



Dynamic evolution of plasma facing surfaces in NSTX: Impact of impurities and substrate composition on fuel recycling

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ABSTRACT

Understanding plasma/complex surfaces interactions in NSTX with liquid lithium on thin porous molybdenum substrate for the divertor, additional PFC surfaces such as carbon tiles, and the presence of gases and impurities require integrated implementation and the interplay of detail various physical processes. These include simultaneous and multiple ion species penetration and mixing, scattering, reflection, physical and chemical sputtering and/or compound formation, dynamic surface evolution/modification, thermal diffusion and segregation, and recombination/desorption of species in this multi-component surface composition.

We enhanced our ITMC-DYN simulation package combining integrated models for studying the time-dependent dynamic surface evolution under impact of plasma particles to address all phenomena self-consistently. These phenomena include the effect of compounds formation and impurities, specific for NSTX design and conditions, the influence of Mo substrate porosity on Li erosion, mixing, and overall fuel recycling. Simulation results showed that formed lithium compounds, filling porous Mo, would reduce diffusion of deuterium into the bulk that will result in accumulation near the surface region. However, inclusion of a thin layer of impurity compounds on the surface would prevent hydrogen motion to surface and leads to a decrease in recombination and desorption rate.

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1. Introduction

Design of liquid lithium divertor (LLD) in NSTX, currently being developed and enhanced, is intended to provide low recycling conditions during discharge. Theoretical predictions of deuterium recycling are based on the low reflection of hydrogen isotopes from Li surface – approximately 10% for 1 keV and ~20% for 100 eV D⁺, and high diffusion and uptake of deuterium in liquid lithium. These predictions were supported by experimental results [1] where almost full retention of deuterium fluence in liquid lithium samples was shown for several relevant temperatures, 523–673 K. However, realistic picture of the reactor environment can significantly change the value of deuterium recycling, obtained theoretically or in the laboratory experiments. Composite/mixed materials as plasma facing components (PFCs) in NSTX device add significant challenge to understanding the effects of core plasma particles impact on LLD surface, lifetime, core plasma contamination, hydrogen recycling, and surface material dynamic properties. High rate of oxygen adsorption from residual gases during lithium deposition on porous

molybdenum and presence of oxygen ions in particle flux to the LLD surface during discharge could potentially affect the successful realization of liquid lithium divertor concept.

Dynamic tracking of surface evolution at nano/micro layers is performed using Monte Carlo binary collision approximation models that include most important processes of ions/atoms interactions and time-dependent evolution of target composition. The dynamic version of ITMC (Ion Transport in Materials and Compounds), i.e., ITMC-DYN code [2–5] includes various implemented interatomic potentials for modeling elastic atomic collisions; several models for inelastic electronic energy loss; dynamic time-dependent update of target composition; numerous number of target layers with unlimited number of composite materials; multiple number of simultaneously incident ion beams with different parameters; implanted atoms diffusion and mixing; molecular surface recombination and desorption; chemical erosion; and surface segregation. Target materials can be composed of several different target layers with various thicknesses. Each layer can be composed of multiple atoms composition as well.

We used ITMC-DYN to analyze NSTX parameters and conditions which can influence deuterium recycling, surface modification and erosion, impurities distribution, and sputtering. We considered typical parameters for the low recycling region of NSTX that were found in various laboratory and recent NSTX experiments [6].

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In such complicated PFC system with lithium, carbon, and molybdenum surfaces, several factors and interplay of different processes – target composition and temperature, deuterium reflection from pure lithium and from compound, particles diffusion and surface molecular recombination – will have significant effect on recycling. Therefore, it is important to predict compounds formation from impurities and components of NSTX chamber on lithium surfaces and to consider and critically review various experimental and calculated values of coefficients for hydrogen behavior in pure materials and in compounds.

2. Models description and application for NSTX conditions

The combination of three main processes should be considered in regard to hydrogen isotope motion and recycling from LLD surfaces – reflection, diffusion, and surface recombination. We did not include in this simulation possible chemical erosion due to hydrocarbon formation and emission since the effect of this process will be very small for the considered surface temperatures and for the low carbon concentrations in lithium layer [7].

