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Experimental studies of lithium-based surface chemistry for fusion plasma-facing materials applications ☆

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ABSTRACT

Lithium has enhanced the operational performance of fusion devices such as: TFTR, CDX-U, FTU, T-11 M, and NSTX. Lithium in the solid and liquid state has been studied extensively in laboratory experiments including its erosion and hydrogen-retaining properties. Reductions in physical sputtering up to 40–60% have been measured for deuterated solid and liquid lithium surfaces. Computational modeling indicates that up to a 1:1 deuterium volumetric retention in lithium is possible. This paper presents the results of systematic in situ laboratory experimental studies on the surface chemistry evolution of ATJ graphite under lithium deposition. Results are compared to post-mortem analysis of similar lithium surface coatings on graphite exposed to deuterium discharge plasmas in NSTX. Lithium coatings on plasma-facing components in NSTX have shown substantial reduction of hydrogenic recycling. Questions remain on the role lithium surface chemistry on a graphite substrate has on particle sputtering (physical and chemical) as well as hydrogen isotope recycling. This is particularly due to the lack of in situ measurements of plasma-surface interactions in tokamaks such as NSTX. Results suggest that the lithium bonding state on ATJ graphite is lithium peroxide and with sufficient exposure to ambient air conditions, lithium carbonate is generated. Correlation between both results is used to assess the role of lithium chemistry on the state of lithium bonding and implications on hydrogen pumping and lithium sputtering. In addition, reduction of factors between 10 and 30 reduction in physical sputtering from lithiated graphite compared to pure lithium or carbon is also measured.

1. Introduction

Lithium has become a potentially viable plasma-facing surface improving particle control and energy confinement in magnetically confined plasmas devices including: TFTR, FTU, T-11 M, CDX-U [1–4], and recently NSTX [5]. Advanced lithium applications include the operation of the lithium tokamak experiment (LTX) and the application of a liquid lithium divertor (LLD) in NSTX. NSTX lithium research is aimed towards sustaining the current non-inductively in H-mode plasmas, which require control of both long pulse density rises and impurity influxes. Lithium wall conditioning provides an enabling technology to control plasma recycling and enhance performance [6–8]. Erosion and redeposition plasma boundary modeling predicted favorable conditions for low-recycling in NSTX using a liquid Li divertor [9]. Recently NSTX has demonstrated that evaporated lithium can improve particle control and energy confinement in diverted H-mode plasmas [5]. Initial results using Li pellet injection (LPI) demonstrated a reduction in deuterium recycling. However after a few plasma shots, pre-lithium conditions returned and high D recycling ensued. Further work evaporated Li on plasma-wetted surfaces of NSTX in larger amounts using a lithium evaporator system known as LiTER-1. During FY2006 runs short-term improvements were found for H-mode discharges with signs indicative of low-recycling regimes including reduction in line average electron density, Z_{eff}, and increase in electron temperature. However, addition of more Li did not improve particle control thus surface passivation of Li coatings by residual water and hydrocarbons were conjectured as one possible reason for the subsequent absence of strong D particle pumping [5]. Recent results by Kugel et al. find that the cumulative lithium wall conditioning has yielded improved density control and noticable D pumping effects [10].

Questions still remain regarding the nature and duration of lithium coatings as well as the role of impurity emission from these lithiated surfaces. This work presents initial results of in situ

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surface chemistry of lithiated ATJ graphite for various deposition conditions simulating the NSTX environment. In addition, we present post-mortem surface characterization of NSTX tiles exposed to lithium deposition runs. Correlation between both results is used to assess the role of lithium chemistry on the state of lithium bonding, lithium erosion, and implications on hydrogen pumping.

