

## Dynamics of deuterium retention and sputtering of Li–C–O surfaces

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### ABSTRACT

Chemistry as well as sputtering and reflection dynamics of lithiated carbon material, bombarded by slow hydrogen atoms are studied. We present a realistic method for computational simulation of the dynamics of the polar Li–C–O–H material dynamics. It is based on an approximate, semi-empirical quantum mechanics of electrons and classical mechanics of nuclei. Results are validated qualitatively by comparison with experiments and with a first principle DFT computations. In particular, we explain observed details of the hydrogen bonding chemistry in lithiated carbon, showing that incoming hydrogen interacts preferably with Li–C rather than C structures.

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### 1. Introduction

The use of lithium as a plasma-facing surface in magnetic confinement fusion devices is increasingly becoming popular. Mostly due to its impurity gettering and ability to retain hydrogen (low recycling regimes). National Spherical Torus Experiment (NSTX) [1] uses lithium deposition on graphite substrates to enable important plasma control. One peculiar mystery in the past few years of lithiation efforts in NSTX is how ultra-thin films of lithium can readily affect the tokamak plasma knowing that Li readily intercalates (diffuses) to the graphite bulk. The mechanism of hydrogen (in NSTX deuterium is used) bonding with lithiated graphite is unknown and this paper seeks to elucidate on this mystery. Laboratory experiments by Taylor et al. [2] have demonstrated a complex rich surface chemistry at play and with XPS analyses found that the presence of lithium has significant effects on the fundamental interactions of hydrogen with C and O atoms on the ATJ graphite surface.

Long range interactions when treating molecular dynamics have been readily “avoided” in the past because of the possible prohibitive computational cost. Namely, it is difficult to study the Li dynamics theoretically because of its polarizing features

when interacting with other elements. These features are most transparently represented by the quantity called electronegativity, i.e. the chemical property of an element which defines its tendency to attract electrons. Li electronegativity is exceptionally low, one of the lowest in nature, and is low in comparison to the elements readily met in NSTX [1], H, C, O, Mo, W. Thus, according to the Pauling scale [3], Li electronegativity is 0.94 as contrasted to 2.2, 2.4, 3.5, and 1.9 of H,C,O, and Mo, respectively. In consequence of partial charge transfer from Li to other atoms, the dominant long-distance binding force is the Coulomb attraction between opposite charges. Bonding between Li and other atoms is mixed covalent and polar (Fig. 1a). The differences in electronegativity between constituent atoms in Li–C, Li–O and Li–H systems are very large and therefore these systems could be considered as ionic solids.

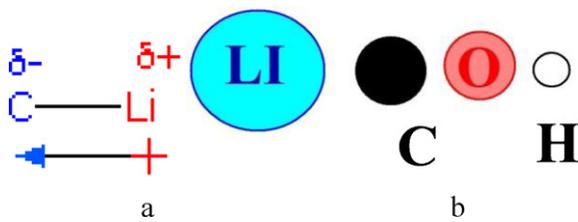
Long-range nonbonding interactions are typically represented as (a) Coulomb type  $E_{coul} = \sum_i \sum_{j>i} (q_i q_j) / r_{ij}$ , as well as (b) Lennard-Jones types [4],  $E_{LJ} = \sum_i \sum_{j>i} D_{ij} [(\sigma_{ij}/r_{ij})^{12} - 2(\sigma_{ij}/r_{ij})^6]$ , resulting in total nonbonding interaction  $E_{nob} = E_{coul} + E_{LJ}$ . Finally the total interaction energy reflects both nonbonding and bonding (covalent,  $E_b$ ) interactions,

$$E_{tot} = E_b + E_{nob}$$

We also note that electronegativity and the size of atoms are mutually related, as shown in Fig. 1b. The bond length of the simple diatomic molecules is typically sum of the so-called covalent radii of the constituting atoms. Thus, covalent radius of C is about 0.7 Å,

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**Fig. 1.** (a) Partial charge transfer in a polar bond. (b) Size of atoms scales inversely proportional to their electronegativities.

