Deuterium Uptake in Magnetic-Fusion Devices with Lithium-Conditioned Carbon Walls

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Lithium wall conditioning has lowered hydrogenic recycling and dramatically improved plasma performance in many magnetic-fusion devices. In this Letter, we report quantum-classical atomistic simulations and laboratory experiments that elucidate the roles of lithium and oxygen in the uptake of hydrogen in amorphous carbon. Surprisingly, we show that lithium creates a high oxygen concentration on a carbon surface when bombarded by deuterium. Furthermore, surface oxygen, rather than lithium, plays the key role in trapping hydrogen.

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Plasma wall interactions profoundly affect the performance of magnetic-fusion devices. Treating the plasma facing components with low-*Z* materials such as boron and lithium has successfully improved plasma performance in many metallic and carbon-walled tokamaks around the world [1–3]. In this Letter, we seek to identify the fundamental physical and chemical mechanisms that occur at a plasma-facing lithiated-carbon surface that lead to improved fusion plasma performance in part by reduced hydrogenic recycling. Prior to this work, these improvements were attributed to be the result of a simple lithium-deuteride (LiD) bond in the context of lithium-based surfaces [4–7]. However, we show that the role of lithium is primarily to bring and retain oxygen at the surface and that the oxygen in turn retains hydrogenic species. Intriguingly, bombardment of the surface by deuterium significantly enhances the surface oxygen concentration. We present experimentally validated computer simulations that show that the dominant mechanism for deuterium uptake in the resulting Li-C-O-D system is the strong interaction between deuterium and oxygen. This surprising result accounts for the beneficial plasma-lithium surface interactions observed in tokamak fusion devices with carbon plasma facing components.

Experiments in tokamaks using lithium conditioning began in 1990 when the Tokamak Fusion Test Reactor achieved record fusion plasma confinement regimes after extensive deposition of lithium on the carbon limiter [8]. Recently Maingi *et al.* [9,10] reported a series of H-mode discharges in the National Spherical Torus Experiment where recycling was reduced, edge-localized modes (ELMs) suppressed, and energy confinement increased continuously as the accumulated lithium dose increased from 0.11 g (nominal Li thickness between 30 and 125 nm) to 8 g. The National Spherical Torus Experiment has mostly ATJ graphite (GrafTech International Ltd.) plasma facing tiles.

Early laboratory experiments with pure lithium surfaces exposed in linear plasma devices showed that liquid lithium could retain deuterium in solution and as solid Li-D precipitates at ratios as high as 1:1 [4,5,11]. However, the intrinsic physics and chemistry in lithiated carbon is significantly different, primarily due to intercalation of lithium atoms into the (carbon) structure [12–16]. Furthermore, the complex chemistry of O and C bonding with Li and D yields a mixture that renders Li-D bonding less likely. Recent studies have in fact indicated that lithium begins to interact with carbon and oxygen immediately upon deposition [14,17].

This work also has ramifications in areas outside fusion such as hydrogen storage (in lithium-carbon based matrices), graphene band-gap engineering, and lithium-air batteries [18,19]. For example, one of the mechanisms for tuning the graphene band gap has focused on the ability for alkali metals (e.g., K and Li) and hydrogen to induce changes in the electronic band states. Deciphering the mechanism for hydrogenation in graphene systems can introduce designed pathways towards graphene-based insulators [20]. Furthermore, the role oxygen can play in the retention of hydrogen in both graphene-based systems and hydrogen and lithium-battery systems needs further elucidation, in part provided in the work presented here.

