Tritium diffusion and formation in the bulk and defective surface of γ-$LiAlO_2$ pellets: First-principles investigation

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Outline

- Introduction
- Main results
  - Tritium Formation
  - Tritium Diffusion Pathways in Bulk & on Surface
  - Tritium Species Formation from $LiAlO_2$ pellet
- Conclusion

Tritium & Its Application

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- Tritium is a radioactive isotope of hydrogen for commercial (400g/yr) and military applications.
  - medical diagnostics and sign illumination, especially EXIT signs.
  - boost the yield of both fission and thermonuclear weapons
- Half-life of 12.3 years and low concentration in nature
- So, to maintain certain amount of ^{3}H, we need to produce ^{3}H.

To produce tritium:

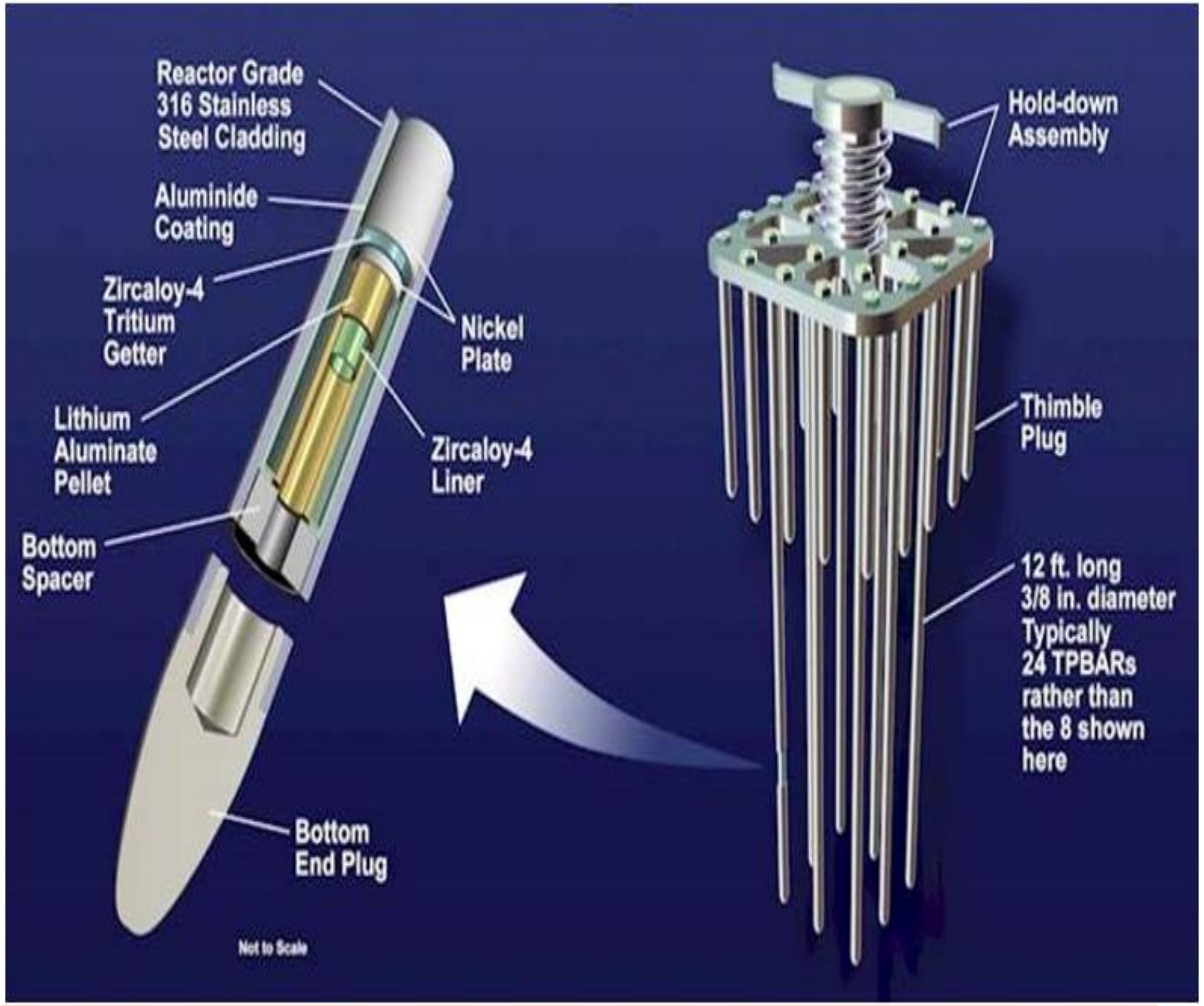
$$^{6}_{3}\mathrm{Li} + \mathrm{n} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H} + 4.8\ \mathrm{MeV}$$

$$^{10}_{5}\mathrm{B} + \mathrm{n} \rightarrow 2\ {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H}$$

$$^{3}_{2}\mathrm{He} + \mathrm{n} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H}$$

$$^{14}_{7}\mathrm{N} + \mathrm{n}\ (\text{cosmic rays} > 4\mathrm{MeV}) \rightarrow {}^{12}_{6}\mathrm{C} + {}^{3}_{1}\mathrm{H}$$

