Release models of hydrogen isotopes irradiated into ternary Li-containing oxides

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Background

- a secure and efficient fuel cycle in fusion reactors

- Release behavior of tritium in breeding blanket

- Li-containing oxides
  - Li$_2$O
  - LiAlO$_2$
  - Li$_2$TiO$_3$
  - LiTaO$_3$
  - LiNbO$_3$

- Defects induced by neutron irradiation: $V_{Li}$, $V_{O}$, $F^+$, $F^0$

- Ions irradiation: deuterium

- Existence states of deuterium correspondence

- Release behavior of irradiated deuterium

- Isotopes
Experiments

- The in-situ Fourier transform infrared spectroscopy (FT-IR) during $D_2^+$ irradiation
- The thermal desorption spectroscopy (TDS) during heating after $D_2^+$ irradiation
  Heating rate: 20 K min$^{-1}$

Ion species: 3keV $D_2^+$
Flux: $1.5 - 6 \times 10^{17}$ ions m$^{-2}$s$^{-1}$

Sample:
- polycrystalline powder: LiAlO$_2$ and Li$_2$TiO$_3$ (99.5%)
Chamber pressure: $<10^{-6}$ Pa

**QMS:** Quadrupole Mass Spectrometer

**TMP:** Turbo Molecular Pump

Top view of the diffuse reflectance system for powder sample

- FTIR
- Ion gun
- Sample
- Reflection mirror
- Heating unit
- Cover

Temperature record: sample holder

QMS: Quadrupole Mass Spectrometer

TMP: Turbo Molecular Pump
Results and Discussion

1. IR spectra for irradiated LiAlO$_2$ and Li$_2$TiO$_3$ powder

- A broad peak observed in LiAlO$_2$ and Li$_2$TiO$_3$

  — Asymmetry of peak implied the possibility of multiple O-D states

- The main O-D peak:
  - LiAlO$_2$ ~ 2600 cm$^{-1}$
  - Li$_2$TiO$_3$ ~ 2580 cm$^{-1}$

  — The average bond energy of O-D in LiAlO$_2$ is higher than that in Li$_2$TiO$_3$
Results and Discussion

2. TDS spectra of powder Li$_2$TiO$_3$

- The thermal desorption peak of D$_2$O is of higher temperature than that of D$_2$
- At higher fluence ($5 \times 10^{21}$ m$^{-2}$), D$_2$O is the dominant release chemical form
- With fluence increasing from $1.7 \times 10^{21}$ m$^{-2}$ to $5 \times 10^{21}$ m$^{-2}$
  - Desorption of D$_2$: no increase (saturation)
  - Desorption of D$_2$O: notable increase
Results and Discussion

3. TDS spectra of powder LiAlO₂

- At lower (1.7×10²¹ m⁻²) and higher fluence (5×10²¹ m⁻²) D₂ is the dominant release chemical form
- Desorption temperatures of D₂O and D₂ change with fluence increasing
- With fluence increasing from 1.7×10²¹ m⁻² to 5×10²¹ m⁻²
  - Desorption of D₂: notable increase (no saturation)
  - Desorption of D₂O: notable increase
Results and Discussion

3. D$_2$O/D$_2$ in TDS

With temperature arising
- Peaks of D$_2$O/D$_2$ in release rate are observed.
- D$_2$O/D$_2$ in total release amount is increasing.
  - Desorption of D$_2$O needs higher temperature than that of D$_2$
Conclusion

- The average bond energy of O-D in LiAlO$_2$ is higher than that in Li$_2$TiO$_3$
  - LiAlO$_2$: the main O-D peak at 2600 cm$^{-1}$
  - Li$_2$TiO$_3$: the main O-D peak at 2580 cm$^{-1}$

- The dominant release chemical form of irradiated deuterium
  - LiAlO$_2$: D$_2$ (Desorption of both D$_2$ and D$_2$O increased with fluence increasing)
  - Li$_2$TiO$_3$: D$_2$O (Desorption of D$_2$ achieved saturation at some fluence while desorption of D$_2$O increased with fluence increasing)