Laboratory experiments with *in situ* x-ray photoelectron spectroscopy (XPS) measurements of carbon, before and after lithium deposition and D bombardment show remarkable changes in the atomic surface concentration of oxygen, see Fig. 1. This figure illustrates that lithium conditioning of carbon increases the surface oxygen content and that ion bombardment greatly amplifies the increase. Before treatment, oxygen accounts for 5 at.% of the near-surface composition (top 5–10 nm) [21]. Following lithium deposition, the oxygen concentration increases modestly. For the sample shown in Fig. 1 the oxygen near-surface concentration reaches 8%. After deuterium irradiation (500 eV/amu), however, the oxygen concentration rises much more dramatically and the elemental near-surface compositions reach 35% oxygen, 10% carbon, and 55% lithium. In stark contrast, irradiating a sample without lithium conditioning actually decreases the amount of oxygen on the surface to 1%.

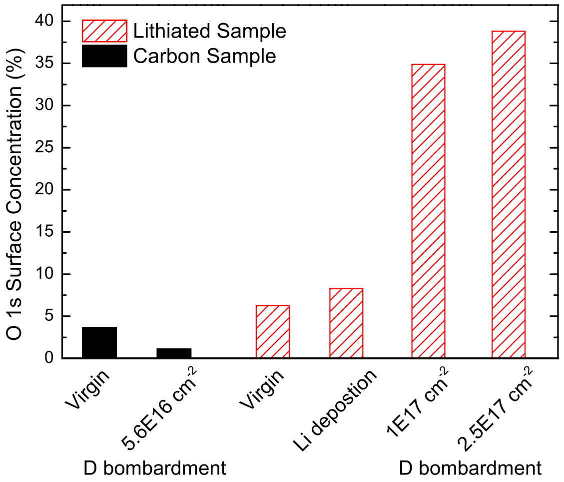

FIG. 1 (color online). Oxygen evolution during irradiation, measured by x-ray photoelectron spectroscopy. Black, filled bar: a sample of polished ATJ graphite without lithium conditioning; red hatched bar: lithium conditioned sample.

This dramatic increase in surface oxygen content during deuterium bombardment is surprising, and leads to unexpected consequences for the deuterium chemistry. In particular we found that when lithiated carbon is bombarded with low-energy deuterium ions (50–500 eV), significant chemical shifts in the oxygen XPS photoelectron O1s spectrum are observed experimentally [14,17,21–23]. The chemical changes were observed as stronger shifts in the O1s spectra when compared to those found in Li1s and C1s XPS spectra for lithiated carbon (and also compared to laboratory XPS experiments with lithium-only foils [21]), challenging the notion that the uptake of deuterium occurred by hydride bonding with lithium atoms. The correlation between the presence of lithium and irradiation with deuterium on the uptake of D atoms is clearly shown in Fig. 1. Our computer simulations below show that the D uptake chemistry is dominantly governed by oxygen if its surface concentration is sufficiently high or comparable to lithium, as was the case in the experimental results shown in Fig. 1 that motivated the present work.

We have applied quantum-classical molecular dynamics (QCMD) modeling [24] based on self-consistent charge density functional tight binding (SCC-DFTB) [25,26] to gain a detailed understanding of the D uptake chemistry. Our approach is similar to the one described in Ref. [27]. Sample matrices of about 250 atoms with five different atomic compositions were bombarded with 5 eV deuterium atoms, defining the size of the computational cell which is limited by the computational capabilities of QCMD. The quantum-mechanical part of the QCMD is required by polarization effects induced by the presence of Li and O. For each matrix composition the calculation was repeated with five thousand trajectories to acquire statistically significant results. We determined the final rest location of the incident deuterium in relation to other elements in the matrix, and tabulated the nearest neighbors of, and partial charge transfer from the deuterium atom. Figure 2 shows the results, averaged over all trajectories that resulted in the uptake of deuterium, with three bars for each of the five matrices labeled P, Q, R, S, T. For each three, the leftmost bar represents the atomic composition prior to impact; the central bar shows the nearest neighbor (NN%) to the final rest location of the incident deuterium; and the rightmost bar the percentage of the retained deuterium atoms that, on