2. Experimental setup

Several off-line experimental ion-beam and surface characterization facilities are used to conduct initial systematic studies on the chemistry of lithiated graphite surfaces exposed to conditions found in NSTX Li runs. For comparison NSTX ATJ graphite tiles exposed to plasma discharges with lithium wall conditioning and deposition are characterized ex situ. Post-mortem analysis is conducted for several NSTX ATJ graphite tiles extracted from the lower inner divertor floor adjacent to the center stack of the machine. These tiles were selected since they covered both the private flux region and outer strike point for NSTX high-triangularity plasmas during lithium-coated shots. Three major experiments were conducted. The first, in situ lithiated graphite experiments under particle irradiation and lithium deposition with simultaneous surface analysis. The second, ex situ lithium depositions and high-intensity deuterium exposures conducted in the IIAX experiment [12] at the University of Illinois and post-mortem characterization in facilities of the Birck Nanotechnology Center at Purdue University. The third, post-mortem analysis of NSTX ATJ graphite tiles.

The IMPACT (Interaction of Materials with Particles and Components Testing) experimental facility was designed and built by Allain et al. at Argonne National Laboratory and has been relocated to Purdue University [11]. The facility provides a number of complementary surface characterization techniques that probe candidate lithiated surfaces while exposing them to a selection of energetic particle beams (e.g. D and He). IMPACT is equipped with a vapor deposition source and filament focused ion-beam source, both used for sample irradiation. Li vapor was deposited onto ATJ graphite samples; thickness of the deposited Li layer varied from 30 to 1400 nm. D_2^+ and He^+ irradiations ranged from 100 to 500 eV/amu on 1000-nm lithium coatings on ATJ graphite deposited at room temperature.

Experiments simulate conditions in NSTX by: (1) calibrating the lithium deposition rate from an e-beam evaporator at a rate between 1 and 10 nm/min, (2) depositing low vs. high deposition doses determined by short and long exposures, (3) bombarding with D or He species at energies between 100 and 500 eV/amu, and (4) exposing lithiated surfaces to D fluencies greater than $10^{20}\ m^{-2}$. In addition, all ion bombardment experiments are conducted at 45-degrees with respect to the surface normal. During ion bombardment and lithium deposition, 1-cm^2 ATJ graphite (Union Carbide) samples are characterized by in situ X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering spectroscopy (LEISS). Details of XPS and LEISS setup can be found in the literature [11]. In addition, during surface characterization and particle bombardment, sputter yields were measured for lithiated graphite using a dual control unit – quartz crystal microbalance system.

For this work the IMPACT facility was retrofitted to accommodate the NSTX ATJ graphite tiles described above (from FY2006 experimental campaign) to measure surface chemistry and structure by means of XPS and LEISS. Poloidal points along the tile axis were characterized with XPS. In situ studies of lithiated ATJ graphite samples exposed to controlled lithium deposition rates are conducted to isolate the effect of ambient air exposure prevalent in all post-mortem analyses of lithiated graphite samples from NSTX. In this work control studies also exposed lithiated ATJ graphite and pure lithium foil samples in IMPACT to ambient air for prescribed time duration of up to 7 days. These samples were exposed to a prescribed time frame and then characterized under vacuum conditions by XPS. XPS data from IMPACT is compared to a charge-compensated high-resolution XPS instrument that uses monochromatic X-rays from a Mg Kα source. This comparison is necessary to identify the effect of surface charging on IMPACT XPS spectra, estimated at about 0.4–0.5 eV. HR-XPS was conducted for D-irradiated samples, which were exposed to ambient air.

