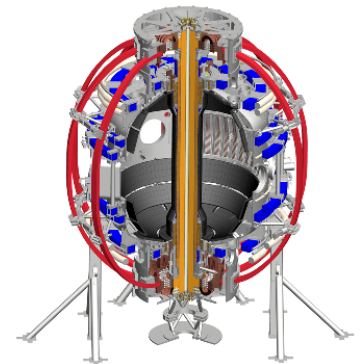


Hydrogen retention in lithium and lithium oxide films

Luxherta Buzi

July 27th 2017



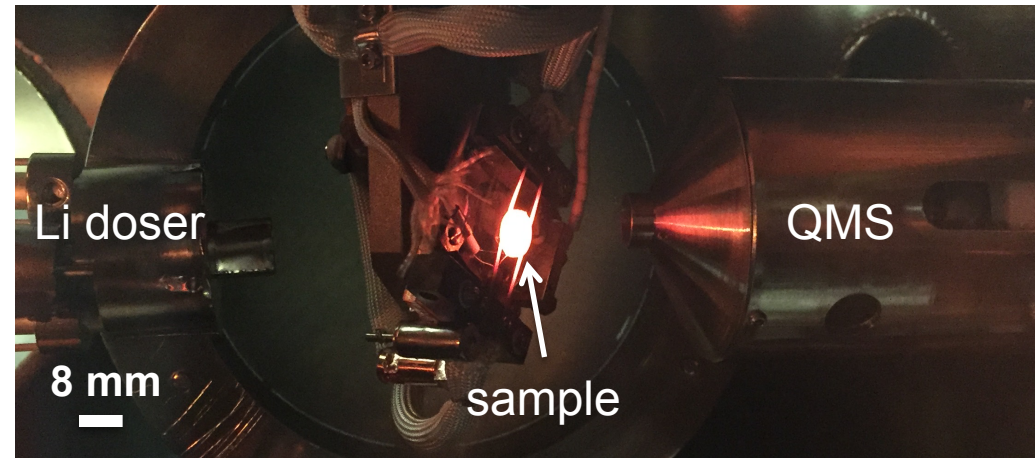
Motivation and outline

- Lithium conditioning of PFCs led to improved plasma performance in NSTX and other fusion experiments
- Lithium is a good getter of hydrogen
- A better understanding of the fundamental mechanisms of H retention and its quantification is needed
- Here we are studying H retention in pure Li and Li_2O as a function of surface temperature

Lab experiments allow for better understanding of PMI processes

PMI processes in fusion reactors:

- Difficult to perform *in-situ* analysis
- Complex environment for plasma and material characterization

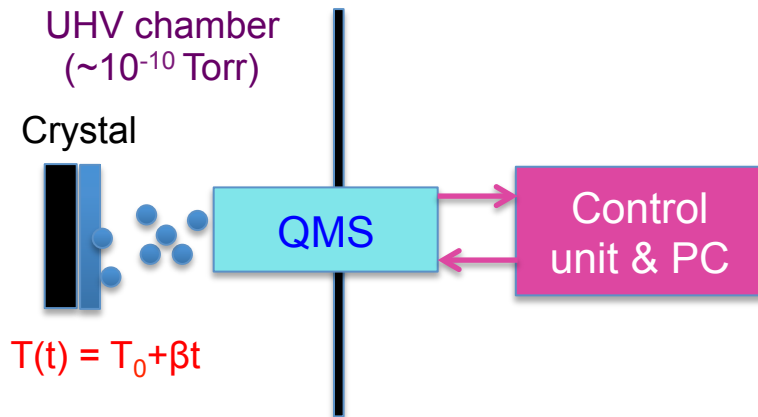


*Resistively heated crystal in a UHV chamber
(QMS-Quadrupole Mass Spectrometer)*

Surface science experiments:

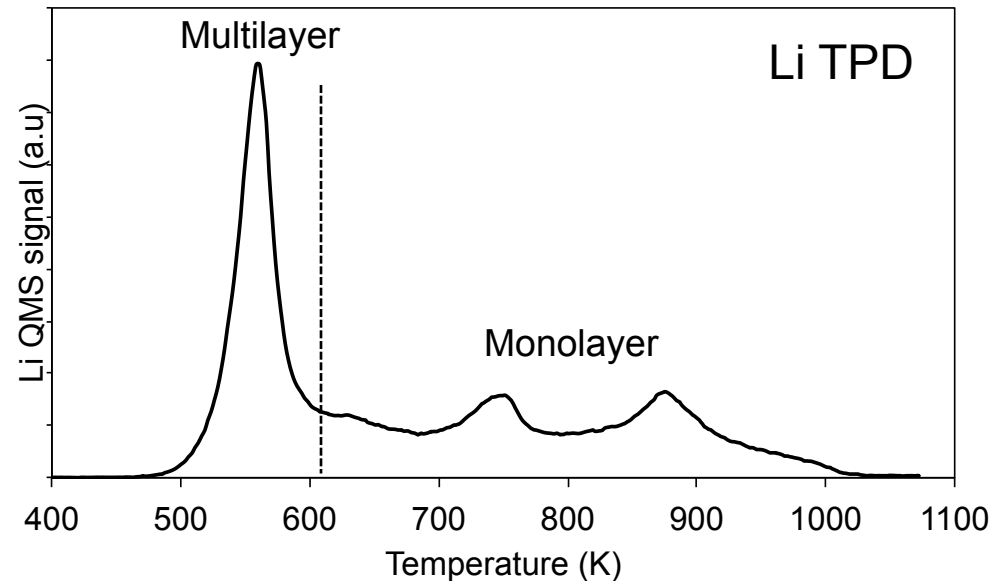
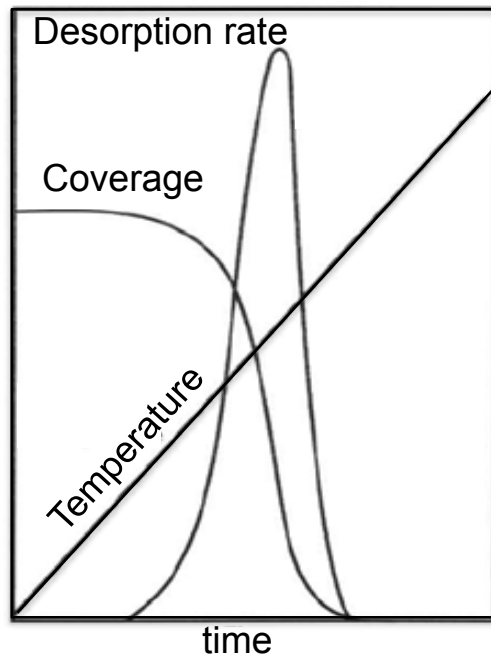
- Understanding fundamental PMI physical and chemical processes
- Analyze materials and coatings in a controlled way
- Well-characterized surfaces and ion beams
- Utilize surface sensitive analytical techniques