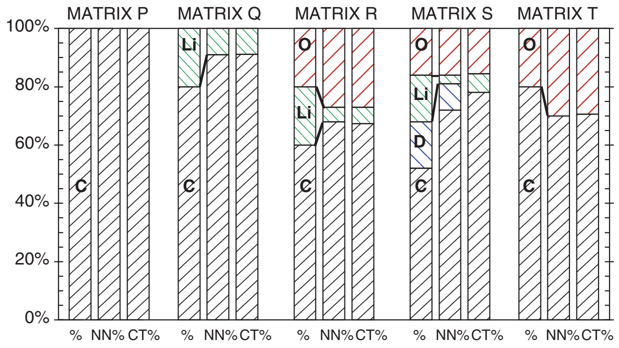

FIG. 2 (color). QCMD results, averaged over a large sample of random impact D trajectories of five surface matrices with different compositions. In each set of three, the leftmost bar shows the atomic composition, the central bar the nearest neighbor (NN%) to the final rest location of the incident D, and the rightmost bar the fraction of the deuterium atoms sharing charges (CT%) with one of the constituents of the matrix.

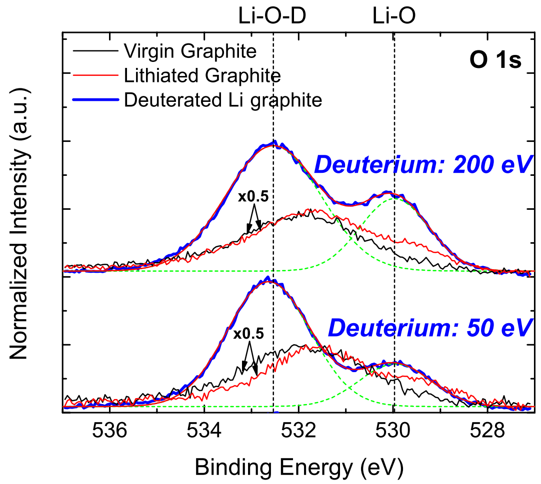

FIG. 3 (color online). Energetic deuterium ions slow down to thermal energies after entering the lithiated carbon substrate. Chemistry occurs at the end of range for the ions. The XPS data here (blue, full height traces) show lithiated carbon bombarded by 50 and 200 eV deuterium ions with nominally identical results. The peak at 530.0 eV represents Li-O bonds and the peak at 532.6 eV represents D-O interactions catalyzed by lithium.

average, share the charge transfer (CT%) with a given matrix constituent (the whole system stays neutral). The NN% and CT% values were obtained independently and are strongly correlated, implying the distribution of the probable binding of the retained deuterium atom in the matrix of the mixed atoms. In Fig. 2, matrix Q has 20% lithium, but deuterium binds to lithium in only 9% of cases ($\mathrm{NN}_{\mathrm{Li}} = 9\%$, $\mathrm{CT}_{\mathrm{Li}} = 8.8\%$). Even when there is an equal 20% quantity of oxygen and lithium in the carbon, as in matrix R, the oxygen by far dominates bonding with deuterium ($\mathrm{NN}_{\mathrm{O}} = \mathrm{CT}_{\mathrm{O}} = 27\%$) while bonding of deuterium with lithium ($\mathrm{NN}_{\mathrm{Li}} = 5\%$, $\mathrm{CT}_{\mathrm{Li}} = 5.7\%$) is suppressed below the lithium atomic concentration of 20%. For matrix T, without lithium, but with 20% of oxygen, 30% of implanted deuterium atoms bind to oxygen; i.e., more than one deuterium atom binds to each oxygen atom. The effect of deuterium accumulation is examined in matrix S which has 16% each of lithium, oxygen, and deuterium. Here the qualitative conclusions are the same; incident deuterium tends to avoid lithium with percentages for nearest neighbor and charge transfer ($\mathrm{NN}_{\mathrm{Li}} = 3\%$, $\mathrm{CT}_{\mathrm{Li}} = 9\%$) lower than the lithium atomic composition percentage of 16%. While the initial deuterium in the matrix S can be a nearest neighbor to the incident deuterium when it has come to rest, they do not mutually bind as indicated by $\mathrm{CT}_{D} = 0\%$.

