Plasma facing surface composition during Li evaporation on NSTX and LTX

PP9.00025

C. H. Skinner, M. Jaworski, H.W. Kugel, R. Majeski, R. Kaita, V. Surla, PPPL.

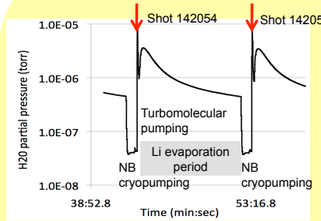
B. E. Koel and R. Sullenberger, Chemical and Biological Engineering Department, Princeton University

Synopsis:

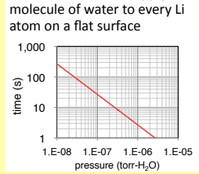
- Lithium evaporation on carbon, stainless, and Mo PFCs has a dramatic effect on plasma performance (53 presentations here).
- Lithium coatings react with residual water in a tokamak vacuum to produce lithium hydroxide and hydrogen:
  $2\ Li + 2\ H_2O \rightarrow 2\ LiOH + H_2$
- This process can occur in the time interval between lithium evaporation and the next discharge.
- The resulting PFC surface should be considered as a mixed material rather than a pure 'lithium coating'.
- To avoid reactions with residual vacuum gasses an ultra-high vacuum (≤1e-8 Torr) is required and may be achievable by techniques such as a large-scale lithium getter pump, discharge cleaning, and/or high temperature bakeout.

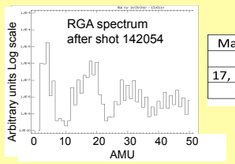
Li / H_2O monolayer formation time

NSTX residual vacuum



Estimate of time to supply one molecule of water to every Li atom on a flat surface





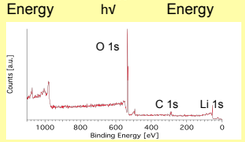
Mass (amu)	Species	Percentage
2,3,4	H, HD, D	76.8%
17, 18, 19, 20	Water	18.0%
other	Not H, not water	5.2%

- Depositing a Li monolayer in NSTX takes ~4.5 s at a typical LiTER evaporation rate of 20 mg/min
  (note this is for an flat mirror-like surface - coating a more realistic rough surface with a monolayer of Li would take longer).
- The water monolayer formation time between shots is estimated from gas kinetics to be ~6s, similar to the Li monolayer time
  (1 minute before shot, LiTER was withdrawn and NB cryopump opened giving ~ 25 sec with water flux lower than the Li flux on flat surface).
- The reaction probability for incident H_2O molecules and surface Li atoms is expected to be near unity.

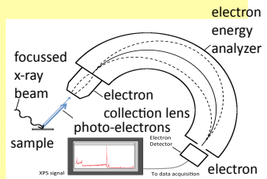
Li surface oxidation tracked by X-ray photoelectron spectroscopy

Monochromatic Al Kα x-rays (1486.6 eV) photoionize atoms.
Emitted photo-electron energies are measured with high resolution 300 mm radius hemispherical electrostatic analyzer.
Photo-electron energy reveals chemical state of top ~ 20 monolayers

Electron Binding Energy = X-ray energy hν − Electron Kinetic Energy



Broad scan XPS spectrum before gas exposure.



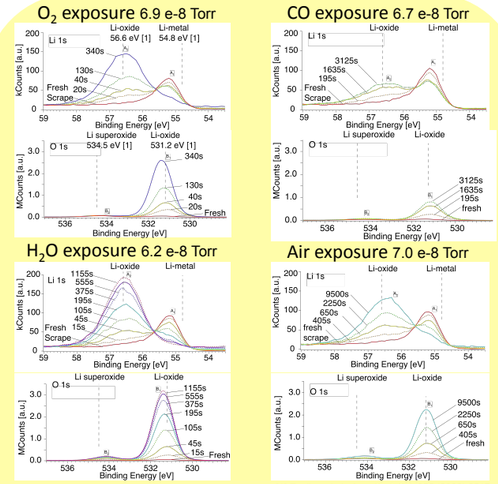
Scienta ESCA -300, resolution 0.4 eV.
Sample exposed to trace O_2, H_2O, CO or air via leak valve.
(base vacuum 5 e-9 torr).
H_2O degassed with freeze/pump/thaw cycles.
Chamber evacuated for ~ 2 min during sequential XPS scans.
XPS spectra fit to Voight profiles by CASA XPS software.