In our simulations, the collision processes responsible for particles reflection are integrated with detailed models of time-dependent atoms diffusion and molecular recombination and desorption. Therefore, we considered actual fluences and exact irradiation times of the discharge. The time step is determined from the processes of diffusion and molecular recombination. An implicit method for modeling atoms diffusion was implemented to increase the time step and reduce required computational time in the simulations, especially for species with high diffusivity.

Diffusion coefficients of hydrogen isotopes in lithium were predicted in several experimental studies [8,9], and the results showed large differences in the diffusion of H and T, approximately three orders of magnitude [10]. Therefore, we used values of the diffusion coefficients for hydrogen isotopes that were predicted by theoretical calculations with approximation of several experimental results [11].

Most probable impurities in NSTX device, carbon and oxygen, can reduce diffusion of deuterium that results in accumulation near the surface region. However, inclusion of a thin layer of impurities on the surface can prevent hydrogen motion to first monolayer and could lead to a decrease in recombination and desorption rate. To take into account changes in the diffusion coefficient in accordance with the modification of surface composition during reactor operation, we analyzed possible chemical reactions of deposited impurities with lithium. We reviewed possible chemical reactions of Li with hydrogen, oxygen, and carbon, and the test results of lithium surfaces and gases content in chamber after NSTX operation [12]. Based on this, we selected several compounds as the most probable components of LLD surface: lithium hydroxide (LiOH), lithium oxide (Li₂O), and lithium carbide (Li₂C₂) – or most likely elemental carbon distributed in lithium. Fig. 1 shows diffusion coefficients of hydrogen isotopes in these compounds and, for comparison, the diffusion coefficient in pure lithium [13–15].

Formation of lithium hydroxide is strongly favored energetically, however it can be transformed to lithium oxide at temperatures >600 K [16,17], which are relevant to NSTX operating temperatures. Therefore, we assumed in our calculations that LiOH as well as Li₂O can be present in liquid lithium layer. Using experimental results for hydrogen isotopes diffusion in compounds, we calculated the diffusion coefficient in multi-component materials depending on target composition as the interpolation of logarithmic values of diffusivity in each compound. Since saturation concentrations of Li₂C₂ in liquid lithium are very low for the considered temperature values [18] and deposited carbon ions

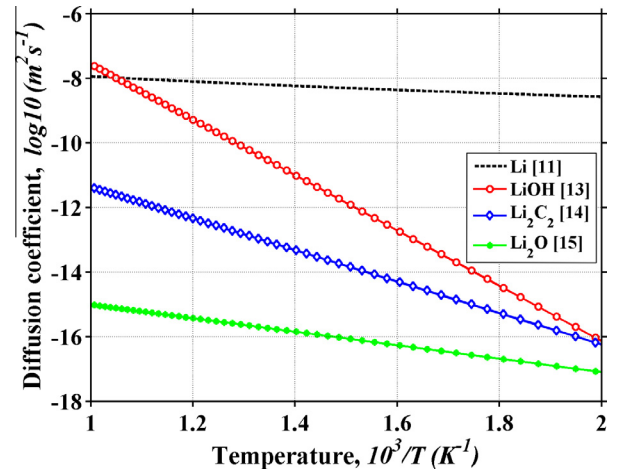


Fig. 1. Diffusion coefficients of hydrogen isotopes in pure lithium and compounds.

most likely be present in the form of elemental carbon, we calculated changes in the diffusion coefficient of deuterium due to carbon species as concentration dependent logarithmic value of diffusion in randomly oriented carbon [19]. Such approach for pure Li₂C₂ compound, e.g., gives approximately the same values of diffusivity that were predicted in experiments [14] (Fig. 2).

We considered two ranges of values for the molecular recombination coefficient of deuterium on lithium surface. First one was derived theoretically and corresponds to the recombination and desorption rate from clean lithium surface. Second one was predicted in experiments where presence of oxides in lithium was found [20]. Common equation for the description of recombination rate for hydrogen isotopes on metallic surfaces is [20]:

$$k_r = 2.63 \times 10^{24} (k_0)^{-2} \sigma (2MT)^{-1/2} \exp(2[E_s - E_c]/kT) \quad (\text{m}^4 \text{s}^{-1})$$

where M is atomic mass of desorbing species, k_0 is pre-exponential factor in Sieverts' constant, T is temperature, E_s is enthalpy of solution, E_c is activation energy of chemisorption at the surface, and σ is constant related to surface-site availability that reflects decrease in recombination rate due to impurities.

