Deuterium interactions with Li-C-O surfaces

Predrag Krstić

Physics Division,
Oak Ridge National Laboratory

Support from: US DOE (OFES)
and
ORNL LDRD program

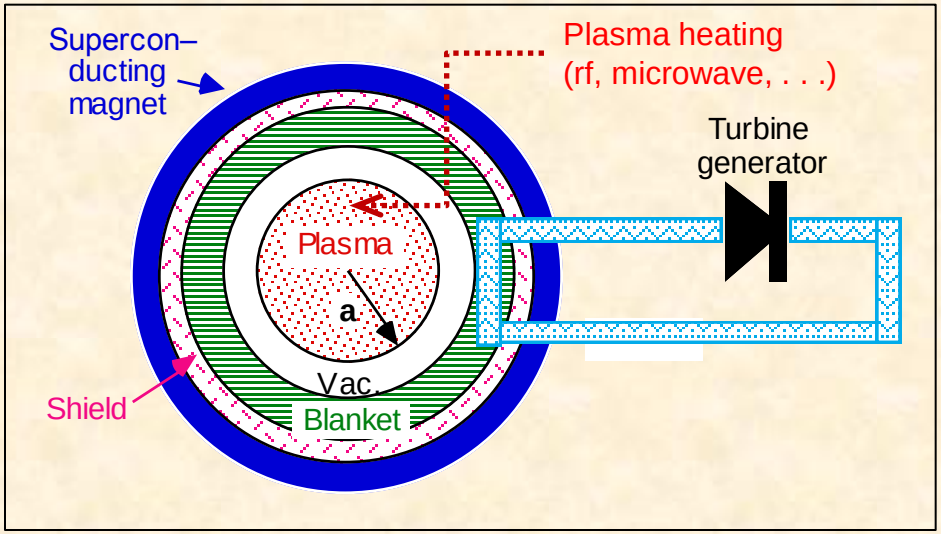
Managed by UT-Battelle
for the Department of Energy

ORNL, 10/27/11

All energy from D-T fusion reactions passes through first wall

- Flux of (particles + heat + 14 MeV neutrons) ~10 MW/m^2

Schematic magnetic fusion reactor



Why is PMI important?

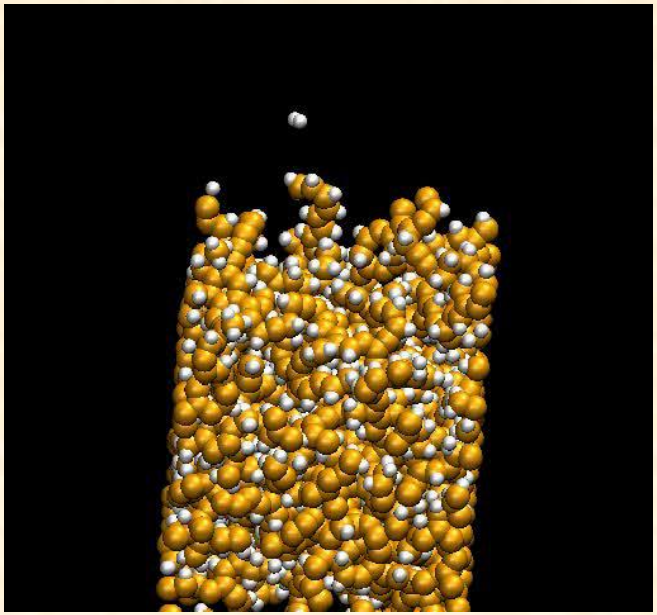
Why lithium? Carbon?

Unlike nuclear fission where energy is volume-distributed

A FUSION REACTOR IMPLIES MANY INTERFACES BETWEEN THE PLASMA AND MATERIALS
Particles and surfaces

Key role of PMI in fusion research well recognized in US and internationally

What does flux of 10^{25} particles/m^{2}s mean (ITER) for a typical atomistic (MD) simulation?



At a box of surface of 3 nm lateral dim? a few thousands atoms (carbon)

The flux is 0.01 particle/nm^{2}ns
1) 1 particle at the interface surface of the cell each 10 ns.

But for deuterium with impact energy less then 100 eV: Penetration is less than 2 nm, typical sputtering process takes up to 50 ps

Is each impact independent, uncorrelated?

Each particle will functionalize the material, change the surface for the subsequent impact!
Processes essentially discrete → Atomistic approach!!!

Guiding principle:

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

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

Close collaborators:

Theory:

CMD | Mat. | PWDFT

Carlos Reinhold
PD, ORNL

Steve Stuart
Clemson U.

Paul Kent
ORNL

Alain Allouche
CNRS, Fr

K. Morokuma,
Kyoto U.

J. Jakowski,
NICS

H. Witek,
Taiwan

Provided Li-C-O-H parameters

Stephan
Irle,
Nagoya U.