3. Results and discussion

3.1. Effects of lithium surface chemistry on surface erosion

The hydrogen pumping performance of lithium surfaces depends among other things on: (1) chemical state of lithium deposited (e.g. bonding with impurity species), (2) any alloying with other metals, and (3) whether the surface is in the solid or liquid state [12]. The hydrogen retention level can also affect particle sputtering. For example, deuterated lithium surfaces were found to have sputtering reductions over 40% when saturation (1:1) levels of exposure were reached [13,14]. In fact, physical sputtering which emanates from the first few monolayers in a metal can have significant sensitivity to the surface chemical state. In particular lithium and deuterium can form strong ionic bonds with heats of formation nearly 50–60% more than the lithium metallic bond. Strong covalent bonding exists for the complex surface chemistry of lithiated graphite indicated by the Li–C data in Fig 1. Fig. 1 shows the sputter yield of Li–C by energetic He ions compared to other lithium-treated or lithium-based surfaces including: pure lithium, alloyed lithium with tin, deuterated lithium, and lithium deposited on ATJ graphite [12]. Comparing these results we find that depending on the state of lithium bonding the yield of sputtered atoms can vary by almost two orders of magnitude near the sputter threshold region. This means that once lithium atoms are bonded to either deuterium or an impurity, the energy needed to break surface bonds leading to sputtering of surface atoms increases. One interesting note is that although the total sputtering yield in Li–C bombardment decreases, the dominant species of sputtered particles is lithium indicated by in situ QCM measurements and low-energy ion scattering spectroscopy measurements in IMPACT. In addition, all sputter yields plotted in Fig. 1 correspond to total particle (ion + neutral) sputtering. This is an important distinction since the ion-induced secondary ion emission (IISIE) is close to 66% for pure lithium surfaces [12].

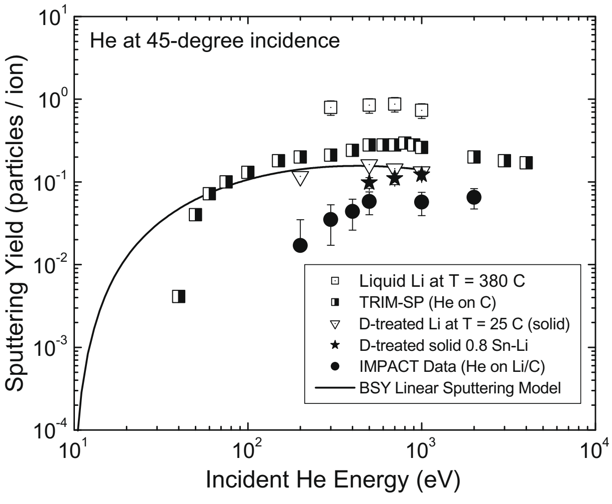

Fig. 1. Sputtering yield comparison for various lithiated surfaces.

3.2. NSTX tile analysis

Several NSTX tiles were removed from the divertor floor and analyzed in the IMPACT experimental facility. The tiles were extracted mostly along a poloidal and radial track on the divertor floor exposed to large amounts of lithium. Fig. 2(a) shows the geometry of the divertor tile set removed for surface characterization. Fig. 2(b) presents XPS data of the C 1s line showing the presence of a strong peak near 290 eV. This particular peak is identified as lithium carbonate. A control NSTX divertor ATJ graphite tile was also analyzed. This tile was located in a location hidden from the lithium vapor flux during NSTX discharges. Note the graphitic state of the control NSTX tile surface indicated by the XPS spectra of the C1s peak. Two clear results from these measurements. One is that the carbonate peak at a binding energy of approximately 290.5 eV and closer to 291 eV after compensating for surface charging (an effect unavoidable in all IMPACT XPS spectra) is associated with lithium deposition. This is evidenced by comparison of the XPS spectra of the 'virgin' or non-Li exposed NSTX graphite tile with a clear C 1s peak at 284.5 eV corresponding to the graphitic state of carbon atoms. The second result is that the chemical state of lithiated graphite along radially (NSTX samples A408-002 and A401-001) measured on the NSTX tiles remains mostly the same. What is yet not clear is the origin of the carbonate peak. That is, lithium is certainly associated with formation of this peak, however oxygen also plays a role and the question is where does it originate? To address this in situ XPS measurement were conducted under vacuum during lithium deposition to identify the dominant bond with lithium atoms and compare to a control experiment exposing the deposited lithium coating to ambient air for at least 24 h.