Temperature Programmed Desorption to quantify H retention and Li thermal stability



Temperature Programmed Desorption (TPD):

- Sample temperature is increased linearly
- Desorbed species are monitored with a QMS
- TPD spectra provide activation energies, reaction orders and total number of desorbed species (area under the desorption curve)



$$N(t) = -d\theta/dt = v\theta \exp(-E_a/RT) \text{ (1st order)}$$

Experiments

- Experiments were performed in a UHV chamber with a 2×10^{-10} Torr base pressure
- Li films were evaporated on a Ni single crystal and exposed to a total dose of 4×10^{15} H⁺cm⁻² during 120 s, while the sample was kept at a temperature in the range 90-520 K
- LEED was performed by using a PHI 15-120 LEED optics
- AES was done using a PHI 15-255G double-pass CMA
- TPD was performed with the sample in line-of-sight of the ionizer of a shielded UTI 100C QMS, using a heating rate of 4 K/s
- 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 04-303A) with adjustable ion energy from 0-5 keV, and a liquid nitrogen trap was used in the H₂ gas line to mitigate H₂O contamination

Experiments

AES - check the purity of the crystal surface

Before deposition, the Ni(110) crystal was sputtered-cleaned (0.5 keV Ar^+ and 1.5 keV D_2^+), annealed at 1000 K in O_2 and H_2 to remove C and O contaminants. The cleanliness of the sample was checked with AES.

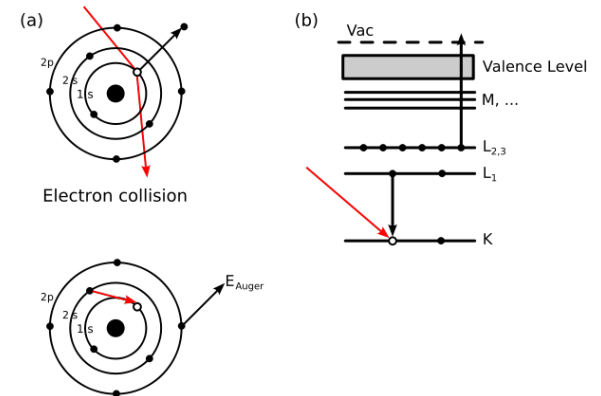
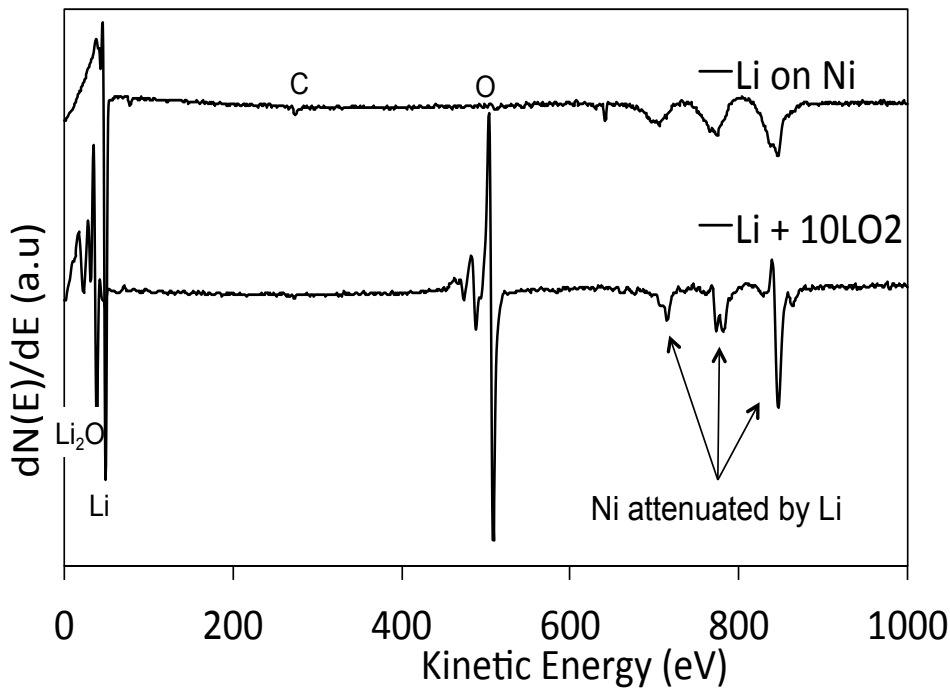


Figure 1. (a) Auger process:

1. An incident electron creates a core hole in the 1s level
2. An electron from the 2s level fills in the 1s hole
3. The transition energy is transferred to a 2p electron that is ejected

The final atomic state has a hole in the 2s orbital and one in the 2p orbital.

