and D₂ (5-200eV) (2019)

Review: Krstic et al, Matter and Radiation at Extremes **3**, 165 (2018), and references therein (on all Li and boron processes) Bedoya et al, Scientific Reports (Nature) **9**, 2435 (2019), and references therein (on boron processes)

D retention in Li-C-O (2013, 2017)

Oxygen role!!!

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What do experiments teach us?

Experiments from Purdue and NSTX (PPPL) indicate higher retention and lower erosion rate with D whenever Li present in C, however XPS diagnostics show dominating D-O-C chemistry. Why – was the question?

From experiments: There was correlation between hydrogen irradiation and the behavior change of the O(1s) and C(1s) peaks ONLY IN THE PRESENCE OF LITHIUM.

The Li(1s) peak was always invariant????



But theory says:

D has only a slight preference for interacting with Li rather than with C. Krstic et al., FED (2012)

Challenge!

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Simulations: How much is uptake of D correlated to O and Li contents?



If there is a SIGNIFICANT amount of oxygen on surface with lithium present in the graphite matrix, OXYGEN becomes the main player in retention-erosion chemistry; NOT LITHIUM!!! SCC--DFTB method, QCMD

How did we do this?

+ REAXFF, QMD

Simulation of deuterium impact to lithiated and oxidized carbon surface (quantum-classical approach, DFTB)

Accepted challenge 🙂



Cell of a few hunreds atoms of lithiated and oxidated amorphous carbon
(~20% of Li, and/or ~20% of O), at 300K
How?

•By random seed of Li and O in **amorphous carbon** and **energy minimization**, followed by thermalization

•bombarded by **5 eV D** atoms, up to 500fs for the full evolution

•Perpendicularly to the shell interface

•5004 **random trajectories** (embarrassingly parallel runs at Jaguar, Kraken); Time step **1 fs;** 30,000-50,000 CPU hours per run, number of runs > 10.

Analysis

Quantitative results



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Here comes the experiment again (Taylor):

How to get high concentrations of Oxygen in the surface? How could we study 100's of eV and keV impacts with 5 eV D?

Sanity check!





D interactions with lithiated graphite



- (left) The surface chemistry is found independent of the incident energy
- (right) With lithium on graphite, surface concentration of Oxygen increased upon bombardment by D

J.P. Allain and C. Taylor, Purdue U.

At most 5% oxygen content on the surface of NON-LITHIATED graphite... AS EXPECTED.

With lithium one gets 10% of Oxygen

IMPORTANT: with LOW-ENERGY IRRADIATION one gets 20-40% oxygen on the surface.

..... B/C LITHIUM BRINGS IT THERE WHEN LITHIATED GRAPHITE IS IRRADIATED.

Normalized Intensity (a.u.)

What have we learned from both T&E?

It is not Lithium that suppresses erosion of C, and increases retention of H

OXYGEN plays the key role in the binding of hydrogen.

Lithium is the oxygen getter: Lithiation of C brings A LOT OF Oxygen inside C and this the main role of Li. If there is a SIGNIFICANT amount of oxygen on surface with lithium present in the graphite matrix, OXYGEN becomes the main player; NOT LITHIUM!!! Oxygen and Oxygen-Carbon bond D strongly: suppressing erosion & increasing D retention. ... consistent with the XPS data!!

Krstic et al, Phys. Rev. Letters, 2013

Chemical sputtering by D impacts of Li-C-O (2018)

Sputtering of lithium configurations

Components Li, C, O 10 Sputtering yield per D 0^{-2} SCC-DFTB Li-C:D Li-C-O:D O Total ∇C ---- Total — Total a-C:D -1-2- $-\Lambda$ – Total 10^{-3} 20 30 10

Total sputtering of the

Impact energy (eV)





large, oxygen suppresses



LiD decreases with energy for LiC:D, and is much smaller for LiCO:D With O the dominant molecular products LiO, OD, OC

Sputtering as would be seen by mass spectrograph



Atomic C and O also the main sputtering products C2D2, CO and LiO at all energies

Sputtered translational energy and angular spectra



Shaded areas: sput distributions at varioua impact energies Symbols: average , solid curves are best fits $(\cos \theta)^a$

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Gray line average over energies

D retention in Li and oxidized Li as function of T (90-650K)

Computation: MD with REAXFF



Temperature (K)		90	305	400	500	600
Pure Li	Li atoms	2000	2000	1998	1995	1991
	Li atoms	1340	1340	1335	1329	1320
	O atoms	660	660	658	656	658

Atomic content for Li and Li₂O target surfaces; Langevin thermostat

O-D and Li-D NNs similarly represented!! Indicates similar efficiency of H or D retention in Li and Li₂O surfaces

Т (К)	90	305	400		500
Li-D (%)	47	45		45	43
O-D (%)	53	55		55	57

Atomic content for Li-D and O-D bonds at various T

Results and comparison with experiment Temper

Temperature programmed desorption (TPD)

Bruce Koel group, PU



Temperature (K)		90	300		400		500		560		600		
	Surface	D_{ret}	%	D _{ret}	%	D_{ret}	%	D _{ret}	%	D_{ret}	%	D _{ret}	%
	Li	4632	91.90	3807	75.53	3472	68.88	3246	64.40			3125	62.00
	Li ₂ O	4842	96.07	4022	79.80	3585	71.11	3316	65.79	2907	57.6 8		
		H_{ret}	%	H_{ret}	%			H_{ret}	%				
	Li	4471	88.701	3630	72.027			3117	61.84				

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D retention and reflection, sputtering of Li by D and D₂ (5-200eV) (In preparation fopr publication)

CONCLUDING REMARKS and LOOK at FUTURE PLANS

- We have shown **published results** for retention, sputtering and surface chemistry of **Li-C-O:D** amorphous mixtures at 300K at chosen impact energies of D, as well as retention of D in Li and Li-O in a range of temperatures (90-650K).
- We have also shown new results for sputtering, reflection and retention of amorphous Li surface by impact of D and D₂,

in range 5-200 eV at room T. Validation with available experiments or computations has been done.

Remarks: The PMI theory has a strong need for exascale (and quantum "if") computing for:

 Integration of the plasma simulation codes and first principles PMI codes at mesoscale (should be doable in next 10 years)

Example: SOL and turbulence transport (XGC1)+neutral particle transport (DEGAS 2) with surface damage & erosion (SPARKS) + particle transport, dust, redeposition (PALABOS)

 Uncertainty Quantification for plasma and PMI modeling Relevant to tokamak plasmas: Data interpretation/analysis, validation of theory, prediction to support "decision making" UQ in tokamak models necessary to support validation (uncertainty in inputs); need for research into the UQ due to model inadequacy; advanced algorithms can help; Should be doable now, but changes in culture of theorists needed.

This year plans:

- Sputtering, reflection and retention of D, D2 (or adequate single charged ions) of **fully deuterated amorphous Li** at 300K (amorphous), range of impact energies 5-200 eV.
- Simulation of evolution of the layers chemistry and morphology upon evaporative deposition techniques of Li and Li₂O Layers on Mo
- Deciphering evolution of the oxidation of Li layers; chemistry and temperature dependence.



Thank you!

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