TBDFT modeling

Experiment:

Fred Meyer
(PD, ORNL)
beam

Eric Hollmann
(UCSD)
plasma

JP Allain
(Purdue)

Chase Taylor
Purdue)

beam and plasma

Students

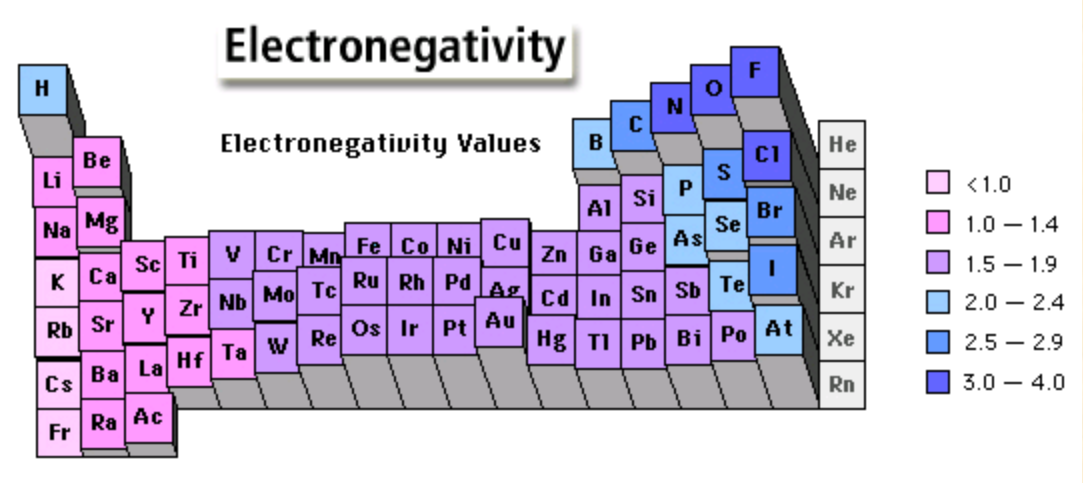
Jae
(ORISE)

Jonny
(UTK)

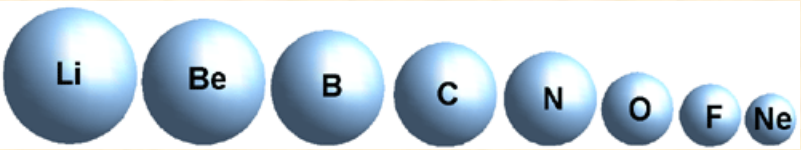
Chris
(MTSU)

Lithium dynamics: Problem to study theoretically because 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.



Consequence: Bonding between Li and other atoms covalent and polar;
Long-range nonbonding:
Coulomb :1/R
Lennard-Jones :$1/R^6$, $1/R^{12}$



Electronegativity and size of atoms related!

How to treat the dynamics in quaternary system Li-C-O-H

- Li-C , Li-H, Li-O are of very different electronegativities and therefore these could be considered as ionic solids/liquids

- As a result of partial charge transfer from one element to the other, the dominant long-distance binding force between particles is the Coulombic attraction between opposite charges, including multipole interactions

- Classical MD is not a good answer, cannot self-consistently calculate charges (EEM+Tersoff-Brenner covalent models too expensive)

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

Simulation Goals:

- Chemistry and sputtering/reflection/retention dynamics in lithiated&oxidized carbon material, bombarded by slow deuterium atoms is studied.

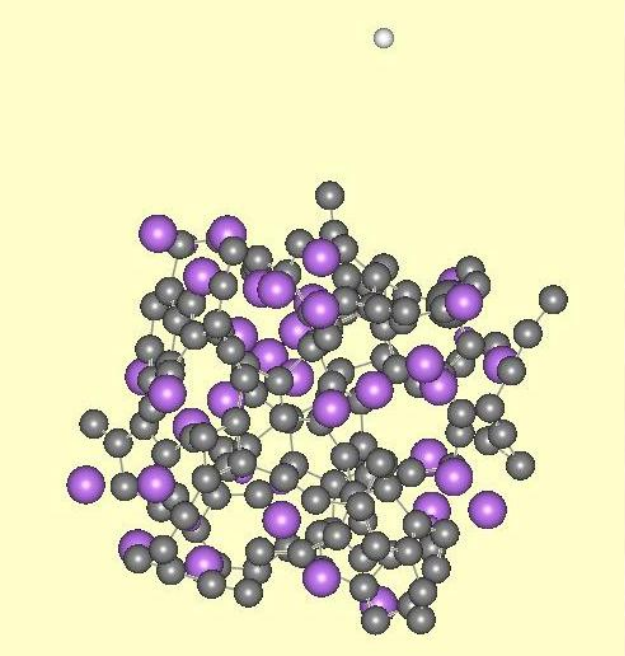
- The objectives of this research are two-fold:

1) To develop the realistic methods for computational simulation of the Li-C-O-H, **validated by experiments.**

2) 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 – is the question now?

C.N. Taylor, B. Heim, J.P. Allain, Journal of Applied Physics 109, 053306 (2011)

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



- 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;** several 10,000 CPU hours per run

What do experiments teach us? I

- We know from in-situ experiments labs, and more than 7 different tokamak machines (TFTR , CDX-U, FTU, DIII-D, TJ-II, EAST , and NSTX) that work with graphite with thin lithium coatings have a "significant" effect on plasma behavior and more specifically on hydrogen recycling.

  Controlled experiments demonstrated reduced recycling, improved energy confinement time t_E, and a reduction of edge instabilities known as edge localized modes (ELMs)

- 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.