(b) The same process using spectroscopic notation, KL1L2,3

Experiments

Experiment 1:

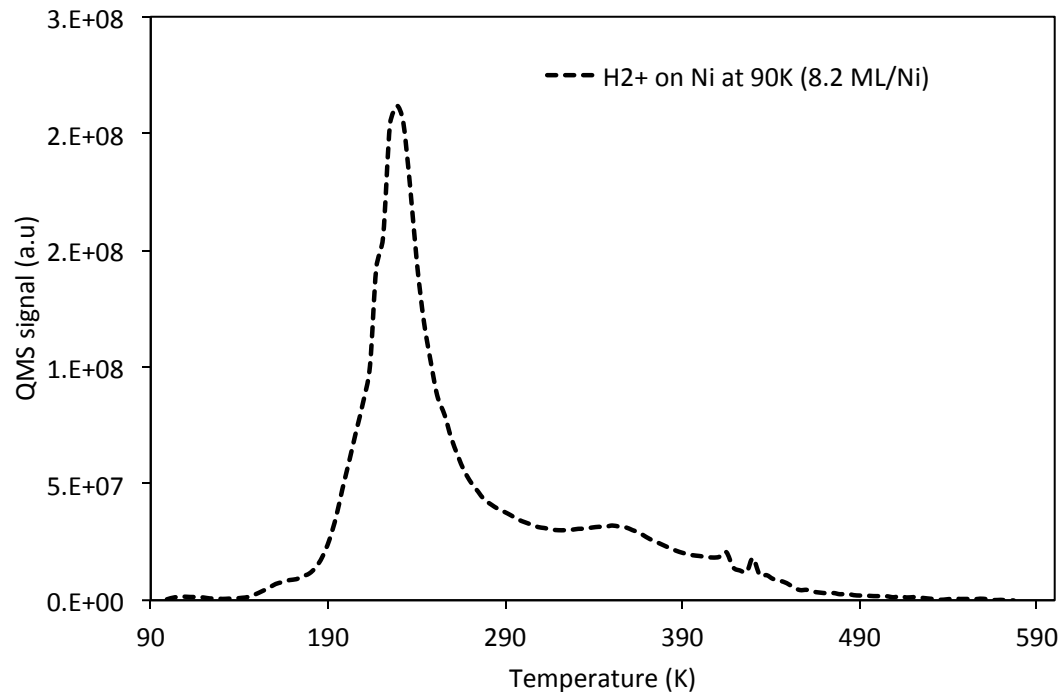
1. Dose Li on Ni (3min20s, 8A, 90-520 K)
 2. Dose H₂⁺ on Ni (2 min, 4E-8Torr, 500eV)
 3. Check O/C with AES
 4. TPD
- } 90-520 K

Experiment 2:

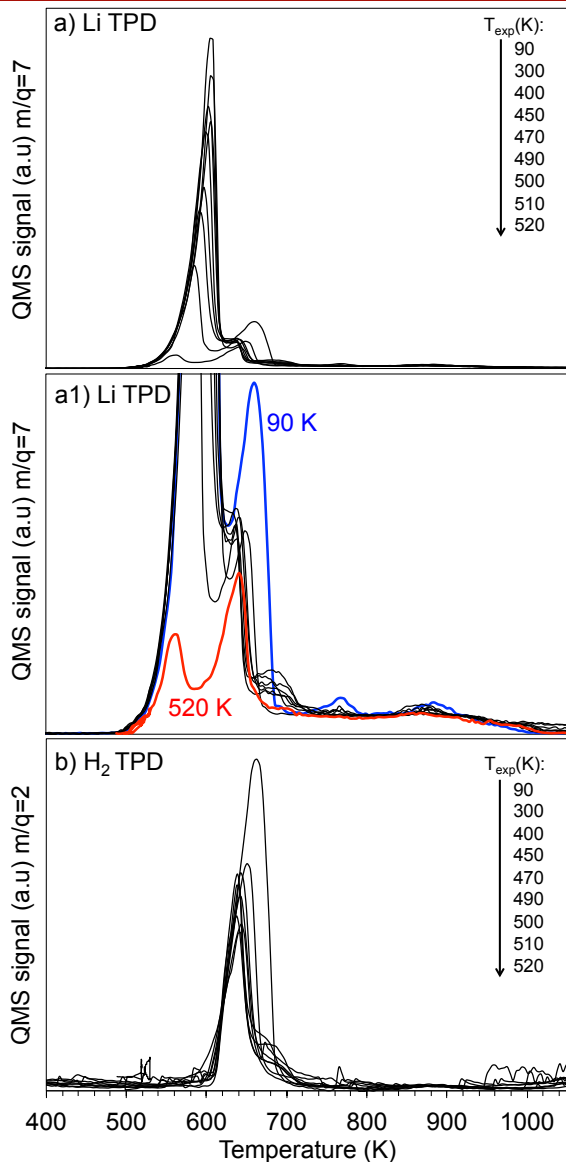
1. Dose Li on Ni (3min20s, 8A, 90-520 K)
 2. Dose 10 L O₂
 3. Dose H₂⁺ on Ni (2min, 4E-8Torr, 500eV)
 4. Check O/C with AES
 5. TPD
- } 90-520 K

