



Hydrogen retention in lithium and lithium oxide films

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ABSTRACT

Pure lithium (Li) surfaces are difficult to maintain in fusion devices due to rapid oxide formation, therefore, parameterizing and understanding the mechanisms of hydrogen (H, D) retention in lithium oxide (Li₂O) in addition to pure Li is crucial for Li plasma-facing material applications. To compare H retention in Li and Li₂O films, measurements were made as a function of surface temperature (90–520 K) under ultrahigh vacuum (UHV) conditions using temperature programmed desorption (TPD). In both cases, the total retention dropped with surface temperature, from 95% at 90 K to 35% at 520 K Li₂O films retained H in similar amounts as pure Li. Molecular Dynamics (MD) modeling was used to elucidate the mechanisms of H retention, and results were consistent with experiments in terms of both retention fraction and the drop of retention with temperature.

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1. Introduction

Li conditioning of plasma facing components (PFCs) has improved plasma performance with energy confinement and lowered H recycling in magnetic fusion devices [1–4], and suppressed edge-localized modes (ELMs) in NSTX [5,6]. Li conditioning of the NSTX divertor resulted in significant reduction (50%) of the heat load due to enhanced radiation [7,8]. These effects may be due in part to lithium's efficiency in binding H isotopes, thereby increasing the H retention and lowering the recycling of these species.

Accordingly, an understanding of H retention mechanisms and parameterization of H uptake in Li is needed for future applications of Li in high heat-flux and long-pulse duration machines, as well as for H storage applications [9–11]. Such information is also needed for Li₂O because at typical base pressures of 1×10^{-8} Torr, which is not uncommon in tokamaks, Li₂O can form rapidly ($2\text{Li} + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{O} + \text{H}_2$ [12]). For instance, in NSTX the walls were exposed to 100–600 L ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr} \times \text{sec}$) of water vapor in-between the plasma shots, during which the Li oxidation occurred.

According to the residual gas analysis, the gas consisted of 77% of hydrogenic species (mass 2, 3, 4) and 18% of water vapor (mass 17, 18, 19, 20) [13]. Li oxidation has also been observed in in-vacuo measurements of Li-coated samples of PFCs in LTX using the Materials Analysis Particle Probe (MAPP) [14–16]. The problem will continue to be important for the high-Z PFC phase of operation in NSTX-U in which Li₂O is also quickly formed, during Li evaporation, under typical water partial pressure conditions in the 1×10^{-9} Torr range.

Several studies have addressed the mechanisms of H retention in Li. Baldwin et al., [17] measured deuterium (D) retention in Li as a function of ion fluence and reported full uptake of D until volumetric conversion to LiD. Ion fluences beyond saturation led to a switch from the low to the high recycling regime (i.e. high retention to low retention), independent of the Li temperature (523–673 K). Taylor et al., [18,19], after analyzing NSTX tiles and performing ex-situ experiments on ATJ graphite samples, reported D bonding with Li after Li interacted with carbon and oxygen. Krstić et al. demonstrated that O concentrations could increase up to 40 at% with significant D fluence, which was later reconfirmed by experiments by Taylor et al. [20]. Using quantum classical molecular dynamics calculations (QCMD) on lithiated graphite surfaces, Krstić et al. [21,22] showed that D is bound to O containing complexes rather

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than to Li, thus promoting oxygen as having a main role in D retention. MAPP results on LTX indicated that it is not crucial to have just elemental Li to bind H, and Li oxide could also act as a binding agent [16]. However, in order to gain a better understanding and evaluate Li oxide's ability to reduce recycling, the efficiency of Li oxide compared to elemental Li in retaining H needs further investigation.

This work is built upon previous experiments where an ultrathin (3 monolayer, ML) Li film was deposited on a polycrystalline TZM sample and irradiated with D ions [23]. Release of oxygen from TZM and subsequent oxidation of Li films during TPD, as well as the complex Li-TZM interface, introduced uncertainties into interpreting those experiments. In order to address these issues, we have conducted a systematic study in which five to seven times thicker Li films were deposited on a nickel (Ni) single crystal. The purity of the Li film was checked with auger electron spectroscopy (AES). Modeling of the results is done by Molecular Dynamics (MD) using REAXFF bond-order potentials [24,25], with correction for dynamical polarization effects due to difference in Li, H and O electronegativities by Electronegativity Equalization Method (EEM) [26,27].

2. Experimental setup

All experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber with a 2×10^{-10} Torr base pressure. Low energy electron diffraction (LEED) was performed by using PHI 15–120 LEED optics. AES was done using a PHI 15-255G double-pass cylindrical mirror analyzer (CMA). TPD experiments were performed with the sample in line-of-sight of the ionizer of a shielded UTI 100C quadrupole mass spectrometer (QMS), with the shield nozzle located 1 mm from the sample, using a heating rate of 4 K/s. A K-type thermocouple (chromel-alumel) was spot-welded directly on the sample to monitor the temperature.