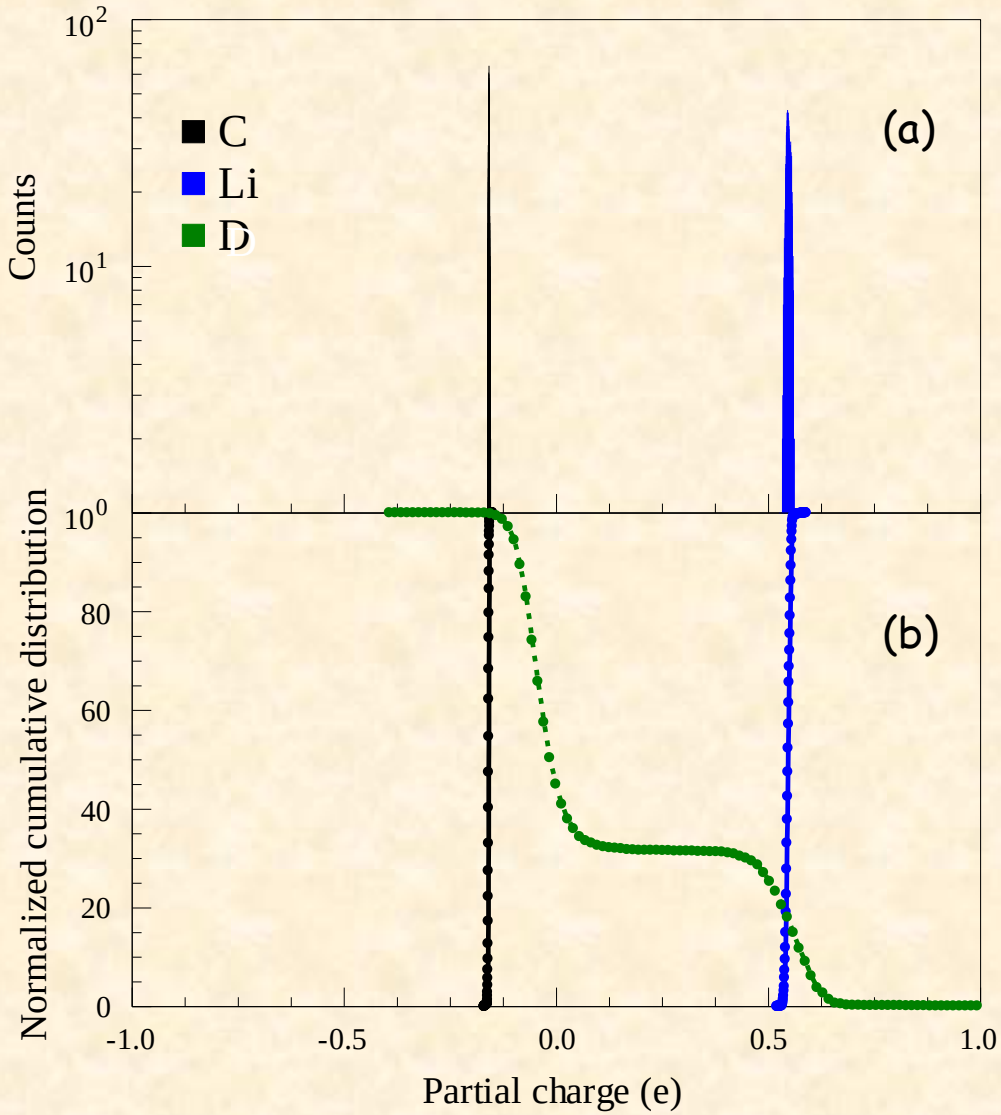
For "some reason" the Li(1s) peaks didn't show much information.

What do experiments teach us? II

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????

Does Li bond more D's?



(a) Distribution of average charges of D, Li and C, with impact of D on a-C:Li surface (~23% Li concentration, Li/(Li+C)).

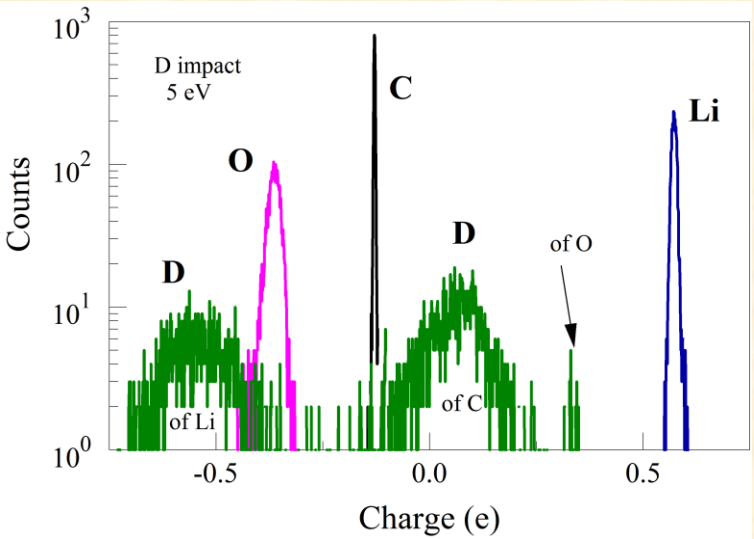
D has a slight preference for interacting with Li rather than with C.