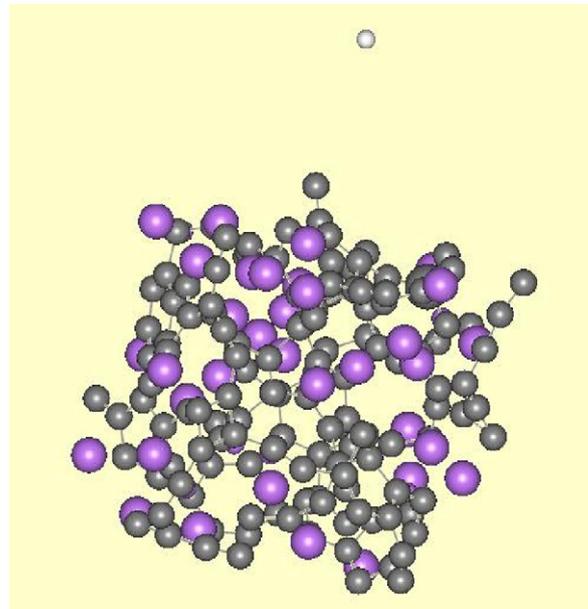
while for Li and H it is close to 1.3 Å and 0.3 Å, respectively. This implies that the density of carbon is lower in lithiated carbon than in a hydrogenated carbon, since Li–C bonds are about twice as long as H–C bonds. Indirect consequence is that the Li–C bond (typically 1.6 eV) could be significantly weaker than the H–C bond (4.5 eV, typically).

However, the charges of the atoms that take part in these polar interactions depend on atomic coordinates. The charges typically change in each simulation step. This narrows down the number of methods that can be used in studies of system dynamics to those that are capable of recalculating accurately the charges at each time step. If the classical molecular dynamics (CMD) is used, with pre-parameterized short range potentials, a semiempirical method like is the Electronegativity Equalization Method (EEM) [5] has to be applied at each step for calculation of the atomic charges. Besides questionable accuracy, this combination of the classical covalent potential with EEM raises a question of numerical efficiency of the approach, and motivates the use of Quantum-Classical Molecular Dynamics (QCMD) as a better candidate for the treatment of the system dynamics.

In the QCMD [6], motion of electrons in the system is treated quantum-mechanically, by solving some form of Schrodinger equation at the beginning of each time step, keeping frozen positions of the nuclei. From this solution the potential energy surface in the hyperspace of all atomic coordinates is found, resulting in instantaneous forces on each atom. Positions of the nuclei are then relaxed, and the whole system is moved during a time step. The main problem is how to solve efficiently the Schrodinger equation for electronic motion. Employing standard Plane Wave (PW) [7] or molecular Density Functional Theory (DFT) to the system of  $N$  atoms (scaling  $\sim N^3$ ) would be too numerically demanding in comparison to the CMD (scaling  $\sim N$ ). For example, at a sample of 1000 atoms the DFT would introduce about  $10^6$  times slower calculations. Having in mind that analog CMD calculation takes of the order of minutes, this is currently a formidable task.

For the quantum-mechanical part of the approach we employ Self Consistent Charge Density Functional Tight Binding (SCC-DFTB) method [8], developed by the Bremen (Germany) Center for Computational Material Sciences, adapted for the trajectory Monte Carlo calculations in a multi-processor super-computer environment. This is an approximation to DFT, in which only valence orbitals are considered and difficult density integrals are parameterized and fitted in advance. In comparison to other tight-binding methods, this one has self-consistent calculation of atomic charges. The method still scales as  $N^3$  (due to diagonalization step), but the corresponding size of basis set (Slater orbitals) is much smaller (up to 10 times) than in first principles DFT. Thus the method is significantly faster, up to a thousand times than first principles DFT, but is also slower than the CMD, falling into the range of current computational capabilities. Parameterization of the pair-parameters for the Li–C–O–H system is provided by the K. Morokuma and S. Maeda [9].