TPBAR Producing Tritium



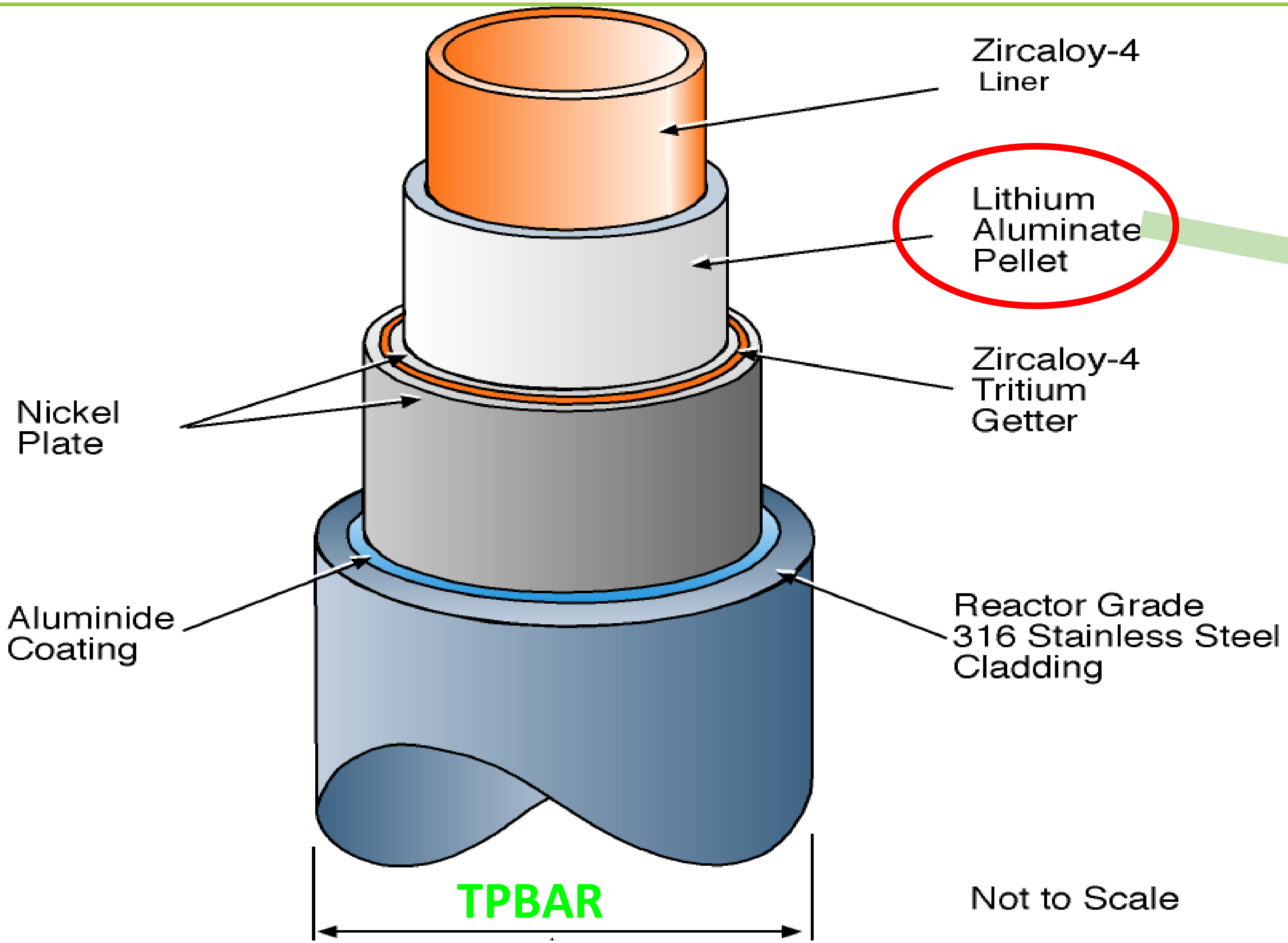
- Anderson, E. S., *et al*, PNNL-14401, (2003), doi:10.2172/15010654

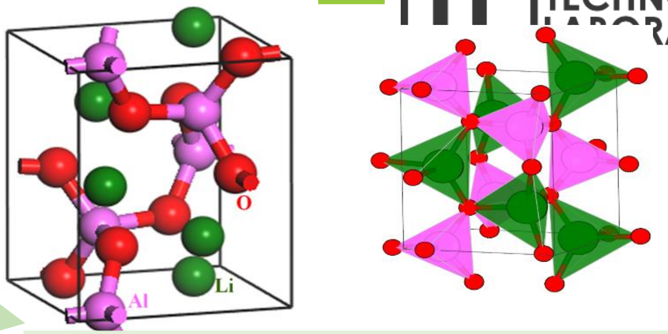
Tritium-Producing Burnable Absorber Rod (TPBAR) in light water reactor to produce tritium through

$$^{6}_{3}\text{Li} + \text{n} \rightarrow \; ^{4}_{2}\text{He} \; + \; ^{3}_{1}\text{H} + 4.8 \text{ MeV}$$

- In TPBAR, due to its high-density, the $LiAlO_2$ is used in the form of an annular ceramic pellet enriched with the ^{6}Li isotope and located between the zircaloy-4 liner and nickel-plated zircaloy-4 tritium getter. When irradiated in a pressurized water reactor (PWR), the ^{6}Li pellets absorb neutrons, simulating the nuclear characteristics of a burnable absorber rod, and produce tritium ($^{3}_{1}$H).

Tritium-Producing Burnable Absorber Rod (TPBAR)





$$^{6}_{3}\mathrm{Li} + \mathrm{n} \longrightarrow\ ^{4}_{2}\mathrm{He} +\ ^{3}_{1}\mathrm{H} + 4.8\ \mathrm{MeV}$$

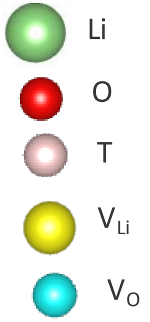
Once T is produced, we need to know:

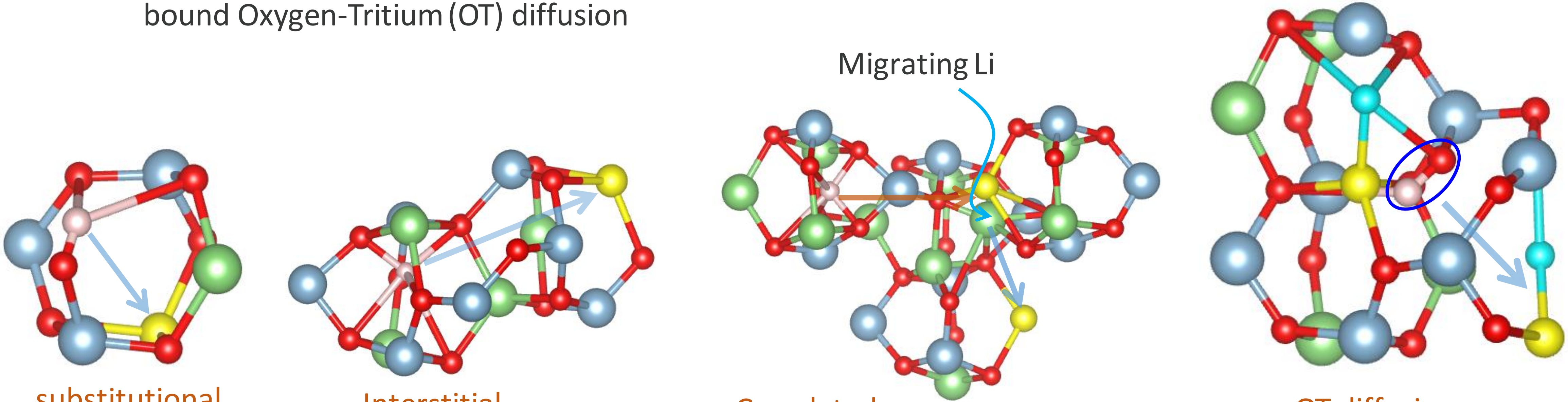
- The T diffusion mechanism in pellet
- The formation of tritium on the surface of pellet.
- T species get off the surface & diffusion into getter to form metal hydrides.

Understanding Tritium Diffusion Process

Proposed possible diffusion pathways:

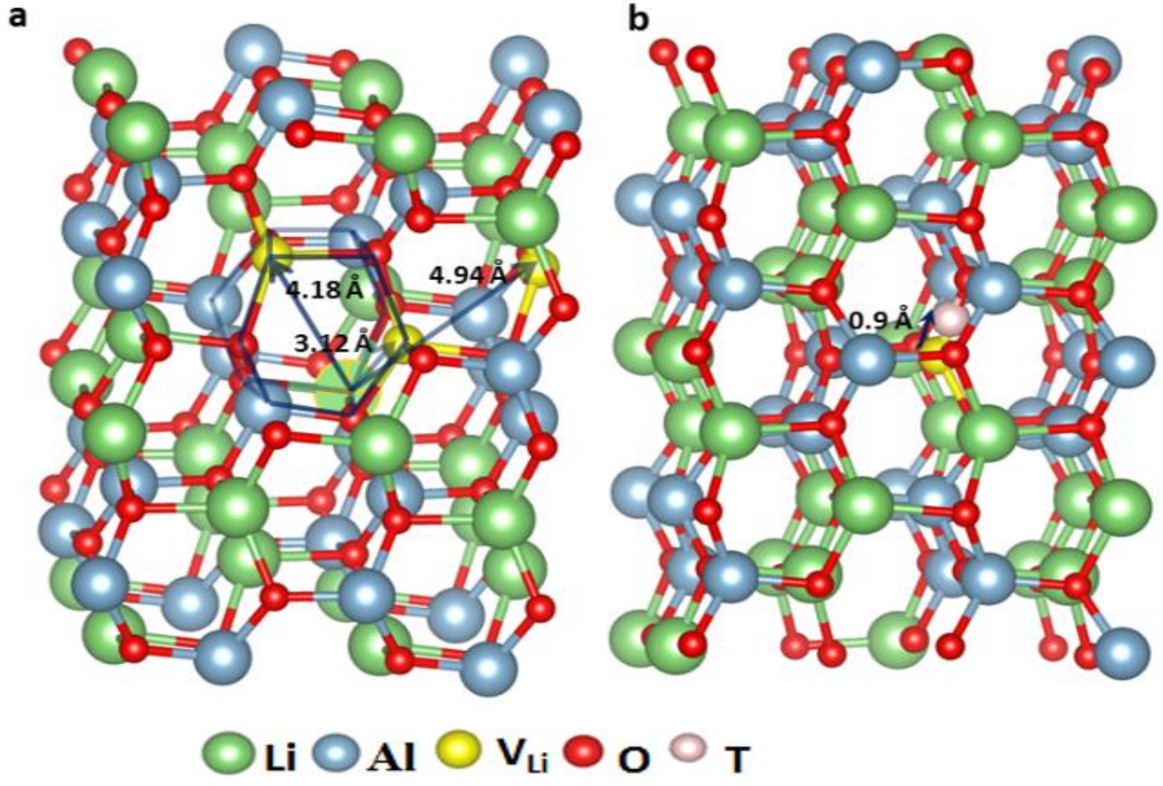
- ➢ Diffusion of Tritium alone
    - i. substitutional Tritium
    - ii. interstitial Tritium
- ➢ Correlated diffusion of Tritium & Lithium
    - i. Lithium moves to vacancy and interstitial Tritium moves to Lithium's place
    - ii. Lithium & Tritium swapping their positions.
- ➢ Diffusion of Oxygen & Tritium as single entity
    - bound Oxygen-Tritium (OT) diffusion