The Ni(110) single crystal (8 mm square, $\pm 0.5^\circ$ orientation) sample was spot-welded onto tantalum (Ta) wires used for resistive heating. The crystal was cleaned using cycles of 1.5-keV Ar⁺ ion sputtering and annealing in vacuum at 1100 K. Oxidation in 4×10^{-8} Torr O₂ with the sample at 1000 K was used to eliminate residual carbon, and reduction in 4×10^{-8} Torr H₂ with the sample at 1000 K was used to eliminate residual oxygen. Good surface order was confirmed with LEED. Surface purity was checked with AES to ensure carbon and oxygen concentrations were below 1%. The quality of the Ni(110) surface was also confirmed to be good using the position and shape of the H₂ desorption peaks in TPD [28]. In these experiments, we used a Ni (110) single crystal as a substrate to avoid effects due to grain boundaries, intrinsic defects, and impurities diffusing to the surface. Moreover, due to the low solubility of alkali metals in Ni, Li and Ni are immiscible, and thus do not form either bulk alloys or two-dimensional surface alloys [9,29].

Li dosing was performed with a commercial Li metal dispenser (Li/NF/7.3/17/FT, SAES Group) by thermal evaporation onto the Ni substrate. H₂⁺ ions were produced in a differentially pumped ion gun (PHI 04–303 A) with adjustable ion energy from 0 to 5 keV, and a liquid nitrogen trap was used in the H₂ gas line to mitigate H₂O contamination. H₂ gas (Praxair, 99.999%) and O₂ gas (Praxair, 99.995%) was introduced into the chamber following a liquid nitrogen trap and using a high precision variable leak valve. Hydrogen, rather than deuterium, was used in these experiments for convenience and H has the same chemistry as D. After surface preparation, Li films were exposed to a 500 eV H₂⁺ ion beam, which is nominally composed of 90% H₂⁺ and 10% H⁺ [30]. The H₂⁺ flux was defocused over the surface and the current measured on the sample was 1.74 μ A. The H₂ pressure in the chamber during H₂⁺ irradiation was 4×10^{-8} Torr and the total exposure time was 120 s.

These conditions provided a total fluence of 4×10^{15} H⁺ cm⁻². The Li areal density was $\sim 3 \times 10^{15}$ Li cm⁻², as discussed later.

3. Computational approach

We simulated these experiments by using Molecular Dynamics. Amorphous target surfaces of pure Li and Li₂O were prepared for a set of temperature values T (90, 300, 400, 500, and 600 K), following the procedure in Refs. [21,22] for each temperature. Computational cells of about 2000 atoms were used. These amorphous cells were created initially at 300 K, one with random distribution of lithium atoms, and another one with a predefined random distribution of 33% O and 67% of Li atoms. These cells were energy optimized in a succession of heating (1000 K max) and annealing processes, and finally thermalized to a desired temperature using a Langevin thermostat with time constant of 100 fs. The final numbers of atoms in the prepared cells at various temperatures are shown in Table 1.

Periodic boundary conditions were applied in the x-y directions to simulate an infinite surface slab, with D impact in the z-direction. The lateral dimensions of the cells were 3.6 nm in z direction and about 3.4 nm in x and y directions for both surfaces (Fig. 1). The cell depth of 3.6 nm is sufficient to prevent penetration of the D atoms to the cell bottom boundary, thus avoiding artificial reflections.

The atomistic simulations were performed by MD, using Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [31] with Reactive Force Field (ReaxFF) Bond Order (BO) potential [24,25,32], and corrections for dynamic atom charge effects by semi-empirical EEM [26,27]. The classical ReaxFF potentials used for Li, O, D were verified in our previous computations [33] of retention and sputtering of Li-C-O-D surfaces by Quantum-Classical Molecular Dynamics (QCMD), using Self Consistent Charge Tight Binding Density Functional Theory (SCC-DFTB) [34]. The ReaxFF potentials implemented in LAMMPS are able to model the dynamics of breaking and forming of chemical bonds [24,32], as well as to calculate the dynamic changes in charges of the atoms in the system with the change of atomic coordinates using the Electronegativity Equalization Method [26,27]. The latter is important in the presence of mutually polarizable materials with very different electronegativities, such as Li (0.94) and O (3.4), while the H electronegativity (2.2) is in the middle.

The prepared computational cells, with various atomic contents and at various temperatures, were bombarded by $N = 5040$ independent 10 eV D atoms, with trajectories starting 1 nm at random location above the surface, in the direction orthogonal to the surface. This large number of trajectories led to the adequate statistics of H retention probability and was done at supercomputing facilities using “embarrassing parallelization”. If the number of D atoms retained in the surface is N_D , then the retention probability per D is calculated as N_D/N . The retention chemistry of D evolves at the end of the collision cascade when the impact particle is thermalized allowing comparison with the experimental results at higher impact energies [21]. We carry out the analysis of the resulting chemistry after the final rest location of each D impact, by performing the nearest-neighbor (NN) estimation for each retained D (H) atom in the surface, defining the most-probable bonds [21]. While role of Li in bonding hydrogen is not challenged in the pure-lithium surface, it is surprising that O-D and Li-D NNs are similarly represented. Although there is two times more Li than oxygen atoms in the surface, oxygen has coordination number 2, two times larger than coordination number of Li (1). This indicates approximate similar efficiency of H (D) retention in Li and Li₂O surfaces. We note that the O-D bond percentage is slightly bigger than Li-D one, and that effectiveness of O to bond D slightly increases with temperature.

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