These simulation results clearly reveal the importance of oxygen surface concentration levels for deuterium uptake chemistry, when the oxygen concentration reaches or exceeds that of lithium. In Ref. [27] much lower concentrations of oxygen did not have any pronounced effects on the deuterium uptake even in the presence of lithium.

The species charge distribution within the matrix confirms that lithium is not playing a major role in retaining deuterium when there is a higher or comparable concentration of oxygen with respect to lithium. Even when lithium is present in the carbon matrix, deuterium preferentially chooses to be in the vicinity of oxygen for its final bonding. These results corroborate the observed XPS spectral shifts that are correlated to the presence of lithium and deuterium where the effect can be seen predominantly in the electronic band states of oxygen atoms [17]. These conclusions are also consistent with the recent first principles computational chemistry calculations [28,29] using plane-wave DFT on binding chemistry of H, O, and Li in the graphite matrix.

At the plasma-material interface in nuclear fusion reactors, the plasma sheath dictates the incident charged-particle bombardment energy, which can influence wall erosion and material mixing. Our focus in this Letter, however, is the D uptake chemistry of hydrogen, which mainly evolves at the end of the collision cascade of the impact particle, when it is almost thermalized. Although the ions incident on surfaces in fusion devices are often more energetic than 5 eV, we experimentally demonstrate and illustrate in Fig. 3 that the near-surface chemistry does not change over a wide range of incident energies. Figure 3 shows XPS analysis of two carbon samples in its virgin and lithiated states, as well as after bombardment with 50 and 200 eV deuterium ions. Irradiation of lithiated graphite by 1 keV deuterium ions (500 eV/amu) results in the formation of Li-O (530.0 eV) and Li-O-D (532.6 eV) chemical complexes [17]. Figure 3 shows the O1s shift to 532.6 eV (corresponding to Li-O-D interactions) develops when bombarded by either 200 or 50 eV deuterium ions. These results imply qualitative independence of the relevant chemistry by the impact energy, at least as long as the impact particle penetration stays within the XPS range

($<$ 10 nm, which is the case at the considered impact energies). Accordingly, 5 eV ion energies in simulations, low energy monoenergetic ions in beam experiments, and the distribution of ion energies in fusion plasmas yield qualitatively identical surface chemistry. Although these results demonstrate favorable binding of impacting deuterium by oxygen, the key issue for their applicability to the fusion plasma-facing surface is the presence of unexpectedly high quantities of oxygen in the surface.

Quantum-classical molecular dynamics modeling was also applied to estimate D uptake and reflection probabilities (a) and ejection yields (b) of various surfaces upon impact of 5 eV D and the results are shown in Fig. 4. As one would expect from the results in Fig. 4, Li does not contribute much to suppress ejection or enhance deuterium uptake. In fact, matrix Q with 20% Li and 80% C shows higher ejection than the other compositions in consideration. The presence of lithium alone (case Q) does not improve deuterium uptake and carbon ejection in comparison to pure carbon (case P); in contrast, it has a negative effect of increasing carbon erosion. It is the presence of oxygen, with or without lithium that suppresses ejection and enhances deuterium uptake. When oxygen is present in amounts greater than or comparable to that of lithium (cases R, S, and T), deuterium recycling and carbon erosion decrease. This conclusion is consistent for single D bombardments as well as the case where deuterium accumulates in the sample (matrix S). Even though the uptake of D is only increased by 10% this is significant because the absolute size of the effect depends on concentration of oxygen and lithium, surface structure, energy deposition by D, and size of the sample, that are difficult to reach in quantum-classical atomistic calculations. Furthermore, simulations are consistent with experimental results of reduction of both chemical and physical sputtering measured by Yagi *et al.* [30] and Allain *et al.* [23]. Deuteration of the lithiated and oxydated carbon (case S) weakly influences this conclusion.