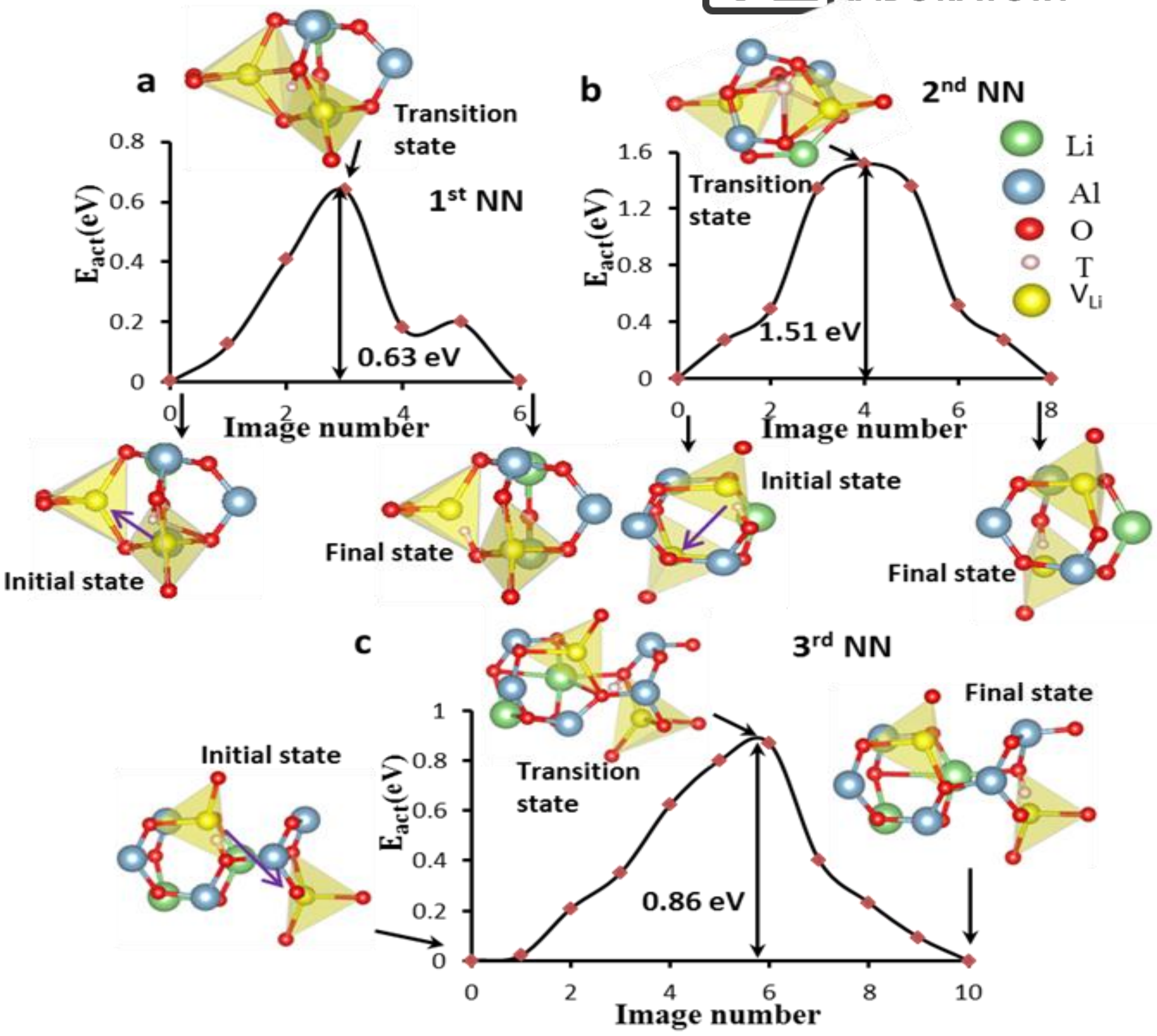




substitutional   Interstitial   Correlated   OT diffusion

Substitutional ^{3}H (T_s) Diffusion



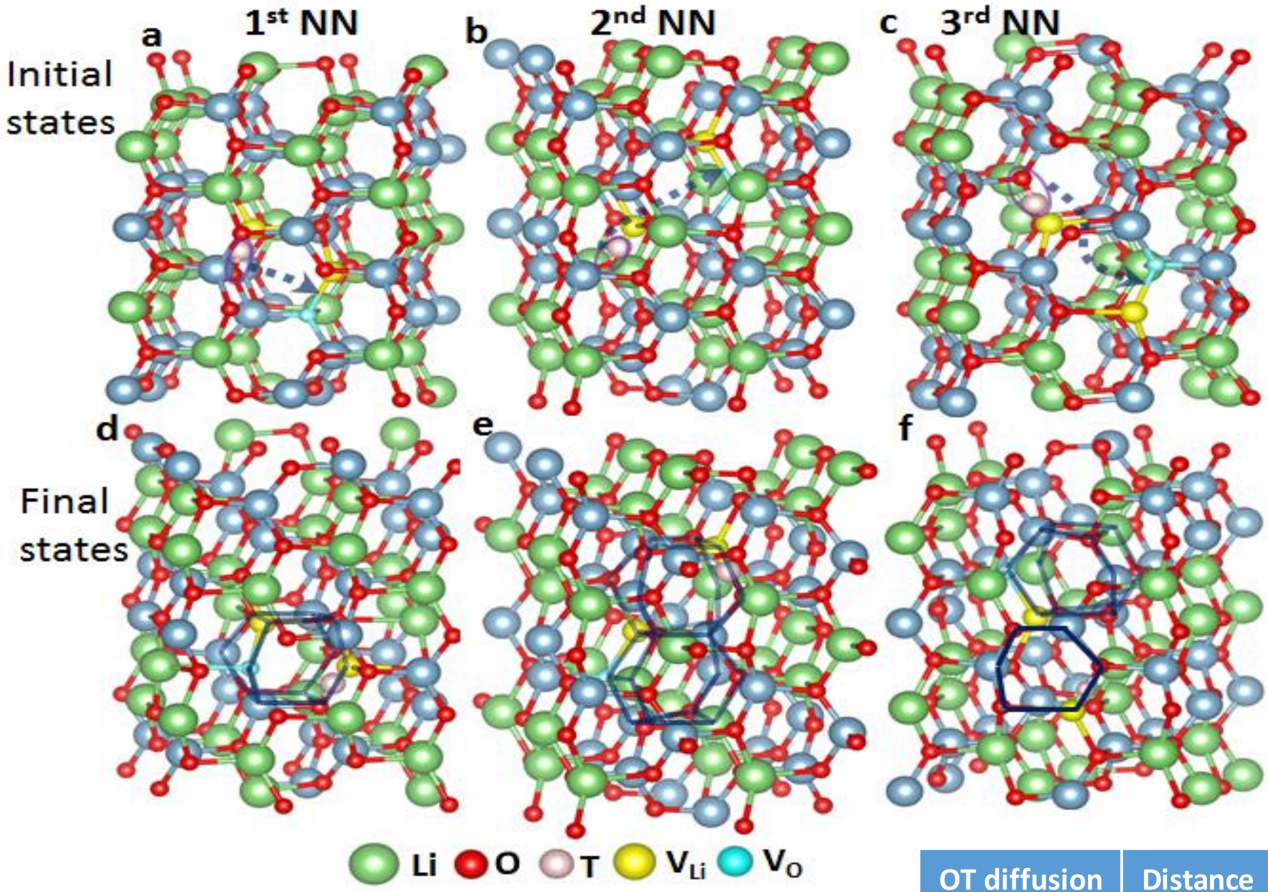


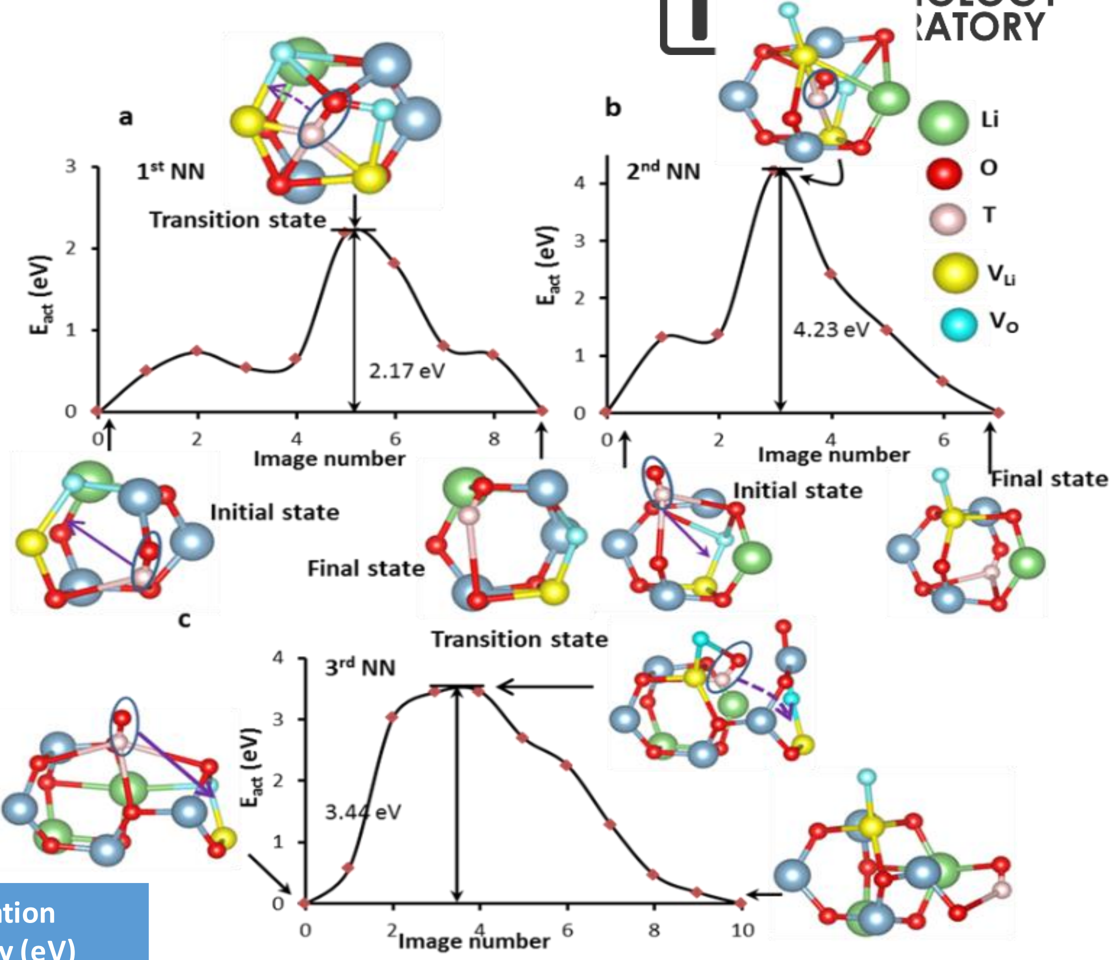
Activation energy (E_{act}) for a substitutional ^{3}H

Nearest Neighbour (NN)	1st NN	2nd NN	3rd NN	Exp. [25] (630–930 K)
Distance (Å)	**3.12**	4.18	4.94	
E_{act} (eV)	0.63	1.51	0.86	0.93

- Paudel, Lee, Senor, Duan, **J. Phys. Chem. C 122**(2018)9755-9765

OT Diffusion





OT diffusion to NN Site	Distance (Å)	Activation energy (eV)
1st NN	3.12	2.17
2nd NN	4.18	4.23
3rd NN	4.94	3.44