H₂⁺ incident on Ni(110)

Gas	Ion energy	H ₂ pressure	H ₂ ⁺ current	H ₂ ⁺ flux	Exposure time	Incident H ⁺ fluence	Incident H ⁺ fluence	Incident H ₂ from BG	H ⁺ H incident fluence	H retained in Ni at 90 K from TPD
H ₂	eV	Torr	nA	H ₂ ⁺ /cm ² s	s	H ⁺ /cm ²	ML per Ni at.den.	ML per Ni at.den.	ML per Ni at.den.	ML per Ni at.den.
	500	4E-8	1745	1.7E+13	120	4.0E+15	3.6	8.4	12.0	flux corrected: 8.2

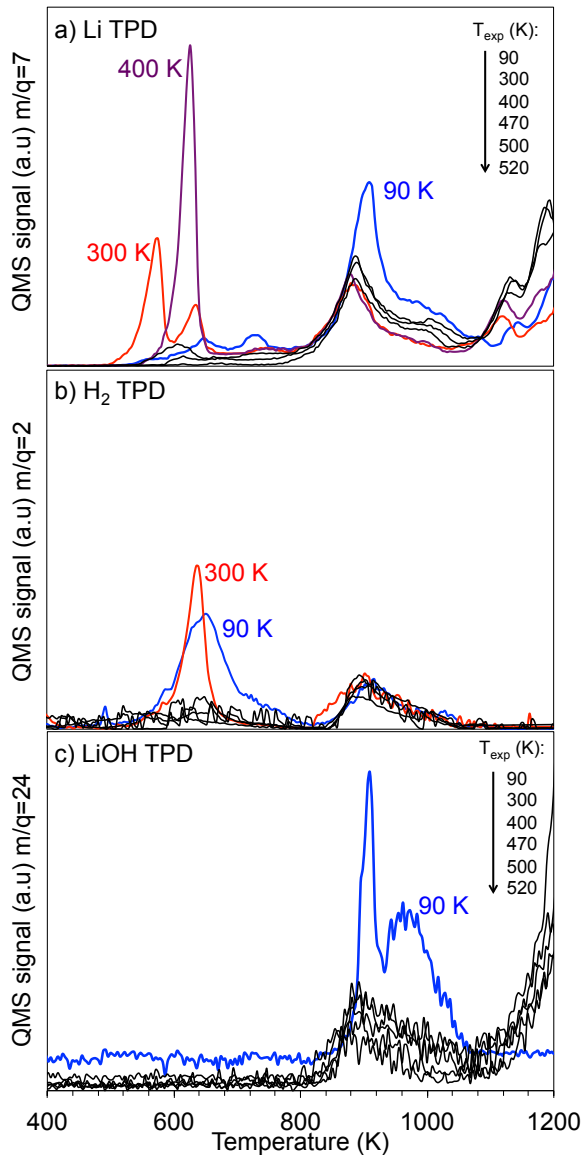


H retention in pure Li



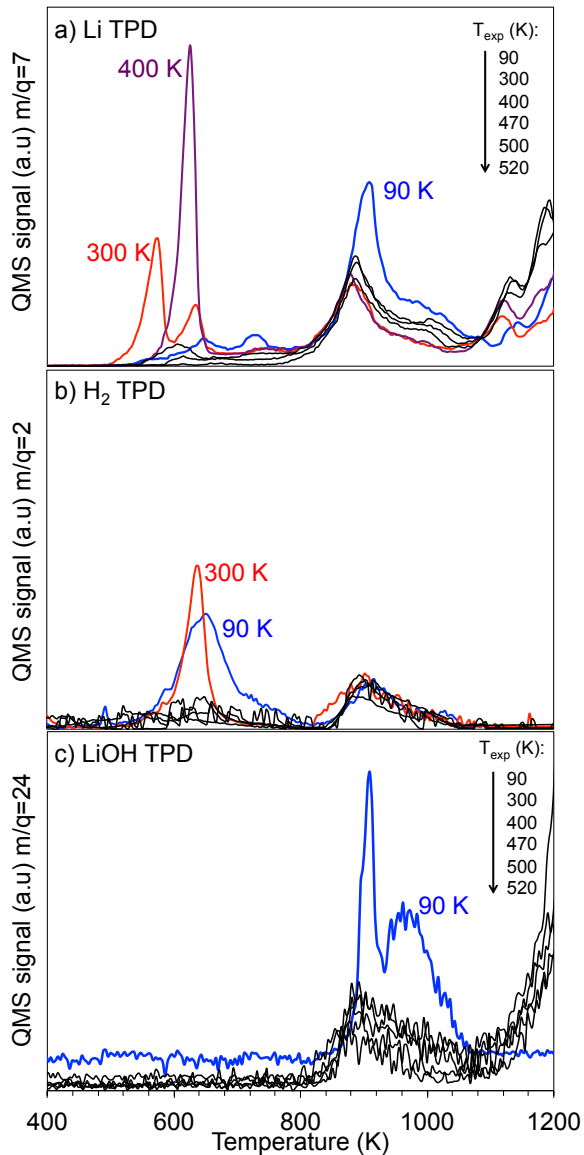
- During the Li and H_2^+ dosing, the Ni substrate was kept at a fixed exposure temperature, ranging from 90 to 520 K
- Since Li starts evaporating significantly with temperature above 500 K, the multilayer peak (near 600 K) starts to decrease above 450 K exposure temperature
- H_2^+ irradiation causes a new Li desorption peak to form at about 650 K due to decomposition of LiH
- This peak is coincident with a H_2 desorption peak, indicating that Li and H_2 evolution is rate-limited by LiH decomposition in the films as previously reported