- D$_2$O/D$_2$ in total release amount is increasing with temperature arising
  — Desorption of D$_2$O needs higher temperature than that of D$_2$
Discussion

Presumption:

Surface reaction for desorption of $D_2$ and $D_2O$:

$D^*$: activated deuterium  A deuterium existing as any state should become $D^*$ and then be desorbed as $D_2$ or $D_2O$

$O^*$: activated oxygen  An oxygen as $O^{2-}$ should become $O^*$ and then be desorbed as $D_2O$

\[
D^* + D^* \rightarrow D_2 \uparrow
\]

\[
D^* + D^* + O^* \rightarrow D_2O \uparrow
\]

\[
\frac{D_2O}{D_2} \propto [O^*]_{surface}
\]
Discussion

Surface equilibrium

\[ O^{2-} \leftrightarrow O^* + F^0 \quad (k_1) \]
\[ O^{2-} \leftrightarrow O^* + F^+ + e \quad (k_2) \]
\[ O^{2-} \leftrightarrow O^* + V_O + 2e \quad (k_3) \]

\[
\begin{align*}
[F^0] &= [F^+] \cdot [e] \frac{k_2}{k_1} \\
[V_O] &= [F^+] \cdot \frac{1}{[e]} \frac{k_2}{k_3}
\end{align*}
\]

\[
\begin{align*}
\left[ O^{2-} \right] + [F^0] + [F^+] + [V_O] &= [O_{\text{origin-site}}] = \text{const} = A \\
&= \text{(oxygen sites conservation)}
\end{align*}
\]

\[
\begin{align*}
2[O^{2-}] + 2[F^0] + [F^+] + [e] &= 2[O_{\text{origin-site}}] = \text{const} \\
&= \text{(electric charge conservation)}
\end{align*}
\]

\[
\begin{align*}
[e] = \frac{[F^+] + \sqrt{[F^+]^2 + 8[F^+]k_2/k_3}}{2} &\approx k[F^+] \\
[O^{2-}] &= A - [F^+] \cdot [e] \frac{k_2}{k_1} - \frac{1}{2} [F^+] - \frac{1}{2} [e] \approx A - m[F^+]^2 - n[F^+] \\
\end{align*}
\]
Discussion

Deduction:

\[ \frac{D_2O}{D_2} \propto [O^*]_{\text{surface}} \propto \left[ \frac{O^{2-}}{F^+} \right] \cdot [e] \approx \frac{a}{[F^+]^2} - \frac{b}{[F^+]} - c \propto \frac{1}{[F^+]} (a, b, c > 0) \]

Deduction-1: when temperature arise, the ratio of $D_2O/D_2$ will be increased with decrease of $F^+$.

Supporting: the increase of $D_2O/D_2$ with temperature arising have been observed in LiAlO$_2$ and Li$_2$TiO$_3$

Deduction-2: In the sample with high activation energy and annihilation temperature of $F^+$, more deuterium will be desorbed as $D_2$.

Supporting: (*reference from M.Oyaidzu in Shizuoka Uni.)

<table>
<thead>
<tr>
<th></th>
<th>* Annihilation temperature /K</th>
<th>* Activation energy /eV</th>
<th>Release chemical form</th>
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</thead>
<tbody>
<tr>
<td>LiAlO$_2$</td>
<td>600-800</td>
<td>0.52</td>
<td>1.4</td>
</tr>
<tr>
<td>Li$_2$TiO$_3$</td>
<td>400-700</td>
<td>0.43</td>
<td>0.41</td>
</tr>
</tbody>
</table>
Thanks!
Appendix

1. Section View of B-O-B in the transmittance system

During irradiation

During TDS

ions

Cover (Mo)

Sample

stage

FT-IR

Sample

stage
During $D_2^+$ irradiation

Instrument for heating after $D_2^+$ irradiation

Cover (Mo)

Mirror

Sample

stage

Mirror

stage
Appendix

O-D on the surface

O-D of sub.D⁺

O-D of int.D⁺
Appendix

$LiAlO_2$

$LiTaO_3$ and $LiNbO_3$