Diffusion Coefficient

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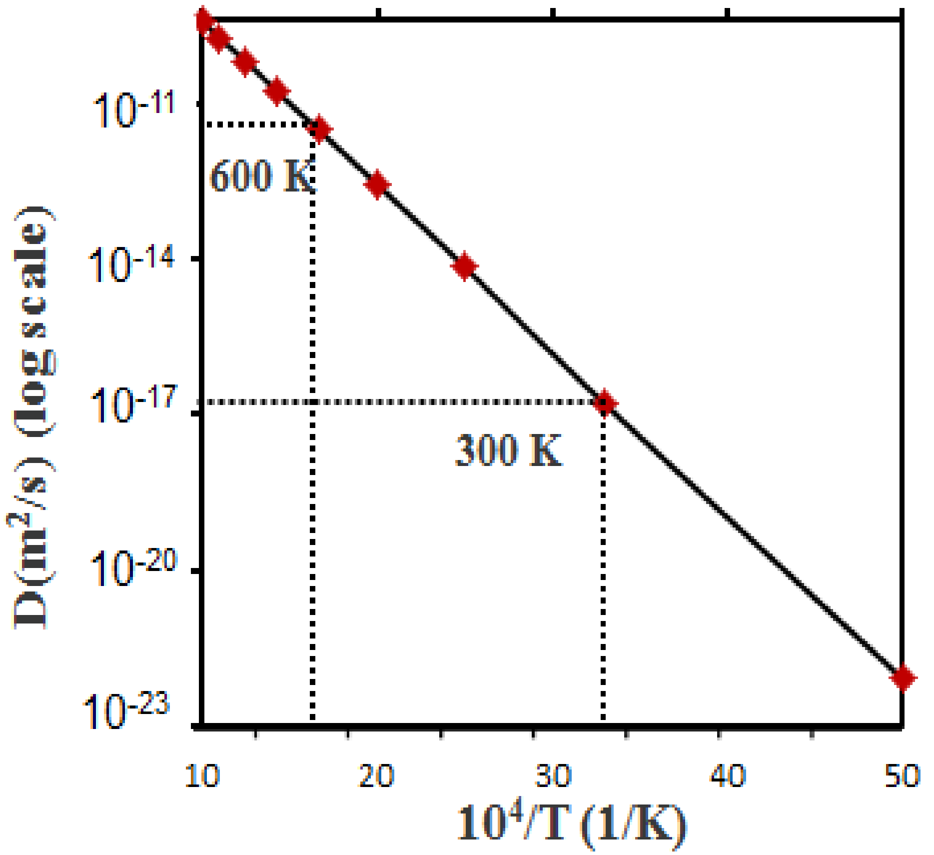


Table 3. Summary of ^3H and OT activation energy barriers (E_{act}), diffusion coefficients (D), and migration distance (L)

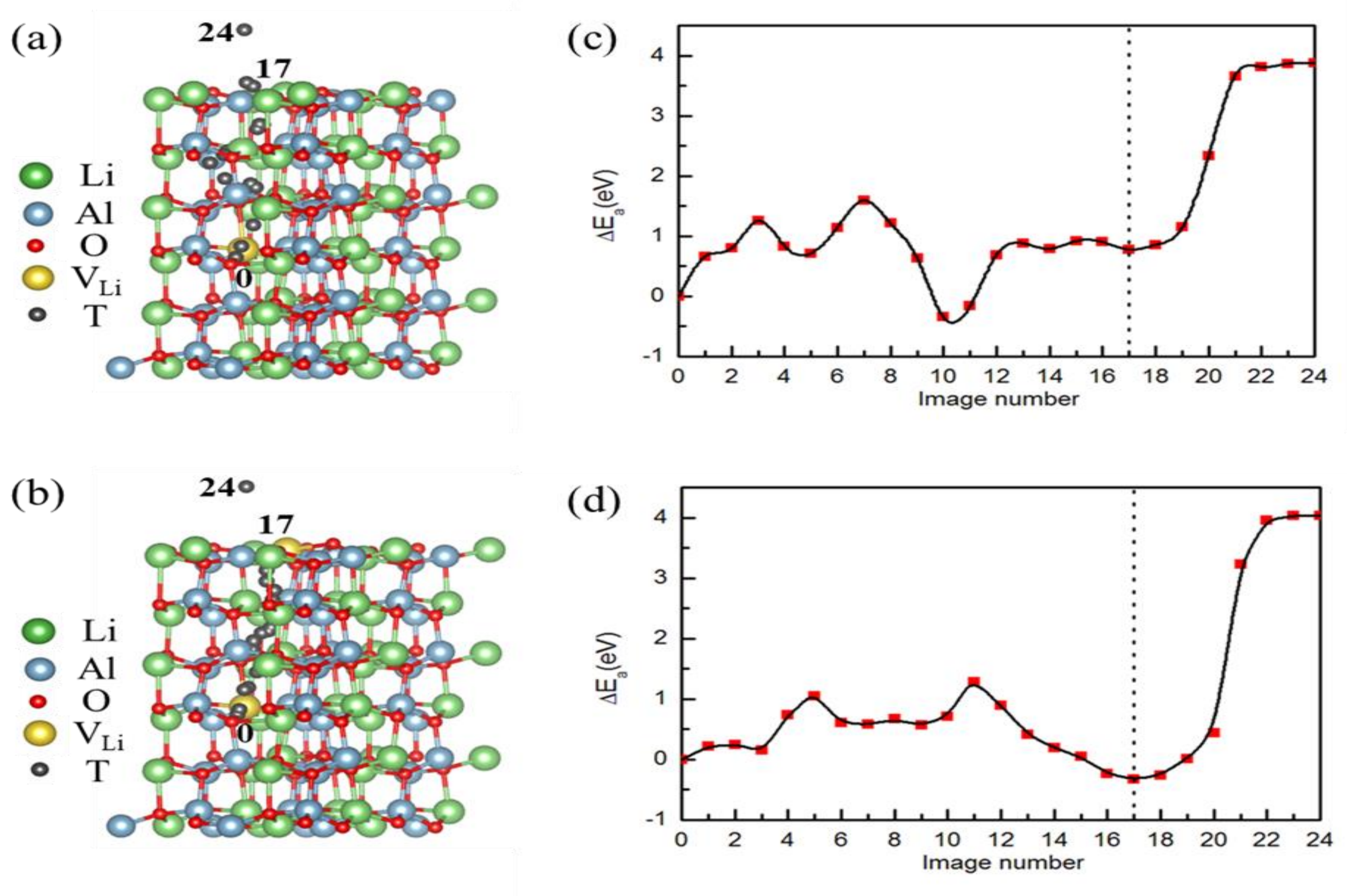
Type of diffusion	Location of V_{Li}	L (Å)	E_{act} (eV)	D at 600 K (m^2/s)
Substitutional	1st NN	3.12	0.63	3.25×10^{-12}
	2nd NN	4.18	1.51	6.45×10^{-20}
	3rd NN	4.94	0.86	3.74×10^{-14}
Interstitial		6.30	0.9	1.72×10^{-14}
Li-T correlated migration (swapping position)	1st NN	3.12	1.18	3.82×10^{-17}
	2nd NN	4.18	1.87	5.96×10^{-23}
	3rd NN	4.94	1.52	1.60×10^{-21}
OT migration	1st NN	3.12	2.17	3.56×10^{-25}
	2nd NN	4.18	4.23	1.17×10^{-42}
	3rd NN	4.94	3.44	7.19×10^{-36}
Two T_i migration (Two Frenkel pairs)	$L(V_{Li})$ = 3.12 Å	6.30	1.29	8.99×10^{-18}
Two T_s migration	$L(V_{Li})$ = 3.12 Å	4.94	1.54	3.53×10^{-20}
Four T_i migration (4 Frenkel pairs)	V_{Li} in random	-	3.41	6.03×10^{-36}
Exp. Data (630-930K) [25]				3.0×10^{-10}