H retention in Li₂O



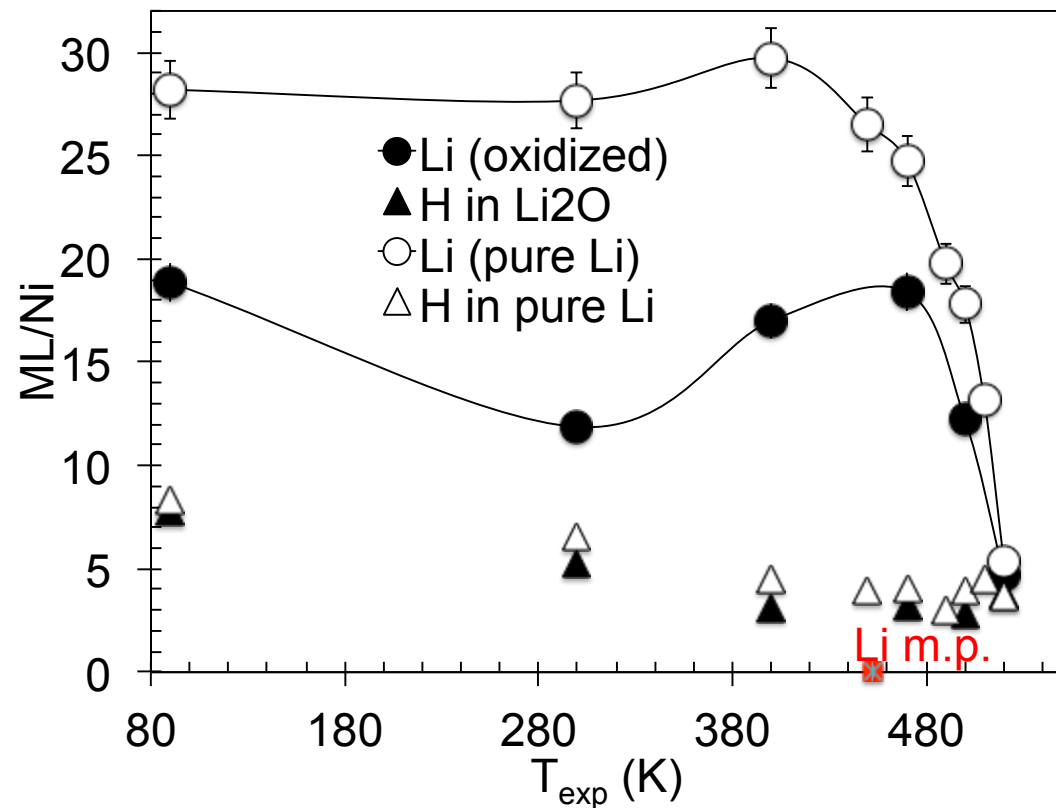
- After irradiation of Li₂O films, TPD detected H₂, Li and LiOH desorption. No desorption of LiO, H₂O or LiH was observed
- After oxidation, Li is retained at the Ni surface until higher temperatures due to the increased thermal stability of Li₂O. In this case Li is only desorbed when Li₂O decomposes, which occurs to yield a Li peak at 900 K
- In the 300 K exposure case, 18% of the Li layer was not oxidized since a Li metallic peak at 570 K was still present (2.2 ML) and about 10% of the Li layer (1.2 ML) formed LiH (Li peak at 630 K)

H retention in Li_2O



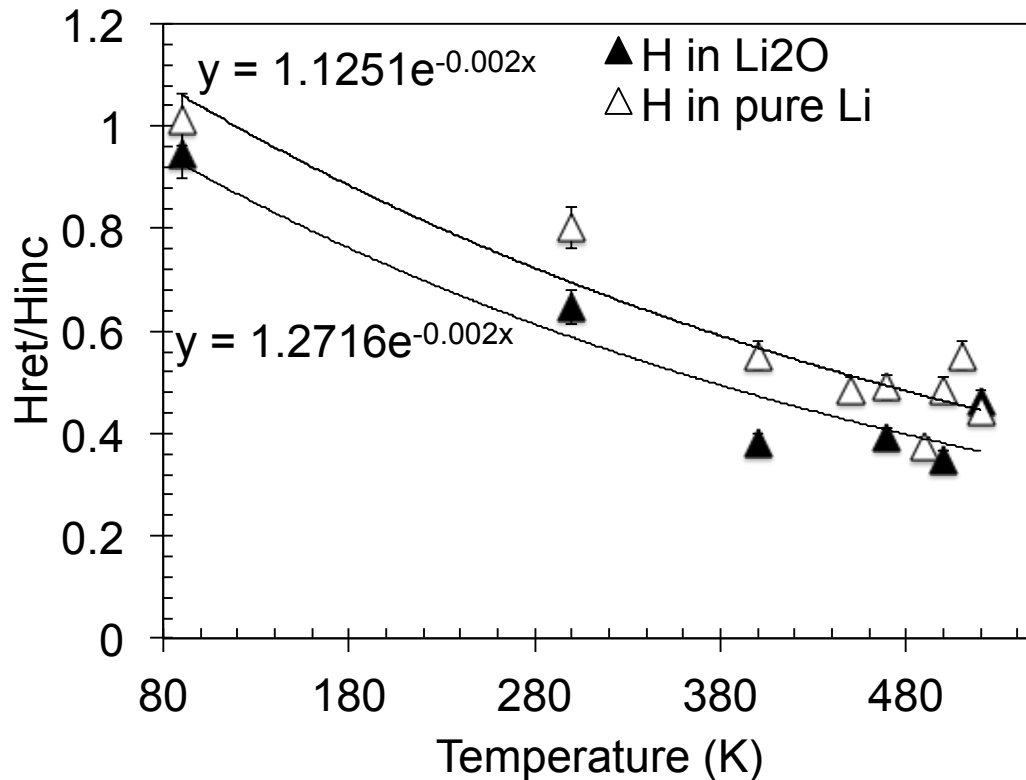
- The exposure to 400 K produced a LiH decomposition peak at 630 K, indicating that about 27% of the Li film formed LiH (4.7 ML)
- H_2 TPD showed a low temperature peak at 630 K only for 90 K and 300 K exposure temperature
- When the temperature increased beyond 300 K, only the high temperature H_2 peak remained at 900 K
- LiOH ($m/q=24$), Li_2O ($m/q=30$) and O_2 ($m/q=32$) were also monitored and desorbed at 900 K, although the calibration for these species is not provided in this work