It is not clear from the experiments the relation between reduction in deuterium recombination and desorption and ratio of oxygen or other impurities on lithium surface. Therefore, we considered the lowest value, predicted in experiments with

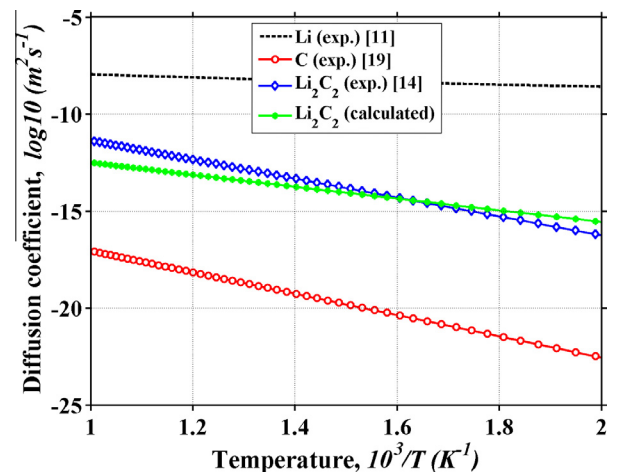


Fig. 2. Experimental and calculated values of hydrogen isotopes diffusion coefficients in various materials.

$\sigma = 0.01$, and the highest value, predicted theoretically with $\sigma = 1$. The last one is closer to the predicted recombination coefficients [21] estimated based on the diffusion coefficient of deuterium in lithium [11].

The diffusion coefficient of hydrogen isotopes in Mo also was chosen based on the review several experimental and theoretical values [22].

3. Modeling results

We used in our simulations parameters for the outer divertor region and LLD surface conditions measured in NSTX device or related laboratory experiments, such as ions temperature <1 keV [23], particle fluxes about $10^{22} \text{ m}^{-2} \text{ s}^{-1}$ [24], LLD surface temperatures is up to 350°C [25], carbon concentration is up to $\sim 3\%$ [6], oxygen concentration is up to 0.3% [26]. Duration of typical plasma discharges in NSTX is ~ 1 s [27]. We used average values for the energy of impurity ions such as 3 keV.

LLD surface is prepared by the deposition of lithium on porous molybdenum substrate. The porosity of substrate and partial filling of porous with evaporated lithium can also influence deuterium recycling. Close location of Mo to the surface can increase the reflection of deuterium that, additionally to the lower diffusion and higher recombination rates of hydrogen in Mo, can switch LLD operation from low recycling PFC to high recycling.

To analyze regimes for such transition we modeled LLD surface with various thicknesses of Li layers on Mo with different surface temperatures.

3.1. Surface composition and deuterium recycling – start from pure Li

If we consider ideally clean lithium layer with 100 nm thickness on Mo substrate at 500 K temperature subjected to $10^{22} \text{ m}^{-2} \text{ s}^{-1}$ flux of 1 keV D^+ with carbon impurities up to 3% , deuterium release can only be from reflection at the surface and is slightly increased with time due to carbon deposition on the top (Fig. 3). The changed diffusion coefficient at location of highest carbon concentration, from 10^{-9} to $10^{-12} \text{ m}^2 \text{ s}^{-1}$, cannot increase the deuterium accumulation enough to be released through the desorption mechanism. The range of 1 keV deuterium ions in lithium for 45° angle of incidence, predicted in modeling for LLD location at/near the strike point [28], is about 60 nm and because of the deuterium high diffusivity in lithium and molybdenum, almost all deuterium diffuses to the bulk.