- Substitutional ^3H diffusion to the 1st NN Li vacancies in $LiAlO_2$ has smallest activation energy barrier (0.63 eV) and has 3.25×10^{-12} m^2/s diffusion coefficient at 600 K.
- The OT diffusion is unfavorable with large E_{act} barrier (>2.17 eV).

- Paudel, Lee, Senor, Duan, **J. Phys. Chem. C** **122**(2018)9755-9765

Tritium trapping and recombination in V_{Li}

T diffusion from bulk to the (100) surface



Pristine surface

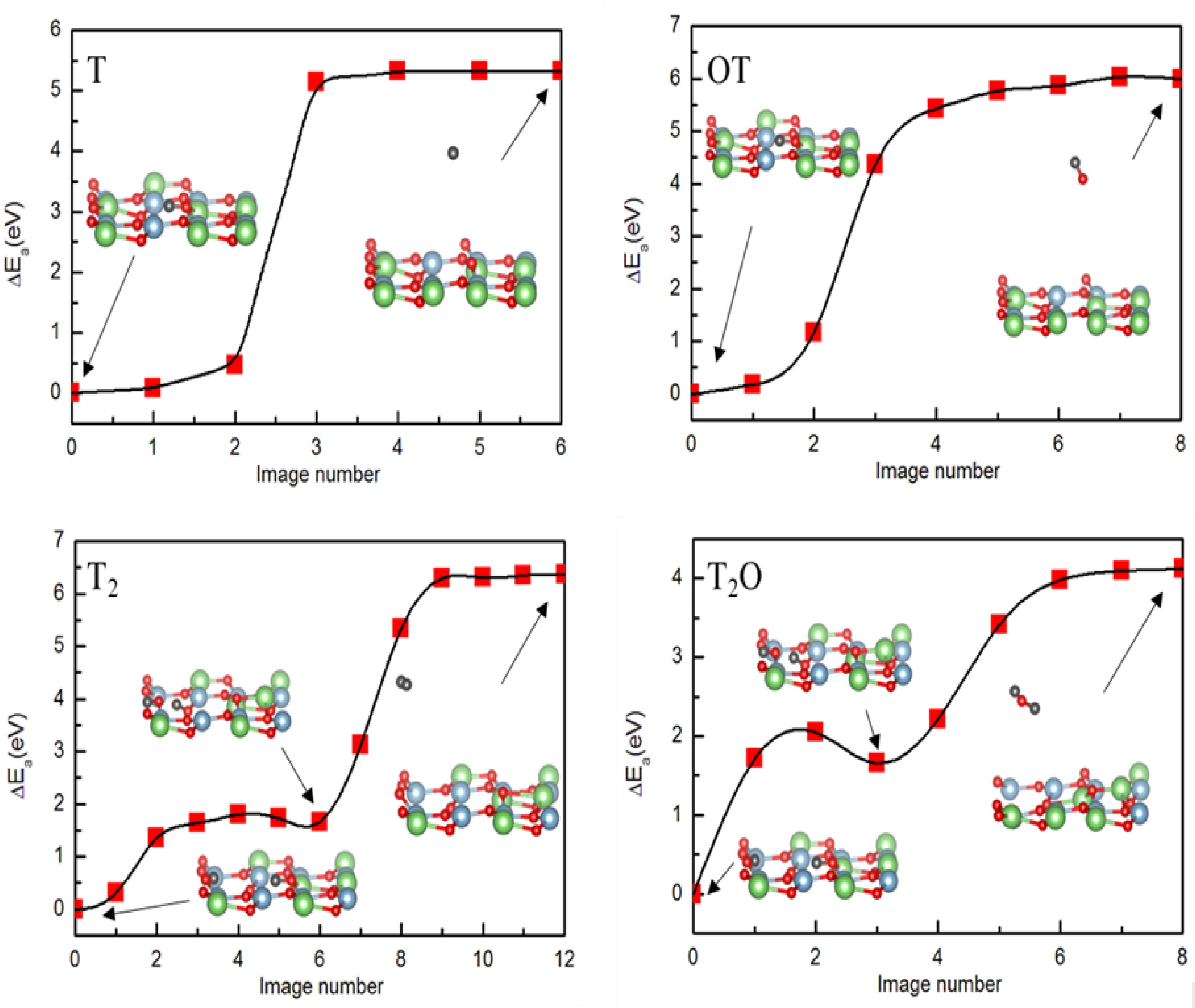
- ✓ The barrier height for T diffusion from bulk towards surface is 1.59 eV.
- ✓ The desorption energy from surface is 3.10 eV.