Lithium surface preparation

- 99.95% pure Li supplied by FMC.
- Sample squeezed between Al plates to get flat surface.
- Surface scraped under N_2 until clean metallic Li surface was visible.
- Transferred to Scienta ESCA-300 and allowed to degas under vacuum.
- Then scraped under vacuum with a tungsten carbide tipped scraper in the Scienta analysis chamber
- O 1s XPS signal monitored until the oxygen peaks were minimized.
- Surface composition by XPS: 91% Li; 6.2% O; 2.45% C

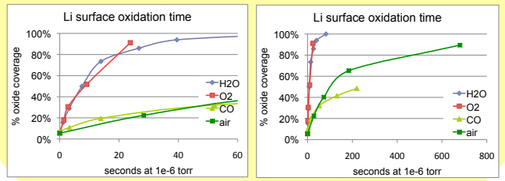
10 mm

Lithium surface oxidation XPS spectra



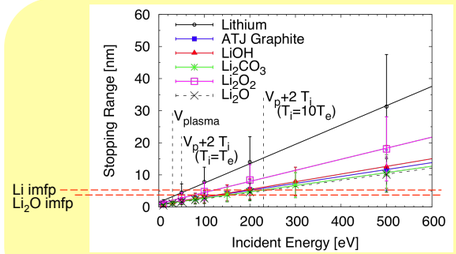
[1] Ensling et al., App. Surf. Sci. 255 (2008) 2517.

Oxidation time @ 1e-6 Torr from Li 1s XPS spectra



same data over longer time

XPS photoelectron range similar to D stopping range

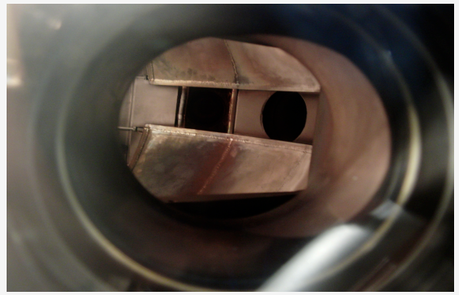


TRIM calculations

Inelastic mean free path of XPS photoelectron in Li = 5.36 nm, in Li_2O = 3.47 nm

LTX operated with a Li-coated 300 °C shell:

- First full high temperature, high Z wall operation of a tokamak
  - Lithium evaporated into 5 mTorr helium fill to disperse coating



- Deposition rate ~0.75 g/hour/evaporator
  - 3 hour duration, plasma operations follow 1 ¼ h later
  - Estimated 1.6 micron average Li thickness.
  - Partial pressure of water: 5e-9 Torr (cold); 2e-8 Torr (hot)
- Lithium coating darkens rapidly.
- No visual evidence of shiny metallic surface
  - Indicative of lithium oxide/hydroxide formation at the surface.
- Li evaporation onto cold walls produced large effect on peak plasma current and discharge duration.
- With hot (300°C) walls - no significant improvement so far over uncoated walls or walls with passivated Li coatings.
- Suspect oxygen segregation to liquid Li surface

Conclusions:

- A clean Li surface is oxidized to > 5 nm depth in about 20 seconds by 1e-6 torr of O_2 or H_2O. Oxidation rate from CO is much slower.
- After a typical NSTX shot the H_2O partial pressure decreases from 3e-6 torr – 3e-8 torr with a corresponding oxidation time of 6s – 600 s.
- The PFC surface after Li evaporation is a mixed material rather than a pure 'lithium coating'.
- Surface composition in flowing Li-PFC system will depend on base vacuum pressure and Li flow rate.

Acknowledgements
The authors would like to acknowledge stimulating conversations with JP Allain, and R. Kaita. We thank the NSTX team for support and assistance. The XPS spectra were taken at the ESCA 300 facility of LeHigh University with technical support by A. Miller.
This work was supported by US DOE Grant No DE AC02-09CH11466 and DE-FG02-08ER54990

Print at 120% 54" x 72" paper size; print dialog, paper quality set to high.