H retention in Li_2O and pure Li



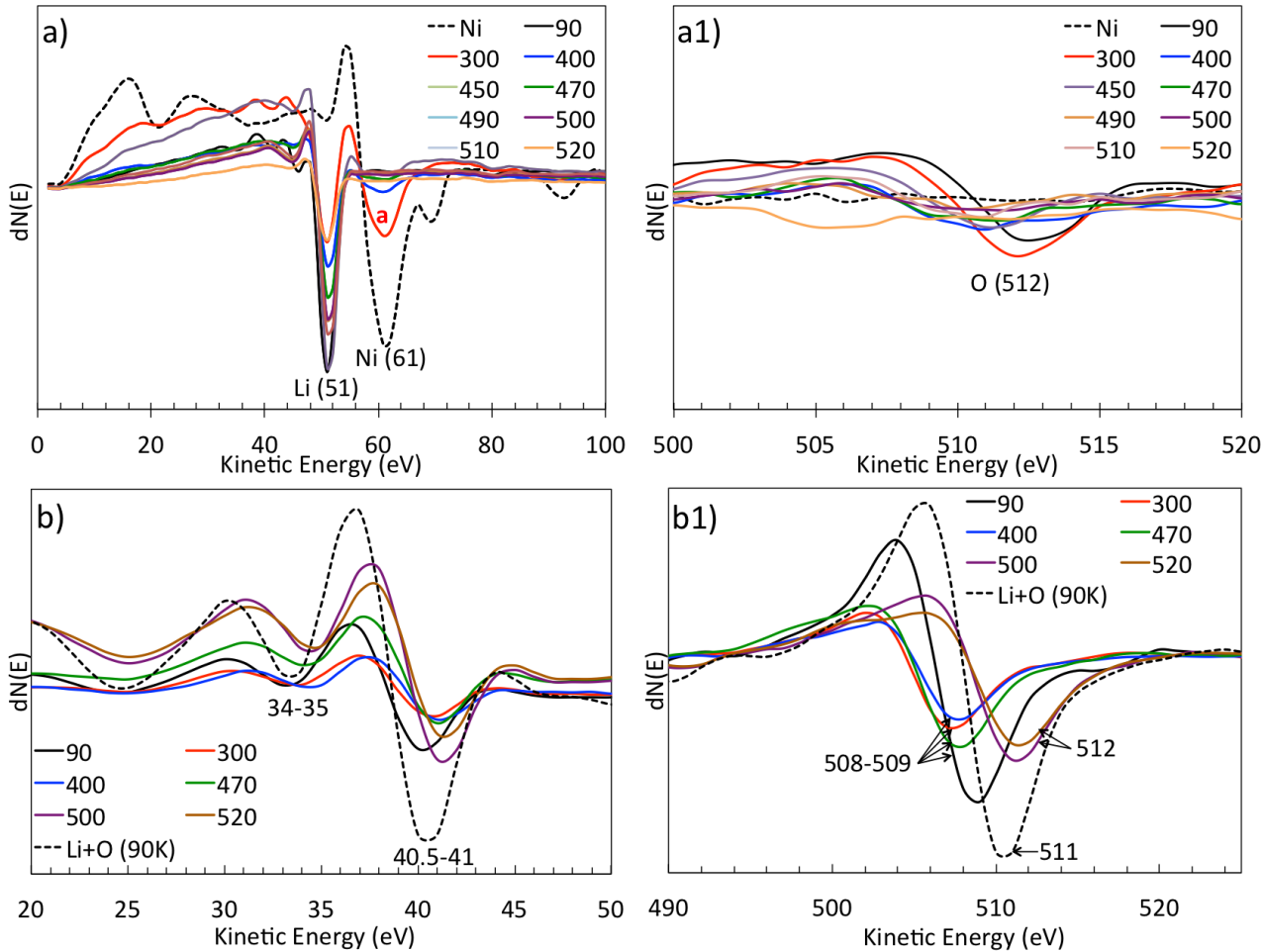
- The total amounts of Li and H_2 are plotted for both cases, i.e., pure and oxidized Li
- The total amount of Li desorbed from the irradiated Li_2O is lower than in pure Li, possibly due to the formation and desorption of other species such as LiOH , which is not calibrated and accounted for
- Since the total amount of H_2 is lower than Li (below the saturation level) it is fair to compare the H retention in both types of films