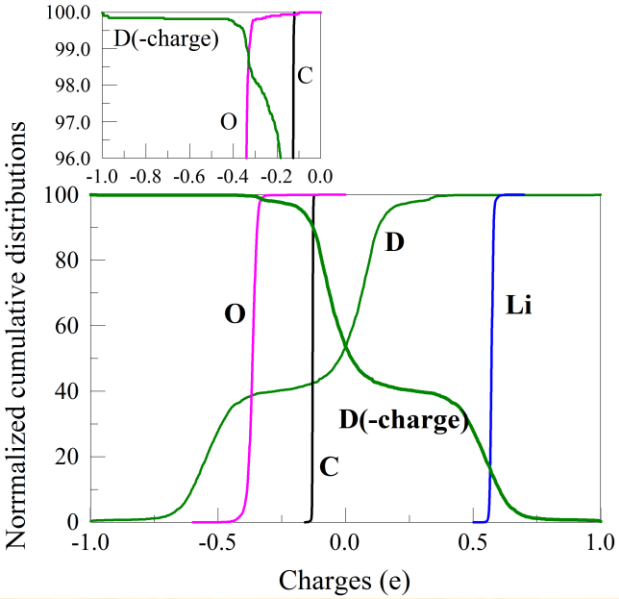
Krstic et al, FE&D, 2011

What is model teaching us (I)?

Large percentage of impact D (40%) prefer closeness of Li to settle down
Not much attention to O (already bonded to Li)

But there is only 20% Li in C, < 5% of O



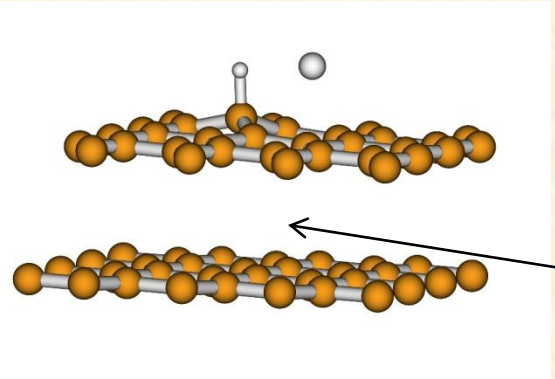


The first try of the model had a nice story. The electropositive nature of Li gave us a clear picture on its influence on hydrogen retention when we compared "with Li" and "without Li" cases in the graphite matrix.

The model remained somewhat unconnected to the XPS data that clearly showed it was the O(1s) that was really active and correlated to hydrogen irradiation. BUT ONLY IN THE PRESENCE OF LITHIUM.
What was missing...???

Quantum-mechanical, PWDFT "static" calculations finger -point in the same direction, Qualitatively benchmark the DFTB findings:

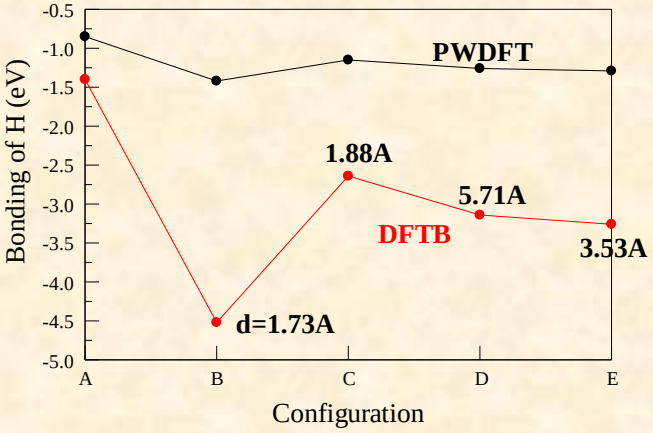
- **graphene bilayer with Li and H on the surface**

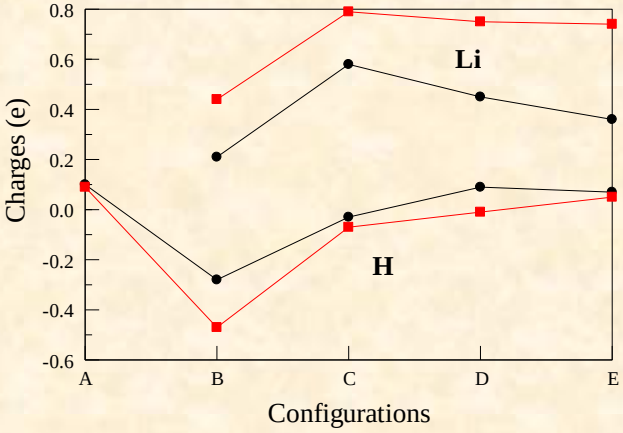


When a lithium atom is co-adsorbed on surface bonding energy of H grows up to values ranging from -2.2 to -2.5 eV, with decreasing the Li-H distance. (compared with -1.9 eV for pure graphite)