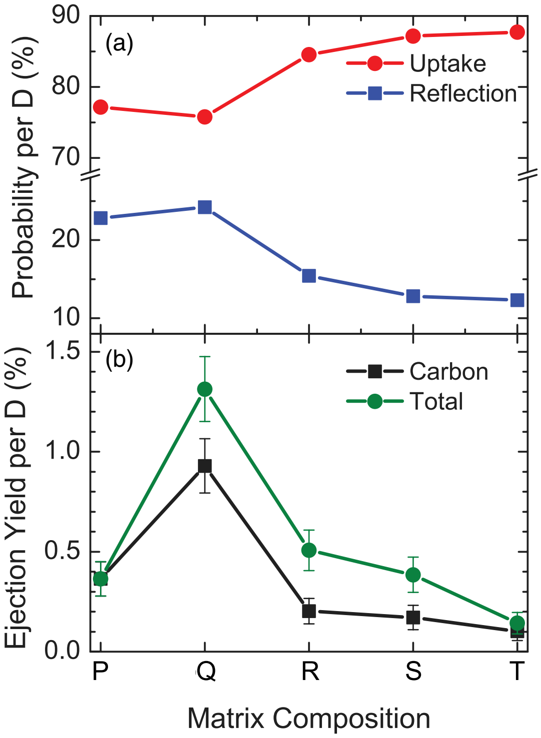

FIG. 4 (color online). Simulation results of D uptake and ejection of the target matrix material. (a) Uptake and reflection probabilities of impact D, and (b) total and C ejection yields for the various matrix compositions, P-T, defined in Fig. 2.

From both experiments and computational modeling we can now summarize the primary mechanisms responsible for trapping of deuterium in lithiated carbon. First, experiments [14] showed that deuterium uptake occurs via mechanisms that include O and C. Next, computational modeling results conclude that deuterium is primarily bound by oxygen in the Li-C-O matrix. Experiments (Figs. 1) showed that once the lithiated carbon (with only 10% oxygen in the top 4–8 nm) is irradiated with deuterium, the concentration of oxygen in the top 10 nm can increase dramatically to as much as 35%. Control experiments (black bars in Fig. 1) of carbon surfaces (with about 5% oxygen) irradiated with deuterium lead to a decrease in oxygen concentration to levels of about 1%–2%, indicating that C + O (without Li) would not be suitable for a plasma-facing wall in a fusion reactor. Lithium therefore is understood as a physical precursor that brings and retains oxygen to the surface (e.g., first 4–8 nm) thereby increasing the probability of D uptake by oxygen atoms. There are three major potential sources of oxygen: (1) impurity oxygen atoms from the Li evaporation source, (2) breakdown of water from the ambient residual gases at the surface during irradiation, and (3) oxygen from within the carbon substrate. Each case includes conditions identical to the case of fusion devices given the average water background is about 10^{-6} Pa or higher. Studies by Nieto *et al.* [31] showed water can readily break down on lithiated graphite surfaces increasing the surface oxygen concentration.

The amount of oxygen found with lithium deposition is well known [7]. The deposited lithium on carbon-based allotropes readily intercalates and when these surfaces are irradiated, additional oxygen can be driven to the surface by radiation-induced segregation and diffusion mechanisms [32].

Our findings, consistent with XPS data presented in Fig. 1, as well as the simulation results in Figs. 2 and 4, have far-reaching consequences for a number of fusion experiments that use lithium conditioning techniques [2,6] on carbon plasma-facing components. We find oxygen plays the key role in the binding of hydrogen, while lithium is the physical precursor for oxygen accumulation in the surface; i.e., lithium is the oxygen getter. When there is a significant amount of oxygen in the surface, compared to that of lithium, oxygen becomes the main player. Lithium has a minor influence on the deuterium chemistry in carbon; however, in practice, lithium is essential in attracting the oxygen, which in turn retains deuterium.

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