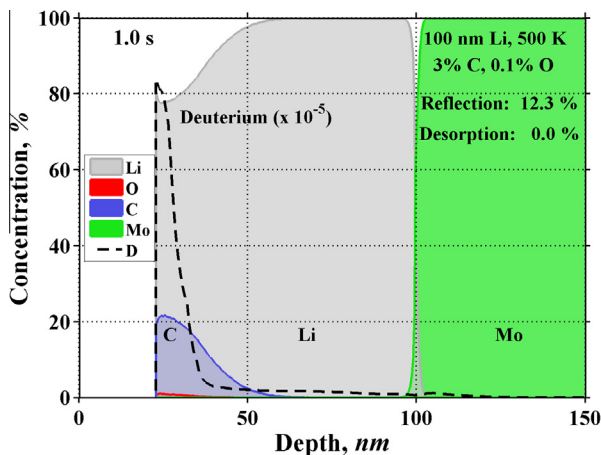


Fig. 3. Lithium surface composition changed by $10^{22} \text{ m}^{-2} \text{ s}^{-1}$ deuterium flux with 3% carbon and 0.1% oxygen.

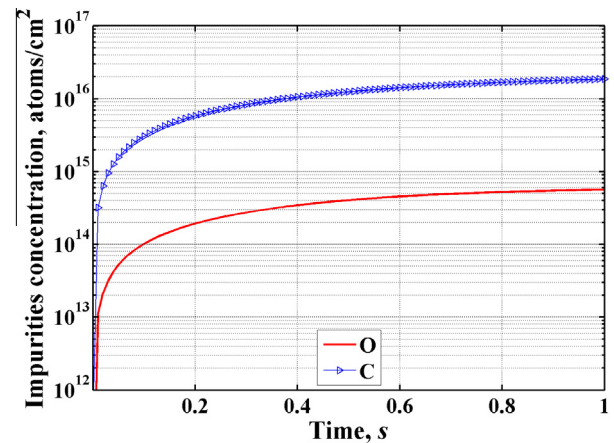


Fig. 4. Impurities concentration in lithium during 1 s discharge.

Maximum concentration of oxygen at the end of discharge is less than 1% and this is almost steady-state concentration value as it is shown in Fig. 4. Erosion of surface by physical sputtering is around 20 nm using 1.68 eV surface binding energy of lithium and deposited impurities. The long range of deuterium ions and the low mass of lithium atoms are the reasons of slight mixing at the Li/Mo interface.

3.2. Effect of lithium oxide and hydroxide on deuterium diffusion and desorption

Laboratory tests of LLD porous molybdenum samples under various possible NSTX operating conditions showed up to 20% oxygen concentration in lithium layer after 30 min of deuterium bombardment [29]. To analyze the effect of oxide layers on deuterium behavior we considered two compounds, LiOH and Li_2O , as initial inclusions in target composition.

Modeling results for target composition, consisted from 40% Li and 60% Li_2O in 100 nm layer on molybdenum substrate, are shown in Figs. 5 and 6. We considered two temperature regimes – 500 K and 600 K . Higher diffusivity at 600 K leads to decrease of deuterium concentration in compound in comparison with the lower temperature case, however higher recombination rate results in almost 6 times higher deuterium release from the surface.

Figs. 5 and 6 show that the desorption rate of deuterium molecules in presence of impurities can be limited by deuterium

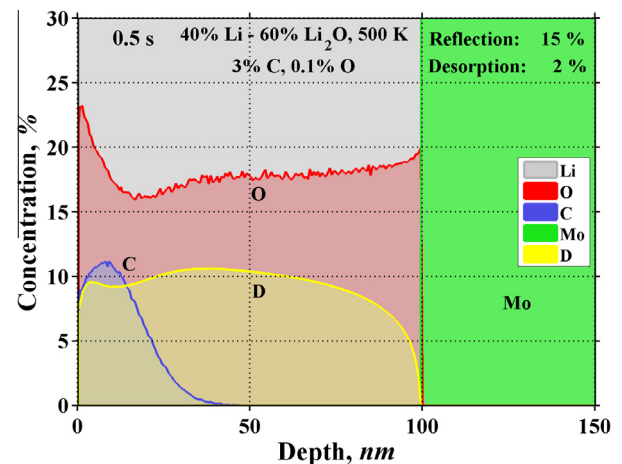


Fig. 5. Deuterium diffusion and desorption in Li/ Li_2O compound at 500 K temperature.