We use a simulation cell of a few hundreds of atoms of lithiated and oxydated amorphous carbon ( $\sim 20\%$  of Li,  $\sim 5\%$  of O), at



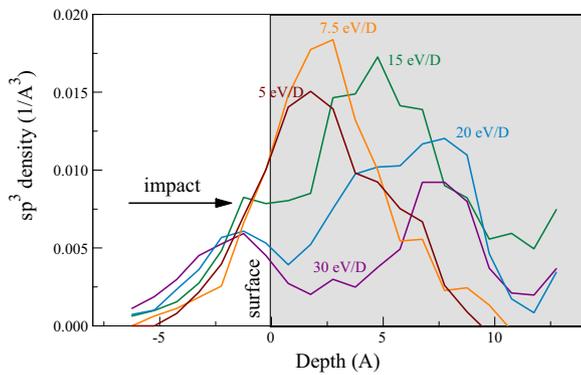
**Fig. 2.** Structure of a typical simulation cell; black (carbon), violet (lithium) and white (hydrogen). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

300 K. This is created by random seeding of Li and O in amorphous hydrogenated carbon, replacing hydrogen by Li and O, followed by quantum-mechanical energy minimization and thermalization to 300 K. This approach also closely resembles the situation in the NSTX where lithium coatings on graphite are used. As expected, during the optimization, the simulation cell swelled about 30% to allow Li and O to create their extended bond lengths (Fig. 2). The swelling decreased the effective carbon density.

The prepared cell was cut into a rectangular box of approximate length of 1.5 nm,  $x$ – $y$  periodic conditions applied, and then optimization and thermalization of the periodic cell was repeated, resulting into a slab, which was periodic in  $x$ – $y$  directions with period of 14 Å while its thickness in  $z$ -direction was close to 20 Å. The slab was bombarded by 5 eV D and 2.5 eV H atoms, perpendicularly to the free cell interface (in  $z$ -direction). 5004 random trajectories were applied to both D and H, each evolving in a separate core of Cray XT5 of NICS (Kraken), with the time step of 0.2 fs. About 24 h was needed for most of the trajectories to finish their evolution, resulting either in reflection (fastest), retention and sputtering (slowest), thus requiring 120,000 CPU hours per impact energy. We note that our simulation had a primary goal to establish the retention chemistry of deuterium with Li–C mixture and was applied to a Li–C–O “virgin” (previously not-hydrogenated and not-bombarded) surface. Realistic experimental conditions would be better approximated if one saturates the Li–C–O surface with deuterium (hydrogen) prior to each prescribed simulation. However, since the saturation process is causal, this would require much more computation effort if done with the SCC-DFTB method. Some combination of the classical MD and the DFTB is a must for creation of a saturated (steady-state) surface [10], and will be a subject of our forthcoming publications.

## 2. Results and discussion

Here we study chemistry and sputtering/reflection dynamics in lithiated (and partially oxydated) carbon material, bombarded by slow deuterium (5 eV) and hydrogen (2.5 eV) atoms. The objectives of this research are two-fold: (a) to develop realistic methods for computational simulation of the polar-covalent bonding of

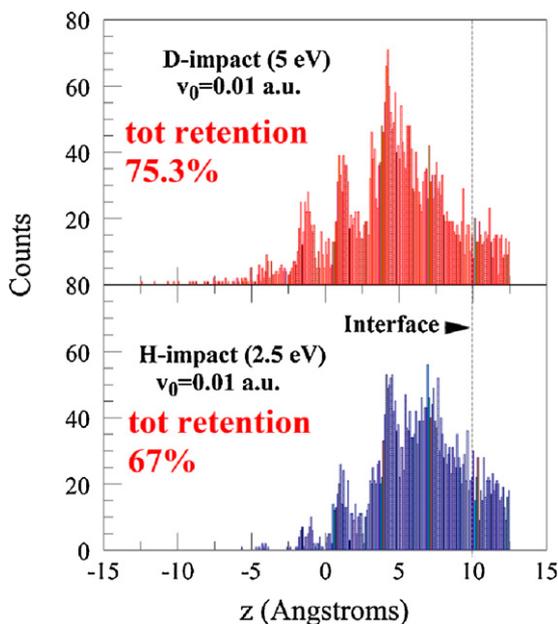


**Fig. 3.** Penetration depth of deuterium into hydrogenated carbon of  $2 \text{ g/cm}^3$ , for various impact energies of D.