3.3. Lithium surface chemistry

Results of in situ lithium deposition exposures are shown in Figs. 3 and 4. Fig. 3(a) consists of in situ deposition of lithium on ATJ graphite samples with concurrent XPS measurement. The data shows a strong graphitic peak near 284.5 eV similar to that measured on the 'virgin' or control NSTX tile sample. This is indicative of a surface with low probability of covalent bonding with impurities. As the ATJ graphite sample is deposited with lithium in situ, XPS spectra show a shoulder in the left side of the C 1s peak indicating some contamination, however the strong lithium carbonate peak is completely absent. After 140 min of deposition, the sample is then exposed to air for 24 h and one notes the rise of a second peak near 290 eV corresponding to lithium carbonate. An additional control experiment is conducted and the results shown in Fig. 3(b). The C 1s peak for pure lithium surface is shown. The sample does not show a graphitic state, rather a peak at a binding energy between 286 and 287 eV corresponding to the carbidic state of carbon bonds (likely C–O bonding). The carbonate peak is also absent, which indicates that the lithium carbonate can only occur for thin-film lithium depositions on graphitic substrates. Fig. 3(c) shows the effect of energetic 500 eV/amu D bombardment for low and high lithium doses. These XPS results are compared to a control case without D bombardment at high lithium doses. All D bombardment cases are samples exposed to ambient air and similar to the NSTX tile samples, a lithium carbonate peak dominates the C 1s spectrum. For the case of low lithium dose, D bombardment is found to have an effect in the competition between carbidic and graphitic bonding states of carbon atoms exposed to lithium. This could have implications in how the complex lithium graphite matrix retains hydrogen during plasma bombardment. Further work on this latter point will be published in future work.

The behavior of lithium bonding is further elucidated by examining the O 1s photoelectron spectra. In Fig. 4(a) spectra are shown for the identical conditions as those shown in Fig. 3(a). As the lithium is deposited in situ a prominent peak at a binding energy of about 530 eV is identified. This is associated with a lithium peroxide bond and likely the bonding state of lithium when deposited under vacuum conditions during NSTX discharges. As the sample in IMPACT is exposed to air, the lithium peroxide peak is lost and only the peak corresponding to strong covalent bonding persists. Fig. 4(b) shows the control experiment with a pure lithium surface. The key result here is that the intrinsic bonding state of lithium in its pure metallic form and that of lithiated graphite is very different. In the case of an unmixed lithium surface, the top layer is dominated by LiOH bonding and once cleaned (Ne^+ bombardment in this experiment) the bonding state of lithium is as an oxide. Measurement of this lithium peroxide bonding state is important in understanding what the state of lithium atoms is during plasma discharges in NSTX. In addition, XPS spectra of ATJ graphite tile surfaces indicate that samples used in off-line experiments closely resemble chemically the ATJ graphite tiles in NSTX.

