Complex chemical interactions of lithium, deuterium, and oxygen on lithium-coated graphite PFC surfaces

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Outline

• Background

• Methodology
  – Control experiments
  – Post-mortem NSTX tile analysis

• Results
  – Oxygen, lithium, deuterium functionality
  – Carbon, lithium, deuterium functionality
  – Post-mortem NSTX FY08 tile samples
  – Summary

• Conclusions and future work
Background

• Lithium has been found to improve plasma performance
  – Lithium pumps deuterium
  – Lithiated graphite also retains deuterium
• The fundamental mechanisms by which lithiated graphite pumps deuterium are unknown
• Offline control experiments simulate fusion reactor environment
  – NSTX
• Correlations observed in comparing control experiments to NSTX post-mortem tiles
# Methodology

## 3 aspects to replicate in offline experiments

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<thead>
<tr>
<th>Component</th>
<th>NSTX</th>
<th>Offline Experiments</th>
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<tr>
<td>Wall/substrate material</td>
<td>ATJ graphite, Tiles</td>
<td>ATJ graphite, Disk cut from rods, polished</td>
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<tr>
<td>Lithium deposition</td>
<td>LITER (Li evaporator), ~1800-7000 nm/discharge&lt;sup&gt;1&lt;/sup&gt;</td>
<td>LEDS (Li Evap and Deposition System), 1000 - 8000 nm per sample</td>
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<td>Ion bombardment</td>
<td>Deuterium plasma, 10&lt;sup&gt;17&lt;/sup&gt; – 10&lt;sup&gt;18&lt;/sup&gt; cm&lt;sup&gt;-2&lt;/sup&gt; per shot along divertor region</td>
<td>Deuterium ion source, 500eV/amu 5.0x10&lt;sup&gt;13&lt;/sup&gt; cm&lt;sup&gt;-2&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Results – Li-D-O functionality

1) The O1s peak on ATJ graphite is located at 532 eV
Results – Li-D-O functionality

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With each surface modification, we are interested in the development of new peaks.

New peaks indicate new chemical functionalities.
Results – Li-D-O functionality

1) The O1s peak on ATJ graphite is located at 532 eV

2) Lithium deposition results in a second peak at ~529.5 eV. A slight shift to lower binding energy in the 532 eV also occurs.
Results – Li-D-O functionality

1) The O1s peak on ATJ graphite is located at 532 eV

2) Lithium deposition results in a new second peak at \( \approx 529.5 \pm 0.5 \) eV. A slight shift to lower binding energy in the 532 eV also occurs.

3) 30 minute deuterium irradiation (\( \Gamma \approx 1.5 \times 10^{15} \) cm\(^{-2}\)) causes a new peak to develop at 533 eV, and a slight shift to higher binding energy for the 529.5 eV peak.
1) The O1s peak on ATJ graphite is located at 532 eV.

2) Lithium deposition results in a second peak at ~529.5 eV. A slight shift to lower binding energy in the 532 eV also occurs.

3) 30 minute deuterium irradiation ($\Gamma \approx 1.5 \times 10^{15}$ cm$^{-2}$) causes a new peak to develop at 533 eV, and a slight shift to higher binding energy for the 529.5 eV peak.

4) The relative intensity of the 533 eV peak compared to the 529.5 eV peak increases with subsequent irradiations.
Results – Li-D-O functionality

1) The O1s peak on ATJ graphite is located at 532 eV

2) Lithium deposition results in a new second peak at ~529.5 ± .5 eV. A slight shift to lower binding energy in the 532 eV also occurs.

3) 30 minute deuterium irradiation (Γ ≈ 1.5 E15 cm⁻²) causes a new peak to develop at 533 eV, and a slight shift to higher binding energy for the 529.5 eV peak.

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5) …and again…
Results – Li-D-O functionality

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5) …and again...