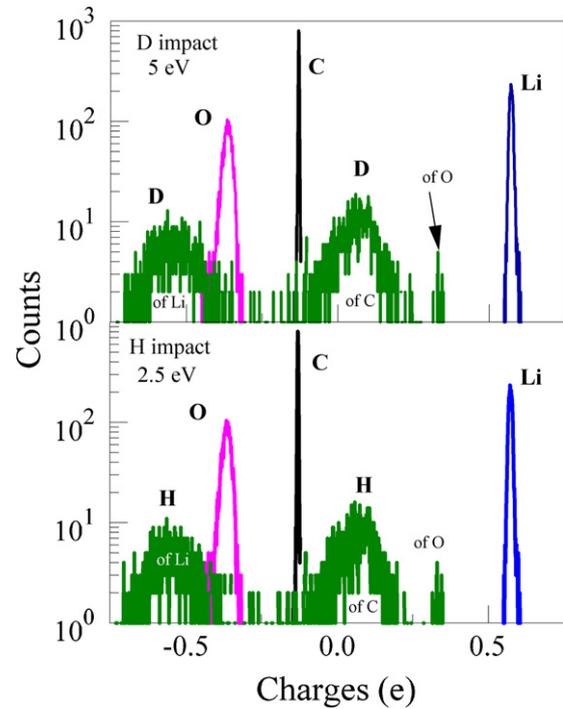
Li–C–O–H, validated by experiments; (b) to explain the specifics of the chemistry of deuterium bonding in lithiated carbon. Namely, experiments from Purdue [2] indicate that Li–C/O sites are preferred by retained D. In short, when deposited on carbon, lithium will always bind with oxygen (when present) and carbon, and incoming deuterium will then interact preferentially with existing Li–O and Li–C structures. We will try to justify this experimentally established hypothesis.

About 70% of impact deuterium in our simulations was retained (exact numbers for D and H are shown in Fig. 4). It is interesting to compare the penetration depth of the impacting atoms into Li–C–O mixture with those previously found in hydrogenated carbon (Fig. 3 [9]). In both cases of Figs. 3 and 4 the surfaces swell by bombardment.

For 5 eV impact energy in Fig. 3, the penetration of D is peaked at about 2 Å, following a distribution which has the half-width of about 5 Å. On the other hand the penetration of D into Li–C–O mixture is peaked around 5 Å. However, its half-width is difficult to define, because the penetration distribution contained a series of narrow peaks whose nature is not yet understood. The penetration of H shows a similar oscillatory structure, somewhat shifted toward shallower depth, showing a weak isotopic effect. A deeper penetration of D into Li–C–O than into a–C:D is a consequence of



**Fig. 4.** Penetration distributions of (a) D and (b) H into Li–C–O mixture. Interface of the surface with vacuum prior to bombardment is presented by vertical dashed line perpendicular to the interface.



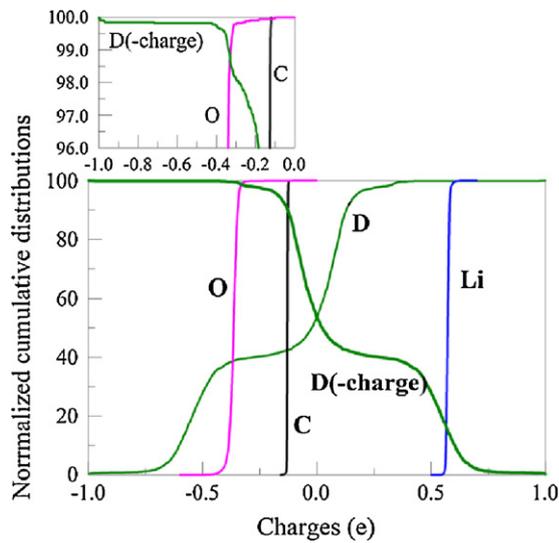
**Fig. 5.** Charge distributions of (a) D and (b) H, as well as of Li, C and O upon the retention process.

the reduced density of C in Li–C–O, as well as the saturated deuterization of the a–C:D in Fig. 3.