H retention in Li₂O and pure Li



- The total amounts of Li and H₂ are plotted for both cases, i.e., pure and oxidized Li
- The total amount of Li desorbed from the irradiated Li₂O is lower than in pure Li, possibly due to the formation and desorption of other species such as LiOH, which is not calibrated and accounted for
- Since the total amount of H₂ is lower than Li (below the saturation level) it is fair to compare the H retention in both types of films

AES analysis



a) Pure Li on Ni (51 eV)

- The reason we don't see LiH (peaks at 36-42 eV) is because H is implanted in Ni (up to 10 nm depth)
- Ni signal is damped by Li.
- When T increased => Li layer is thinner => Ni peak increased

b) LiH or Li₂O from literature form at 40±1 eV (38 eV)

Slow (in minutes-time frame) conversion of LiOH at T>~450 K:
 $2\text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O}(\text{g})$

a) Li and a1) O AES signal after H₂⁺ exposure of pure Li and b) Li and b1) O AES signal after H₂⁺ exposure of Li₂O

Conclusions

- H retention in pure Li and Li₂O films was measured as a function of surface temperature under UHV conditions
- It was shown that both pure Li and Li₂O are able to retain H suggesting that low H recycling can be achieved if Li₂O is formed under fusion reactor conditions, as both Li and Li₂O are comparable in efficiency in trapping H
- The experiments have shown that H is retained as LiH in pure Li. This was confirmed by TPD profiles, which show the Li and H peaks formed at the same temperature (650 K), corresponding to the LiH decomposition
- In addition to TPD, AES measurements supported the fact that LiOH was formed after Li₂O film was irradiated with H ions and it decomposed to Li₂O and H₂O at exposure temperatures higher than 470 K
- Experiments showed that H retention drops exponentially with surface temperature in the range 90-520 K from 95% to 35% due to outwards diffusion of H at high temperatures

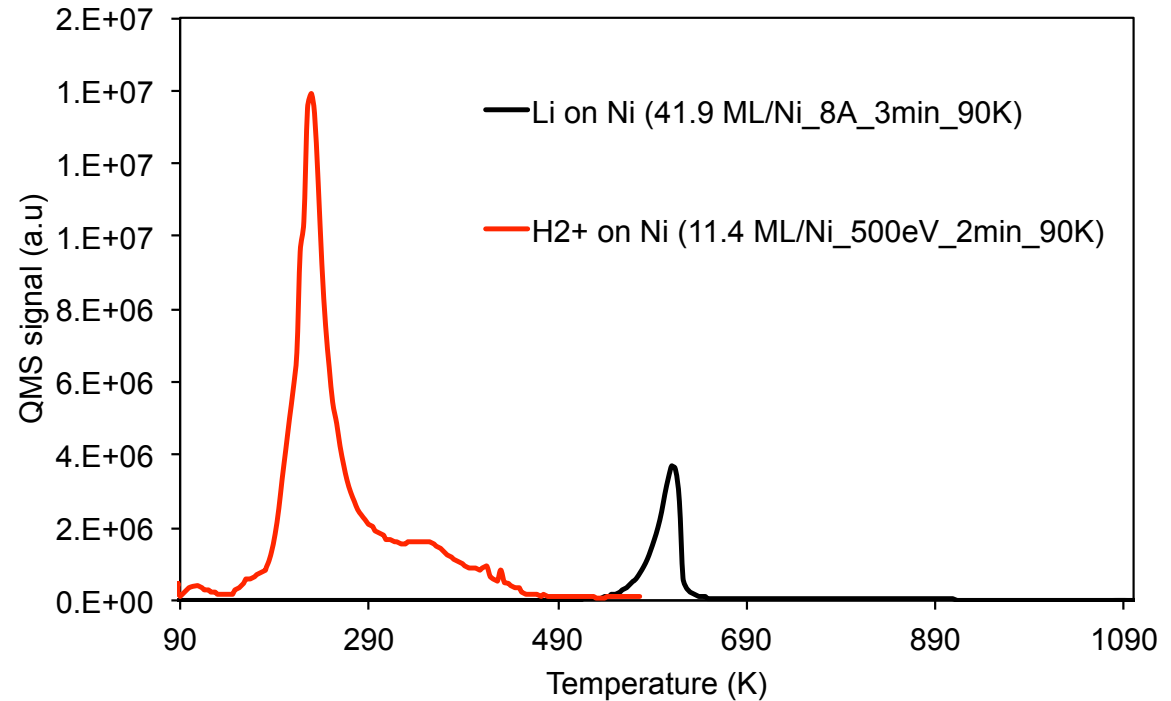
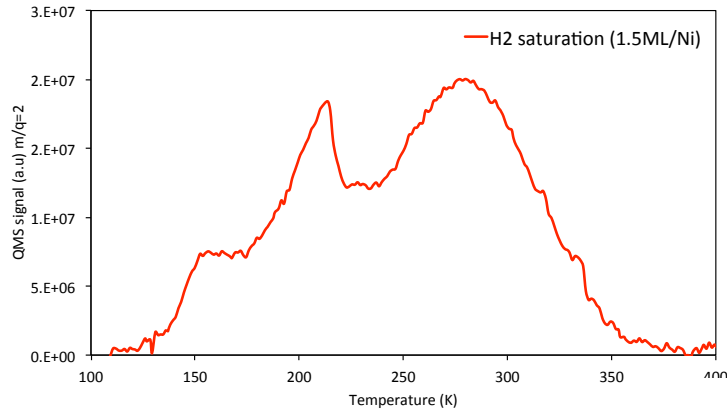
Acknowledgements