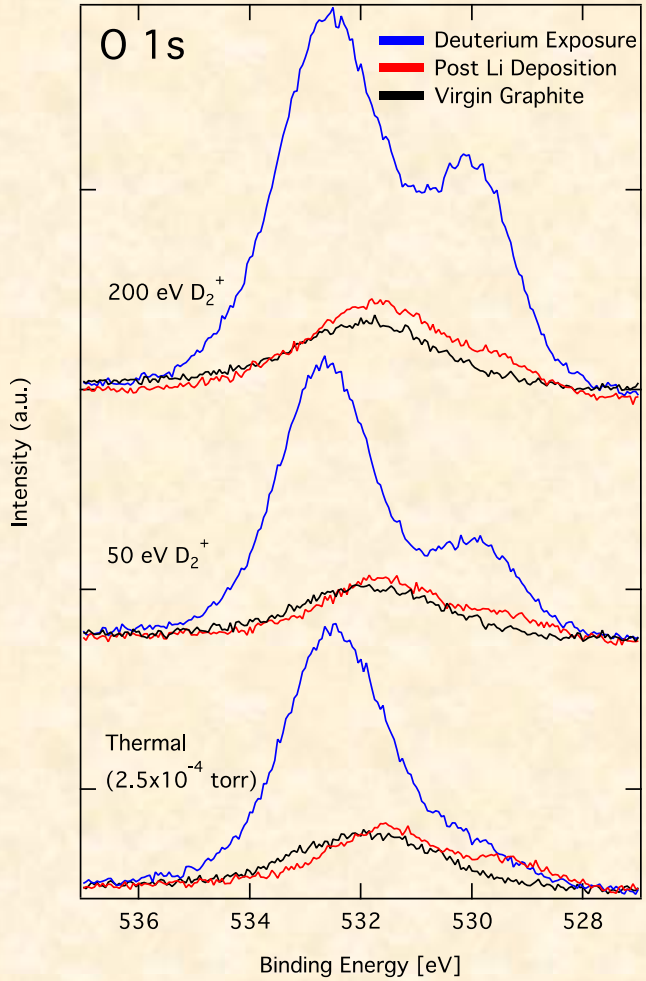
The bonding E enhancement is also observed when Li is sandwiched 1 layer below the surface layer (**conf. E)**

Allouche&Krstic, Carbon (2011)





What do experiments teach us? III



Is it the impact energy?
Model used 5 eV and experiment …

Comes very interesting and theoretically anticipated result:

C. Taylor shows that the chemistry is incident particle energy independent… as expected.

But, again a result came by observing the O(1s); in presence of Li
Not even the C(1s) showed much.

No problem with impact energy!!!

What do experiments teach us? IV

Result: The quantitative amount of lithium deposition in the in-situ Purdue studies correlated DIRECTLY with results by Maingi et al on amounts of Li deposited in NSTX and subsequent changes on plasma behavior.

300-500 nm THIN FILM only OF LITHIUM MADE A SIGNIFICANT CHANGE IN PLASMA BEHAVIOR of spatial scales of meters!! NO ELMS. But this behavior was limited in time and for some reason saturated.

Then comes another pioneering result by C. Taylor showing how this saturation is attained in lithiated graphite: Connected with O saturation

What do experiments teach us? V

Here comes the experiment again (Chase):

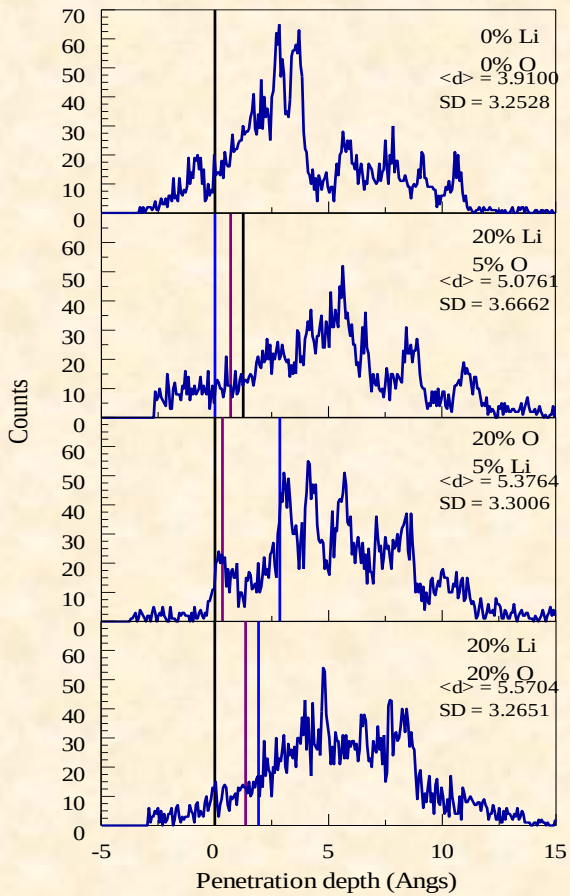
1) At most 5% oxygen content on the surface of NON-LITHIATED graphite... AS EXPECTED.