Certainly the most interesting result of the present work arises from analysis of the distributions of the charges in Fig. 5. Average charge of Li, C, and O is calculated for the final distribution of each retained trajectory, while the D (or H) charge is recorded at the termination point of a retaining trajectory. Therefore, for each trajectory any of Li, C, O, D appears once and so the heights of the peaks do not have any absolute meaning. The integral below distributions of each of the atoms describes only the number of retained trajectories. Li and O peaks appear lower because of their width. We note that the charge distributions in Fig. 5 show almost no isotope effect, and we will focus in Fig. 5 on the case of D impact.

It is obvious, because of the present screening, that D charges are distributed in accordance to their closest neighbors, revealing the place where a D atom is retained. Thus, the wide peak around  $-0.55e$  obviously represents D's in the vicinity of Li; peaked at  $+0.55e$ . The peak around  $+0.12e$  are from D's in the vicinity of C, peaked at  $-0.12e$ , while the small peak at  $+0.35e$  is for D's "neutralizing" O at  $-0.35e$ . Neither height of the peaks, nor their total contributions are proportional to the number content of the respective atoms.

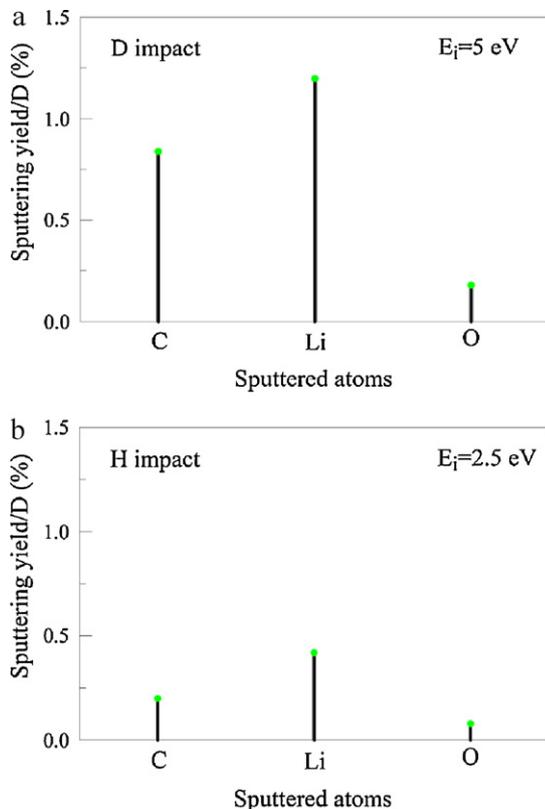
This is best seen in Fig. 6, which represents integrals of distributions in Fig. 5b, normalized to 1. In order to be able to visually compare different contributions we also add a cumulative curve for D as a function of the negative of its charge. One can see that the contribution of retained D's which are bound in the vicinity of Li is about 40%, while about 56% D's bonds to C's, and only 4% to O. Having in mind that the total content of Li in the sample is 20.3%, while of O is only 5.4%, the binding of D to oxygen is approximately following the oxygen concentration. This is not a case for lithium, which is about a factor two more efficient in retaining deuterium than pure carbon. This quite clearly qualitatively explains the results of the Purdue experiments: the long-range polarization of the material by the presence of lithium induces preferentially negative charge on D, which is then driven by nonbonding forces toward the sites of positive charge, i.e. toward the sites which neighbor lithium. The positive polarization of D by oxygen does not show such



**Fig. 6.** Normalized cumulated distributions of retained D in comparison to C, Li and O.

preference. This is in disagreement with the experimental findings, and it is reasonable to assume that it is a consequence of much lower concentration of oxygen than of lithium set in our simulation. In experiments, the transient oxygen gettering by lithium increases the oxygen content levels significantly beyond 4%. We will include concentration of oxygen comparable to lithium in future work, to check the concentration-competition effects.