6) …and again.
Results – Li-D-O functionality

Observations
Based on these results and control experiments

1) As is
2) Post 2km
Li deposition
3) D2-30m
4) D2-1.5h
total
5) D2-2.5h
total
6) D2-5h
total
Results – Li-D-O functionality

Observations
Based on these results and control experiments

529 eV
- Only develops after Li deposition
- Shifts slightly (~.5 eV) after D2.
- Relative intensity decreases with higher D2 fluence

1) As is
2) Post 2 knm Li deposition
3) D2-30m
4) D2-1.5h total
5) D2-2.5h total
6) D2-5h total

O1s
Results – Li-D-O functionality

Observations
Based on these results and control experiments

533 eV
- Only develops after irradiating a *lithiated* sample.
- Relative intensity increases with higher D2 fluence

529 eV
- Only develops after Li deposition
- Shifts slightly (~.5 eV) after D2.
- Relative intensity decreases with higher D2 fluence
Results – Li-D-O functionality

Control experiment

Procedure:
ATJ graphite was irradiated with D without any lithium conditioning.

Result:
No shifts or new peaks were observed.
Results – Li-D-O functionality

Control experiment

Procedure:
ATJ graphite was irradiated with D without any lithium conditioning.

Result:
No shifts or new peaks were observed.

Therefore:
533 eV peak is a result of D irradiation on a lithiated graphite sample.
1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.
Results – Li-D-O and C functionality

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

2) Lithium deposition results cause the FWHM of the primary peak to increase. Peak shifts ~1eV to higher binding energy.
Results – Li-D-O and C functionality

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

2) Lithium deposition results causes the FWHM of the primary peak to increase. Peak shifts ~1eV to higher binding energy.

3) 30 minute deuterium irradiation ($\Gamma \approx 1.5 \times 10^{15}$ cm$^{-2}$) causes a new peak to develop at 291 eV. The 284 eV peak shifts again to higher binding energy, now residing ~285 eV.
**Results – Li-D-O and C functionality**

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

2) Lithium deposition results causes the FWHM of the primary peak to increase. Peak shifts ~1 eV to higher binding energy.

3) 30 minute deuterium irradiation (Γ ≈ 1.5 E15 cm⁻²) causes a new peak to develop at 291 eV. The 284 eV peak shifts again to higher binding energy, now residing ~285 eV.

4) The relative intensity of the 291 eV peak compared to the 529.5 eV peak increases with subsequent irradiations. Peak at 285 eV ceases to change.
Results – Li-D-O and C functionality

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

2) Lithium deposition results cause the FWHM of the primary peak to increase. Peak shifts ~1 eV to higher binding energy.

3) 30 minute deuterium irradiation ($\Gamma \approx 1.5 \times 10^{15}$ cm$^{-2}$) causes a new peak to develop at 291 eV. The 284 eV peak shifts again to higher binding energy, now residing ~285 eV.

4) The relative intensity of the 291 eV peak compared to the 529.5 eV peak increases with subsequent irradiations. Peak at 285 eV ceases to change.

5,6) Change of relative intensity slows at some D fluence threshold.
Results – Li-D-O and C functionality

1) ATJ graphite shows a graphitic C1s peak at 284 eV. Carbonate presence is observed at 290 eV.

2) Lithium deposition results causes the FWHM of the primary peak to increase. Peak shifts ~1 eV to higher binding energy.

3) 30 minute deuterium irradiation (Γ ≈ 1.5 E15 cm^-2) causes a new peak to develop at 291 eV. The 284 eV peak shifts again to higher binding energy, now residing ~285 eV.

4) The relative intensity of the 291 eV peak compared to the 529.5 eV peak increases with subsequent irradiations. Peak at 285 eV ceases to change.

5,6) Change of relative intensity slows at some D fluence threshold.
Results – Li-D-O and C functionality

Observations
Based on these results and control experiments

1) As is
2) Post 2 knm Li deposition
3) D2-30m
4) D2-1.5h total
5) D2-2.5h total
6) D2-5h total

Results

Based on these results and control experiments, C1s binding energy was measured for different conditions.

- **As is**: The initial condition without any treatment.
- **Post 2 knm Li deposition**: After 2 knm of Li deposition.
- **D2-30m**: Treatment with D2 for 30 minutes.
- **D2-1.5h total**: Total treatment with D2 for 1.5 hours.
- **D2-2.5h total**: Total treatment with D2 for 2.5 hours.
- **D2-5h total**: Total treatment with D2 for 5 hours.