2) With lithium you get 10% of Oxygen

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

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

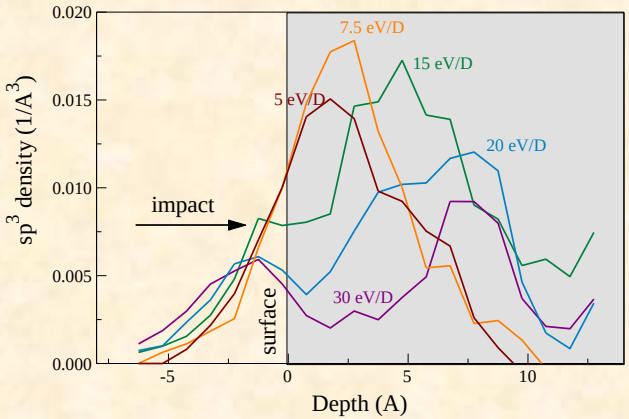
What is modeling teaching us? II



Quantal (250 atoms)

Multipeak structure is consequence of the discrete structure of the bonding centers

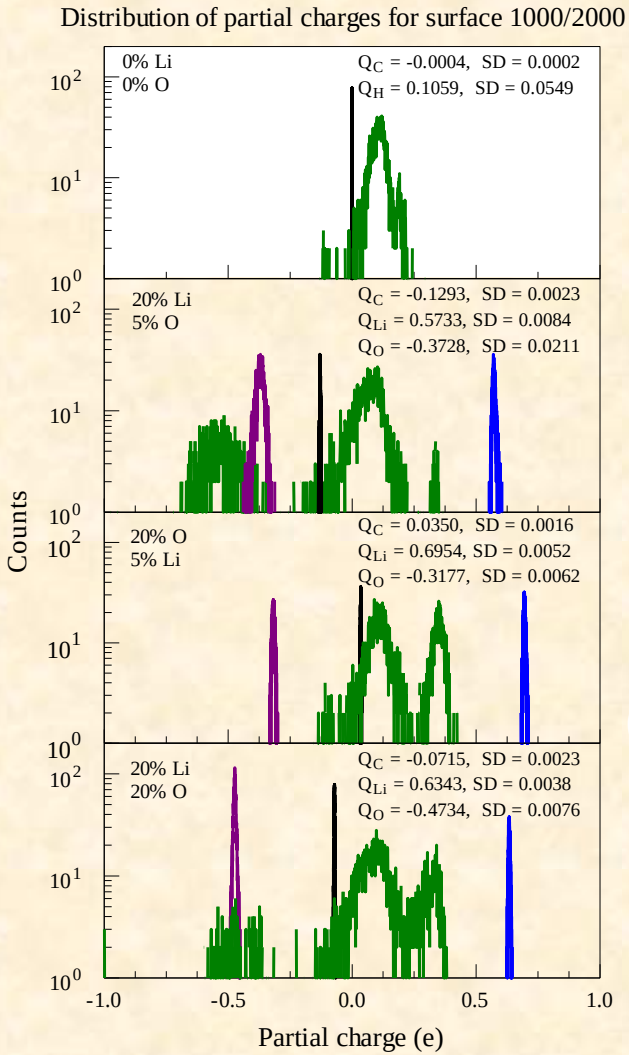
Penetration depth?



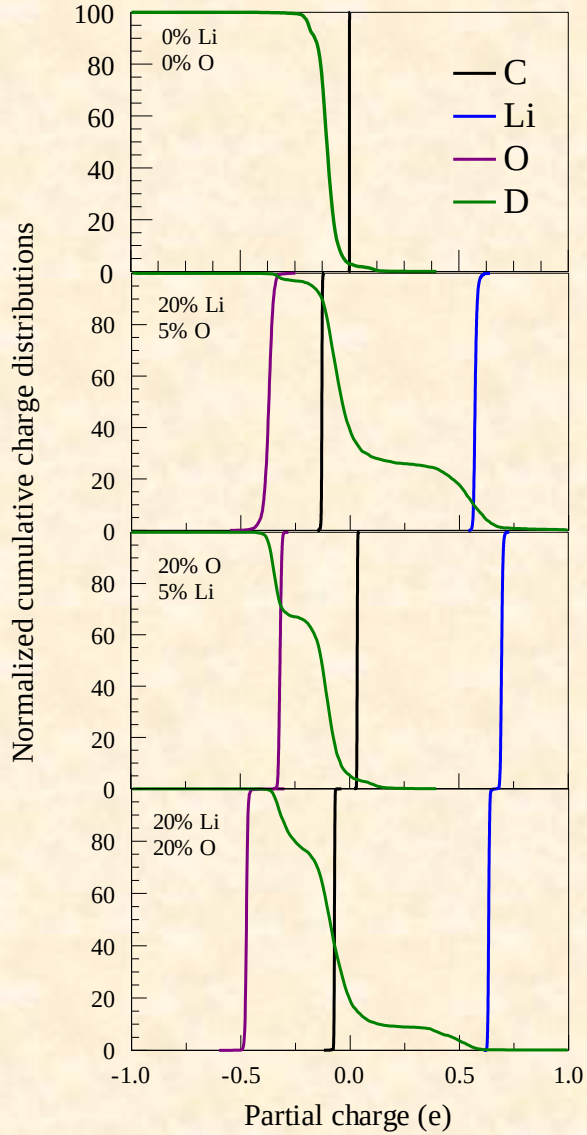
Classical (2500 atoms)

Interestingly: QM and classical give similar penetrations for a:C (deut.)

How do Li and O compete?