A product of our simulations are the sputtering yields of Li, C, and O atoms. We note that no molecular products were observed in emission spectra. As can be seen from Fig. 7a and b, there is a significant isotope effect in the sputtering yields: the yields by D impact are about a factor 3 larger than those by H impact.



**Fig. 7.** Sputtering yields (in %) of the Li-C-O surface by (a) D impact and (b) H impact.

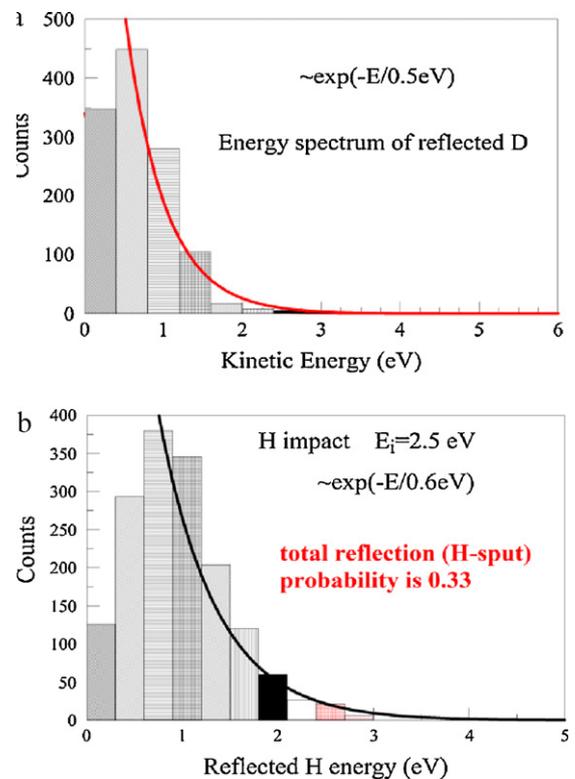
Most of this isotope effect can be explained by having in mind that the transfer of energy in an elastic binary collision of a projectile of kinetic energy  $E_1$  and mass  $m_1$  on a target atom of mass  $m_2$  is

$$\Delta E = 4m_1m_2E_1/(m_1 + m_2)^2$$

Considering the fact that the yields in Fig. 7 are defined per impact particle (rather than per nucleon), we obtain  $\Delta E_D/\Delta E_H \approx 3.2$  for the energy transferred to Li, which is close to the found ratio of 3.

The obtained sputtering yields are relatively large in comparison to those obtained by sputtering of D of deuterated carbon [10]. The bonding of Li to C is about 1.6 eV, i.e. almost 3 times smaller than C-C binding (4.5 eV), therefore the high sputtering yields for Li are not surprising, and were seen in the experiments [11,12]. It is more mysterious why the carbon sputtering yield is so much increased by the presence of lithium. A possible explanation is weakening of the carbon-carbon bonds by the presence of Li, accompanied by a drop of the carbon density. We note that our finding partially opposes to experimental ones of Yagi et al [11], and Kato et al [12] who found that intercalated lithium into graphite suppresses chemical and physical carbon sputtering of hydrogenated graphite surface. However, as elaborated in [10], the agreement of the computer simulations of particle-surface interactions with experiments are strongly conditioned by the level to which simulations mimic the experiment. In the present case this level is very low (amorphous structure against the crystal, graphitic ones in the experiments, different densities of carbon, not cumulated D in the simulation which prevents the chemical sputtering, large difference in the impact energies, etc.) The present finding indicates that suppression of the carbon sputtering by lithium presence might not be a general phenomena, but rather dependent on the type of the carbon surface and its conditioning with Li.

It is interesting to show the kinetic energy distribution of the reflected deuterium and hydrogen atoms (Fig. 8). Both distributions



**Fig. 8.** Energy distribution of the reflected (a) deuterium, (b) hydrogen atoms. Solid lines: Boltzman distribution fit.