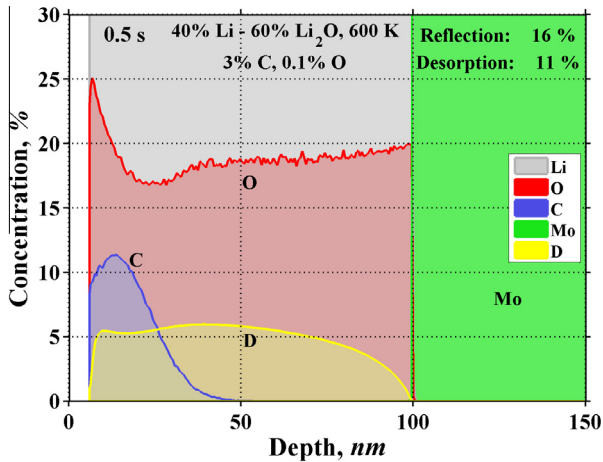


Fig. 6. Deuterium diffusion and desorption in Li/Li₂O compound at 600 K temperature.

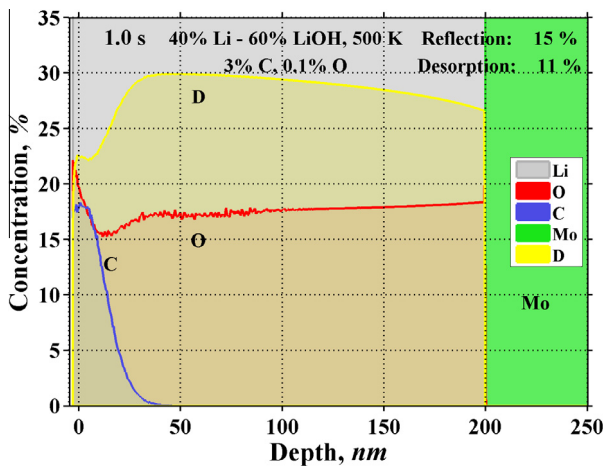


Fig. 7. Deuterium diffusion and desorption in Li/LiOH compound at 500 K temperature.

diffusion to the surface. It is better illustrated in Fig. 7 of deuterium diffusion and desorption in Li/LiOH composition with 200 nm thickness on Mo at 500 K. Thus, we took into account changes in desorption rate due to impurities effect on deuterium diffusion and, as consequence, on recombination rate.

Modeling results for target composition of 40% lithium and 60% lithium hydroxide with 200 nm thickness, showed that deuterium desorption rate is around 10% even at 500 K surface temperature since of initial presence of hydrogen in compound, increase of its concentration due to deuterium influx, and low diffusion coefficient of around $10^{-13} \text{ m}^2 \text{ s}^{-1}$.

We also calculated deuterium desorption rate using lowest values of the recombination coefficient [20], and these calculations predicted maximum of $\sim 3\%$ of deuterium release through the desorption mechanism.

3.3. Lithium thickness effect on recycling

Simulation results for different thicknesses of lithium compounds on molybdenum substrate showed that closer locations

of Mo to the surface, e.g., with 10 nm Li layer on top, will result in an increase in reflection rate up to 50%. A thicker layer of lithium oxide, e.g., 200 nm, can reduce deuterium diffusion to the bulk, that result in rapid increase of its concentration near the surface and, therefore, increase of deuterium desorption. An increase of carbon concentration in ions from 1% to 3% will result in 30% reduction of desorption rate of deuterium from lithium oxide.

4. Conclusion

We modeled lithium surface evolution and hydrogen isotope behavior in pure lithium and compounds under the impact of deuterium ions with impurities for conditions relevant to NSTX operation. Using our dynamic Monte Carlo code, ITMC-DYN, we simulated deuterium release from the surface due to reflection, molecular recombination, and desorption for various lithium compounds, layers thicknesses, temperatures, and impurities concentrations. Thicker layer of lithium oxide or hydroxide will result in deuterium accumulation near the surface due to the reduced diffusion to the bulk, that can slightly increase desorption rate. Increase of carbon impurities in edge plasma will lead to carbon accumulation on LLD that will act as barrier to deuterium release from the surface. The interplay of lithium compounds formation, deuterium diffusion, surface recombination, and desorption depends critically on LLD parameters and operation. Therefore, detailed analysis of lithium coating porous Mo, its compounds formation and saturation limits, and deuterium desorption during and in between discharges need further studies both experimentally as well as modeling since these issues critically affect the overall performance of liquid metals operation in tokamak environment.

Acknowledgment

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