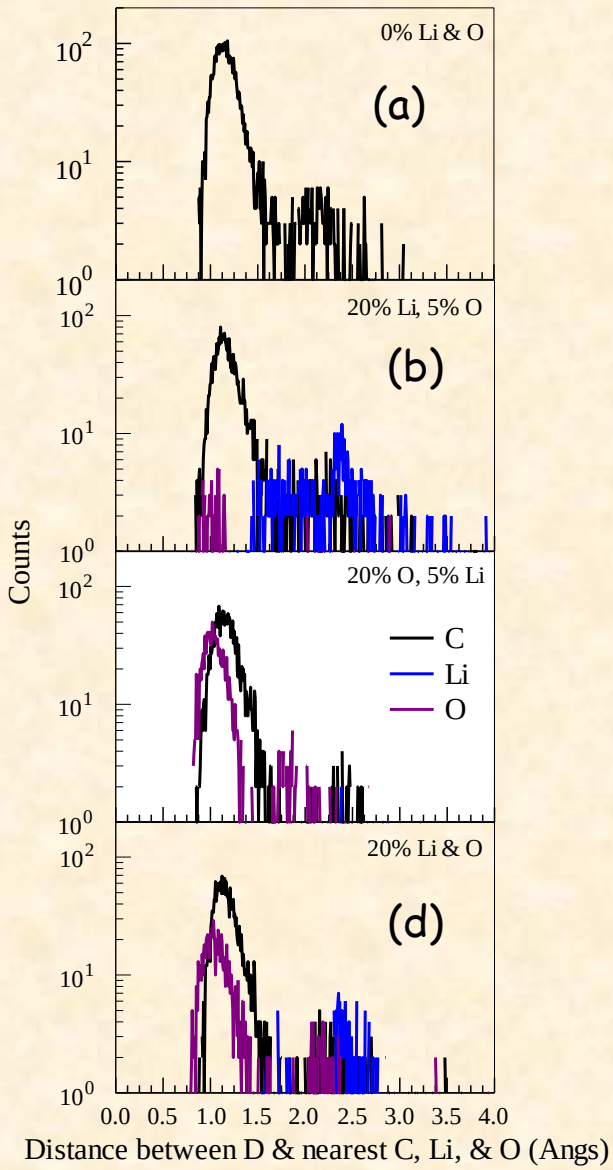
MODEL

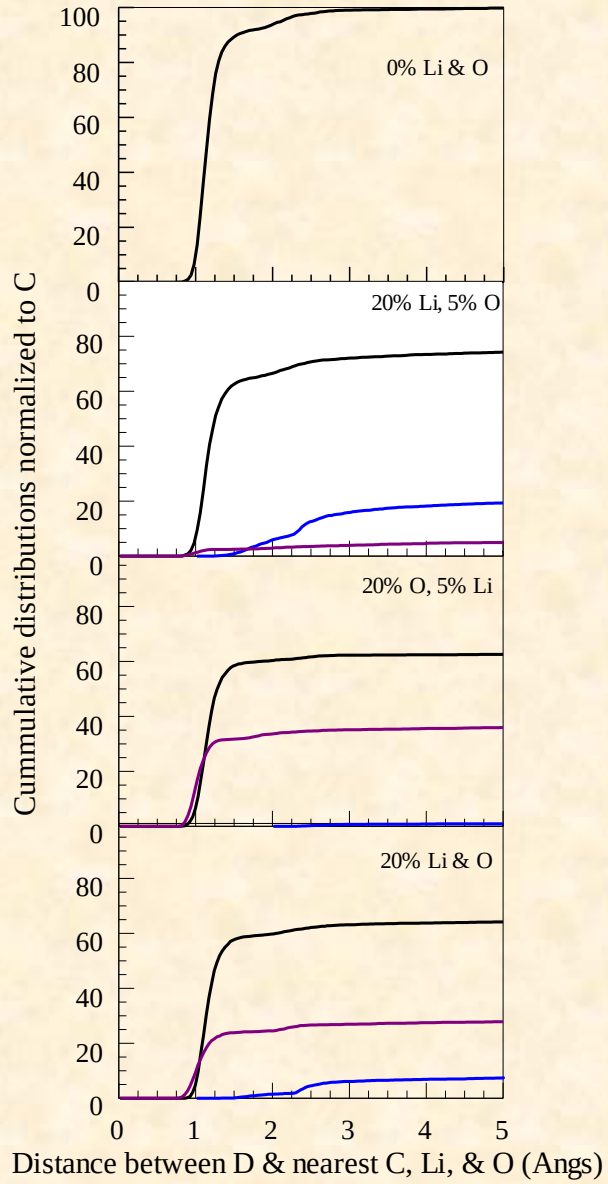


Indicate that D has a preference for interacting with O and C-O structures rather than with Li or Li-C structures **when there is enough O**