This material is based upon work supported by the U.S. Department of Energy, Office of Science/Fusion Energy Sciences under Award Number DE-SC0012890

Backups

Surface temperature effect on clean Li: Li, H₂, CO calibration

Dose $4e-8$ Torr H₂ for 2min at 90K



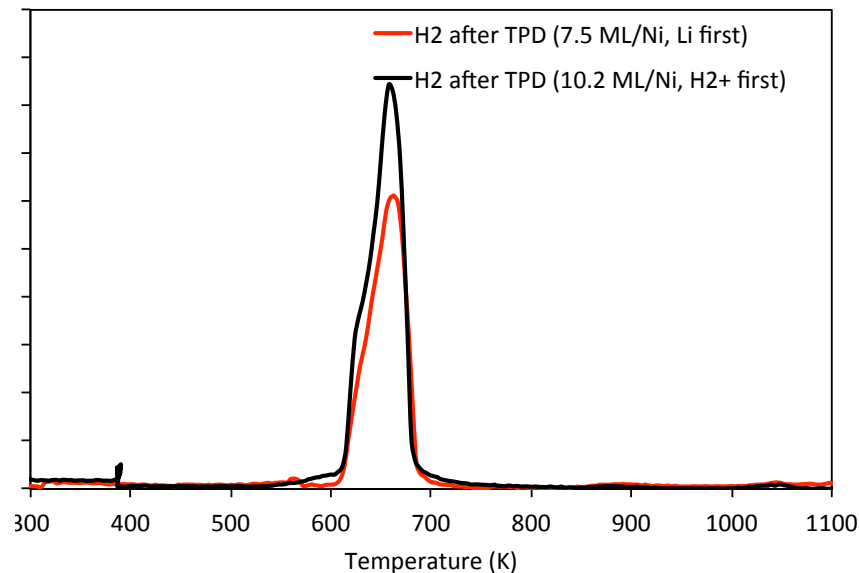
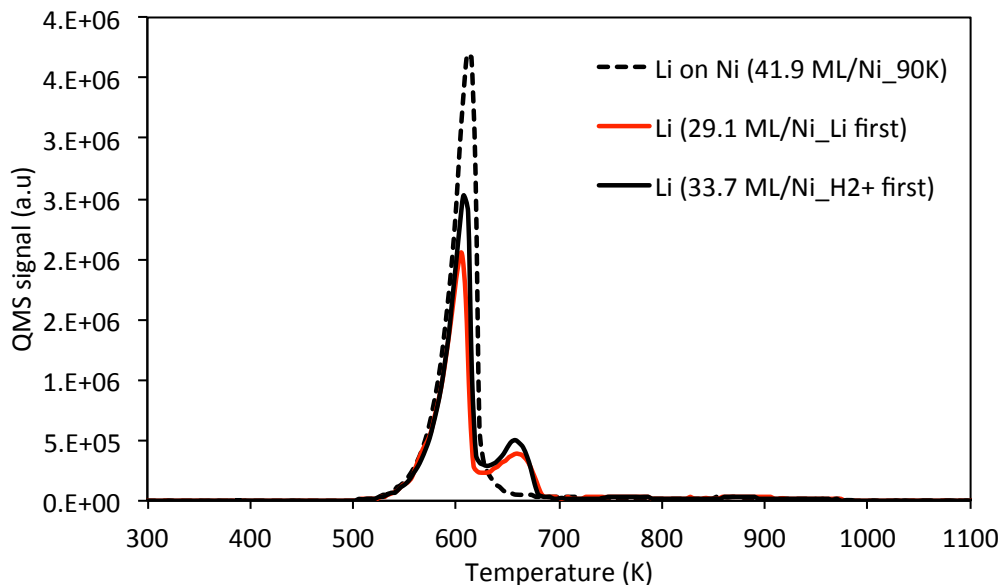
Surface temperature effect on pure Li: H retention at 90 K - more H is retained if H_2^+ is dosed first

Dose H_2^+ first

1. Dose H_2^+ on Ni (2min, $4E-8$ Torr, 500eV, 90K)
2. Dose Li on Ni (3min20s, 8A, 90K)
3. Check O/C with AES
4. TPD

Dose Li first

1. Dose Li on Ni (3min20s, 8A, 90K)
2. Dose H_2^+ on Ni (2min, $4E-8$ Torr, 500eV, 90K)
3. Check O/C with AES
4. TPD



In both cases LiH was formed

Surface temperature effect on oxidized Li: H retention at 90 K – Li₂O formed

Dose H₂⁺ first

1. Dose H₂⁺ on Ni (2min, 4E-8Torr, 500eV, 90K)
2. Dose Li on Ni (3min20s, 8A, 90K)
3. Expose to 10 L of O₂
4. Check O/C with AES
5. TPD

Dose Li first

1. Dose Li on Ni (3min20s, 8A, 90K)
2. Expose to 10 L of O₂
3. Dose H₂⁺ on Ni (2min, 4E-8Torr, 500eV, 90K)
4. Check O/C with AES
5. TPD