The graph shows the intensity of C1s as a function of binding energy, with different treatments clearly marked.

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**Caption for Diagram**

Observations
Based on these results and control experiments, C1s binding energy was measured for different conditions. The graph shows the intensity of C1s as a function of binding energy, with different treatments clearly marked.
Results – Li-D-O and C functionality

Observations
Based on these results and control experiments

- **284-285 eV**
  - Control experiments have shown that 2 peaks momentarily coexist.
  - Development of new peak indicates new bonding functionality.

1) As is
2) Post 2knm Li deposition
3) D2-30m
4) D2-1.5h total
5) D2-2.5h total
6) D2-5h total
Results – Li-D-O and C functionality

Observations
Based on these results and control experiments

291 eV
- Only develops after irradiating a *lithiated* sample.
- Relative intensity increases with higher D2 fluence.
- Eventually peak “saturates” and does not respond to increased D fluence.

290 eV
- Slight carbonate influence observed.
- Air exposure of a lithiated sample results in a carbonate peak (not shown).

284-285 eV
- Control experiments have shown that 2 peaks momentarily coexist.
- Development of new peak indicates new bonding functionality.
Results – Li-D-O and C functionality

Control experiments

Procedure (repeat): ATJ graphite was irradiated with D \textit{without} any lithium conditioning.

Result:
Graphitic peak (284 eV) shifted slightly to higher binding energy.
Carbonate peak (290 eV) diminished.
No new peaks were observed.
Results – Li-D-O and C functionality

Control experiments

Procedure (repeat):
ATJ graphite was irradiated with D without any lithium conditioning.

Result:
Graphitic peak (284 eV) shifted slightly to higher binding energy.
Carbonate peak (290 eV) diminished.
No new peaks were observed.

Therefore:
291 eV peak is a result of D irradiation on a lithiated graphite sample.
Results – Post mortem NSTX FY08 tiles

1) As is
2) Post Ar cleaning and TDS

Before treatment procedure, passivated tiles exhibit broad peaks. After cleaning, tiles resemble peaks found in control experiments.
Results - Summary

• Oxygen
  – Li and O interactions, on a graphite substrate, are manifest at 529.5 eV in the XPS spectrum. Peak diminishes with larger D fluence.
  – Li, O, and D interactions, on a graphite substrate, are manifest at 533 eV. Peak dominates with larger D fluence.

• Carbon
  – Li, D, and C interactions are manifest at 291 eV. Relative peak energy increases with increased D fluence. Changes cease to occur at a yet to be discovered D fluence threshold.

• Post-mortem tiles
  – Treatment (Ar sputtering and heating) changes passivated, broad, inconsistent peaks to align with consistently produced peaks found in controlled experiments.
Conclusions

• Specific photoelectron energy ranges identified that correlate with Li, O, D and C binding.

• Lithium binds with oxygen and carbon and is actively interacting with deuterium.
  – We conclude that D retention in lithiated graphite is dictated by more than simple interactions between Li and D alone. The presence of carbon and oxygen plays a major role in dictating how D is bound in the lithiated graphite system.

• Controlled experiments show a compelling link to post-mortem tiles.
Conclusions – Qualitative representation

Processes

1) Fresh ATJ sample
2) Post Li deposition
3) Post D bombardment
4) Post air exposure

polycrystalline surface

Li-C-O

C-O

532 eV

0

Li-O

529.5 eV

Li-O-C-D

Li-O-C

Li-Ox

Li-Ox

533 eV

531.5 eV

529.5 eV

passivated layer

Li-D-O dominant functionality

Li-Ox dominant functionality

Bulk graphite (C-O)

Legend of functionality states

most dominant interaction

less dominant interaction

least dominant interaction

ATJ sample

4) Post air exposure
Future work

- Investigate and distinguish differences between physical and chemical response of irradiations.
  - Using inert species (He) to isolate chemical effects.
- What thickness of lithium is most effective for pumping deuterium?
- What are the time dependent effects of lithium deposition and deuterium irradiation?
- Interrogate sample surface at various depths to determine chemical functionalities throughout specimen

Questions

- Does the lithium-carbon functionality actually allow more pumping of D to occur compared to liquid lithium?