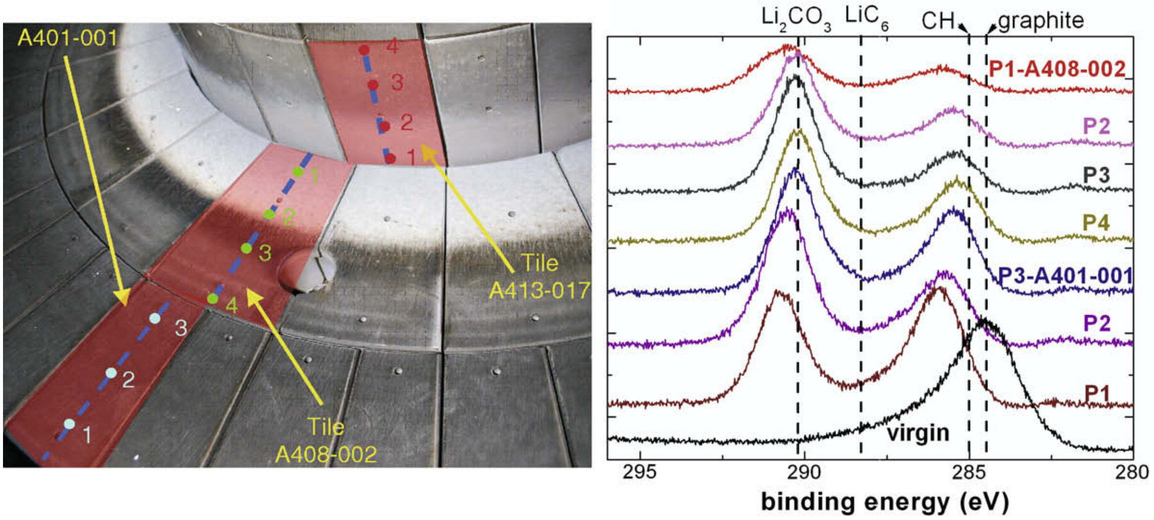

Fig. 2. (a) The NSTX divertor floor tiles after Li evaporation runs in FY2006. Picture shows points of XPS analysis in IMPACT. (b) XPS data of points shown on left along the NSTX divertor floor ATJ graphite tiles. 'virgin' tile A408-003 tile is defined by its location hidden from the lithium flux during NSTX discharges.

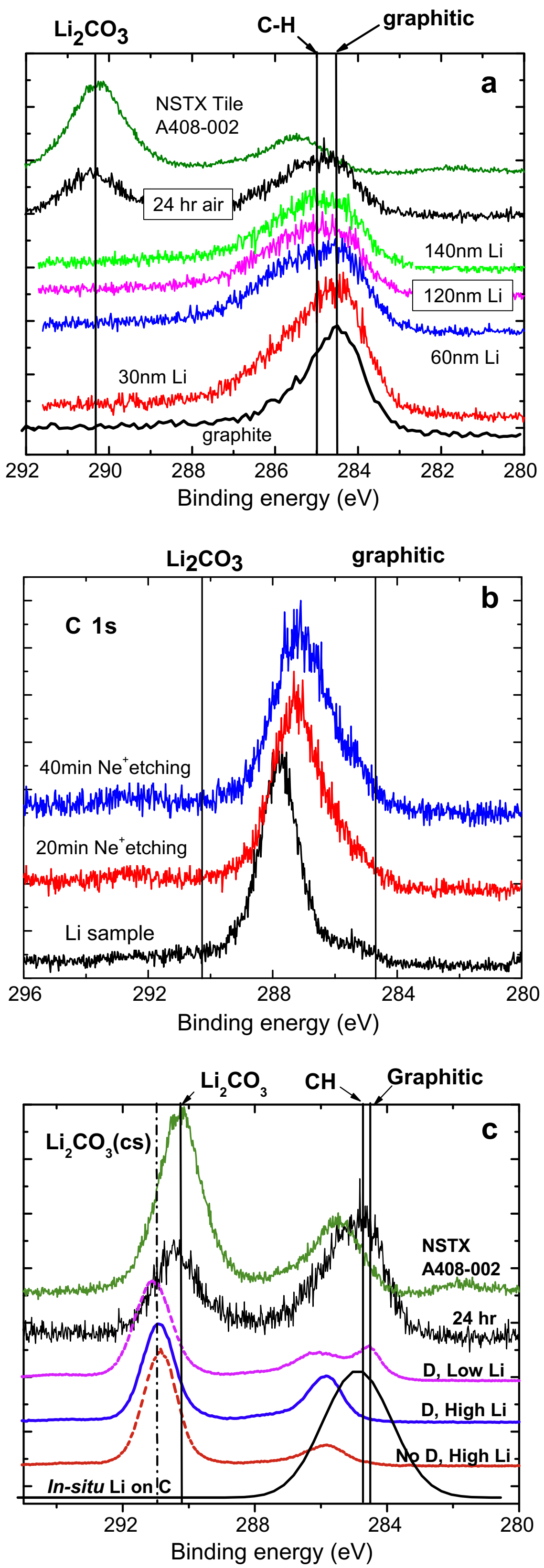

Fig. 3. (a) XPS data of C 1s photoelectron spectra from in situ IMPACT measurements on lithiated graphite with controlled lithium deposition rate. (b) XPS data of C 1s photoelectron spectra from in situ IMPACT measurements on pure lithium metal with impurity coating and post-irradiation with Ne ion-beam. (c) XPS data of C 1s photoelectron spectra comparing in situ IMPACT measurements and ex situ data of lithiated graphite with high-resolution XPS compensated for charge (cs) accumulation, which shifts peaks about 400–500 meV.