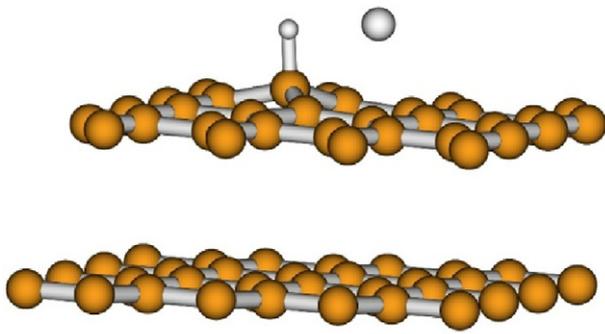


Fig. 9. Double-layer graphitic slab with Li and H atoms.

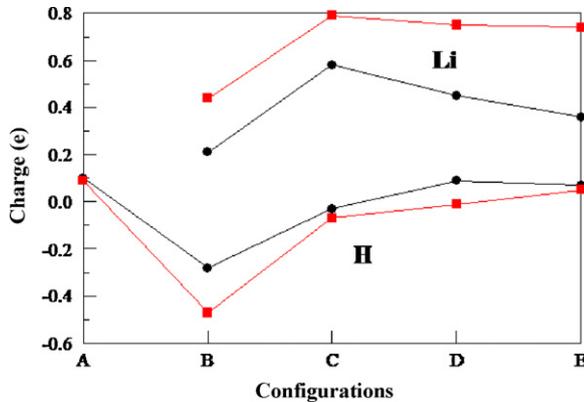


Fig. 10. Charges of Li and H atoms for various positions of the H atom. A–D: increasing distance Li–H. E: corresponding to Li intercalated between two planes.

have a Maxwellian shape whose high energy wings are well fitted to the Boltzmann distribution corresponding to energy of 0.5 eV for D, and 0.6 eV for H. This surprising thermalization can be realized if the impact particle makes a cascade through the surface before the ejection through the “hot” void created by the particle.

We show a comparison of the two static calculations: SCC-DFTB and PW-DFT [13,14] for a double-layer graphene infinite sheet ( $x$ - $y$  periodic boundary conditions applied to the cell in Fig. 9), varying positions of Li and H with respect to the graphene. A single H is bounded to the graphene from the top and configuration optimized (configuration A); a Li atom is bounded to a C atom the top, configuration optimized and then the hydrogen atom placed at different distances from the Li atom, above the top layer (configurations B–D); finally a lithium atom is intercalated between the graphene layer, and H bounded above the top layer and optimized (configuration E).

A good comparison of the absolute values obtained by PW-DFT and SCC-DFTB is hard to obtain. However, like for comparisons of the values obtained by various DFT functionals in the DFT calculations, here we consider the qualitative trend in the curves. Fig. 10 shows comparison of the charges obtained by the two methods, for the described configurations of the graphene-Li-H. The charges of Li and H follow the same trend. While H shows even a good agreement of quantitative values of the charges, Li charges by SCC-DFT are almost factor two larger than with PW-DFT.

### 3. Conclusions

We have studied the polar-covalent interactions that emerge in mixtures of lithium with carbon-hydrogen-oxygen. The swelling of the Li–C surface due to the larger size of Li–C bonds is reflected by a increased penetration of D and H into the surface. We found that the influence of O, present in small quantities, is of negligible influence to the dynamics of retention. However Li, present at 20% of the total number of atoms in the cell, substantially changes the retention chemistry, significantly increasing the probability of collecting the H atoms in its neighborhood, in accordance with the observations. These results have very important ramifications for our understanding of the use of lithium surface coatings and lithiation strategies in magnetic fusion confinement plasmas. In particular, the role of lithium-carbon complexes and their influence on deuterium retention elucidated by the atomistic simulations presented here have now uncovered the enhanced ability of lithiated graphite to retain hydrogen, in qualitative agreement with the experimental findings [15].

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