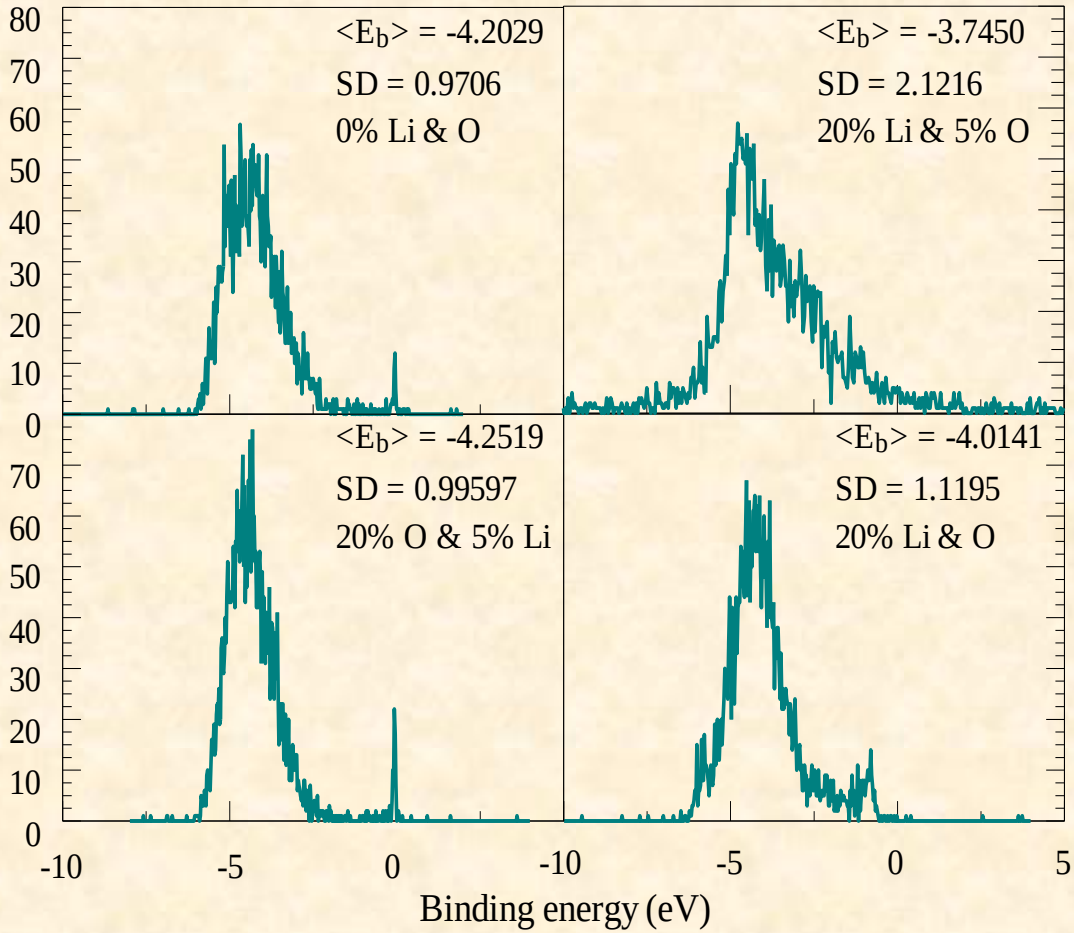
What do the first neighbors to D say?

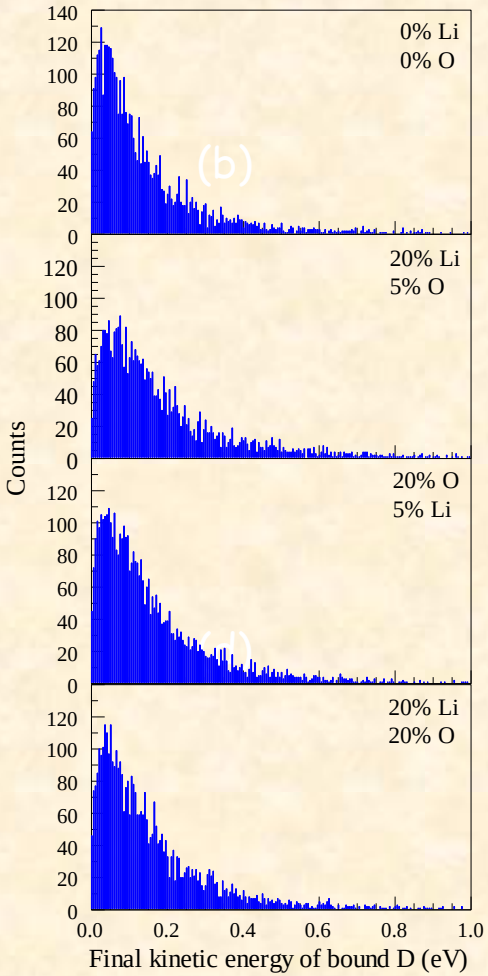
Again: O preference!





Distribution of binding energies of D in various mixtures consistent with O dominance





Widths are signatures of various bonding sites

Most of the bound D's in the ground Vib state – width 0.2 eV)

CONCLUSIONS

%	20%O 5%Li	20%Li&O	20%Li 5%O	a-C
C	0.080176388	0.28548124	0.549898167	0.364004
Li	0	0.14274062	0.99796334	0
O	0.020044097	0.061174551	0.142566191	0
Ref D	15.51413109	18.55628059	24.70468432	22.83114
Ret D	84.48586891	81.44371941	75.29531568	77.16886
Confirm	100	100	100	100
BAD/Trans	15	100	94	59

Li is an excellent oxygen getter: Lithiation of C brings A LOT OF Oxygen inside C and this the main role of Li.

Oxygen and Oxygen-Carbon bond D strongly, suppressing erosion & increasing D retention.

Li mainly ineffective in this process.

What is model teaching us?

A beautiful music of full harmony of theory and experiments

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

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

... consistent with the XPS data!!