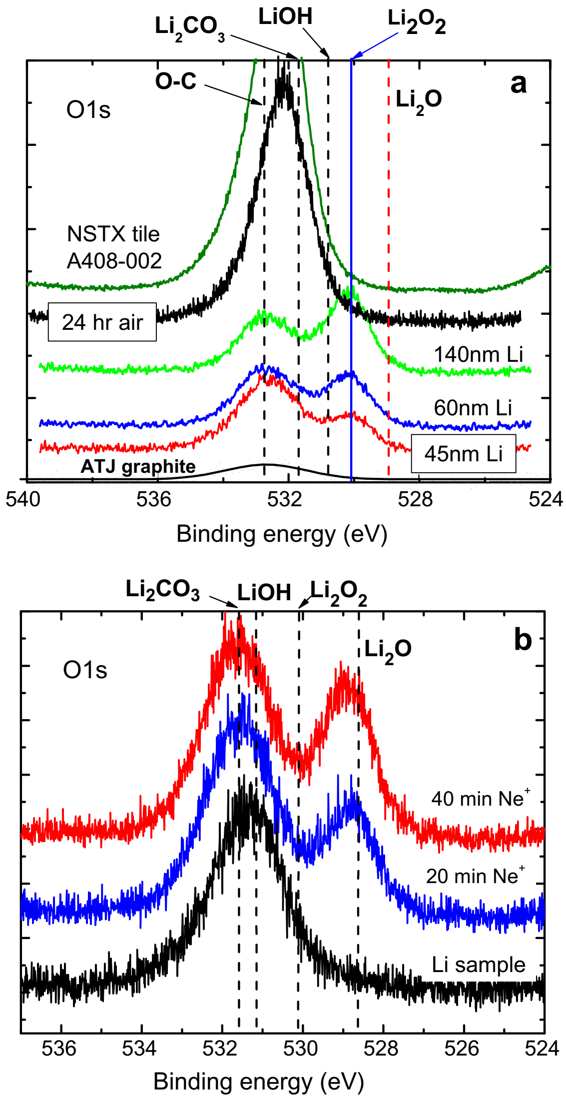

Fig. 4. (a) XPS data of O 1s photoelectron spectra from in situ IMPACT measurements on lithiated graphite with controlled lithium deposition rate. (b) XPS data of O 1s photoelectron spectra from in situ IMPACT measurements on pure lithium metal with impurity coating and post-irradiation with Ne ion-beam.

4. Conclusion

Both in situ and ex situ surface characterization of lithiated graphite show strong bonding states for lithium atoms at the surface. Lithium in lithiated graphite binds with oxygen as a peroxide and produces lithium carbonate when surface is exposed to air. During irradiation with energetic He or D particles, the total physical sputtering is reduced although dominated by sputtered Li atoms consistent with the literature. Lithium is found to intercalate the graphite matrix, although strong bonding yields an equilibrium concentration on the surface of about 30% as indicated by XPS data. The implications for NSTX lithium wall conditioning from these results are twofold: (1) lithium bonding state is dominated by presence of oxygen at the surface preventing effective D pumping, and (2) large lithium deposition studies indicate that over the course of time there may be more lithium available to pump hydrogen and thus provide more reliable particle control properties. However, as long as the lithium is mixed with carbon and no substantial amount of lithium is provided for lithium coating, particle density control may be challenging.

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