Surface with one V_{Li}

- ✓ The barrier height for T from bulk towards surface is 1.28 eV.
- ✓ The desorption energy from surface is 4.36 eV.

The ^3H atoms diffusion from bulk would be accumulated on the surface, trapping in V_{Li}.

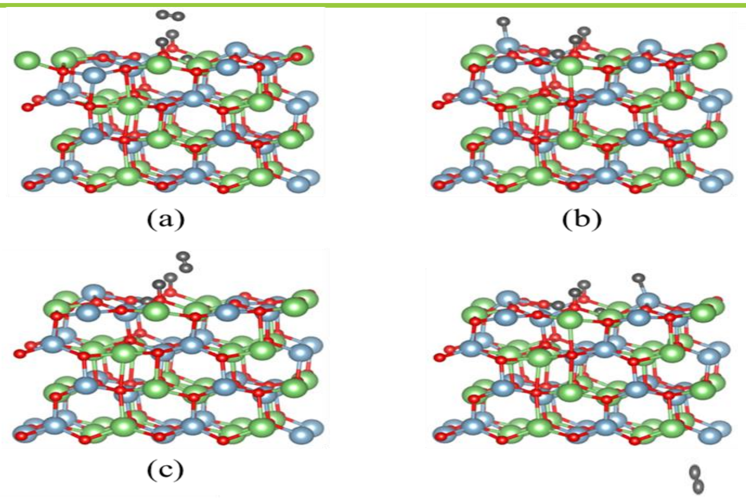
T-species desorption from (100) surface of γ-$LiAlO_2$

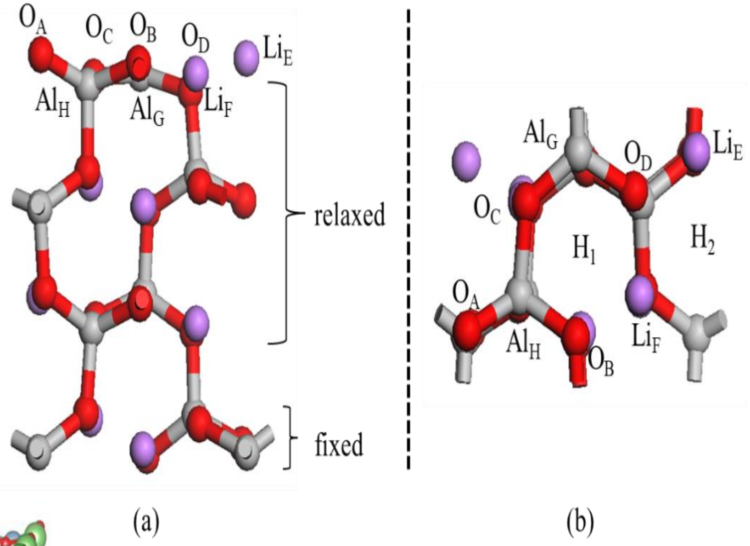


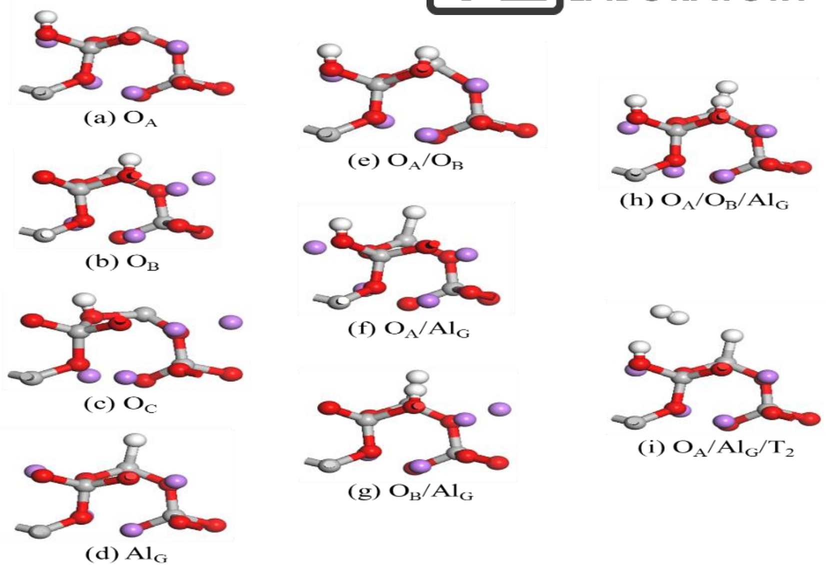
- ✓ The most stable (100) surface;
- ✓ The surface O sites are the most favorable adsorption site for T;
- ✓ the energy barrier for substitution T diffusion is bulk < surface < defective surface;
- ✓ the energy barrier for substitution OT diffusion is bulk > surface > defective surface;
- ✓ the desorption behavior of all the substitution T-related species (T, OT, T_2, and T_2O) is nearly prohibited, due to the high desorption energy.

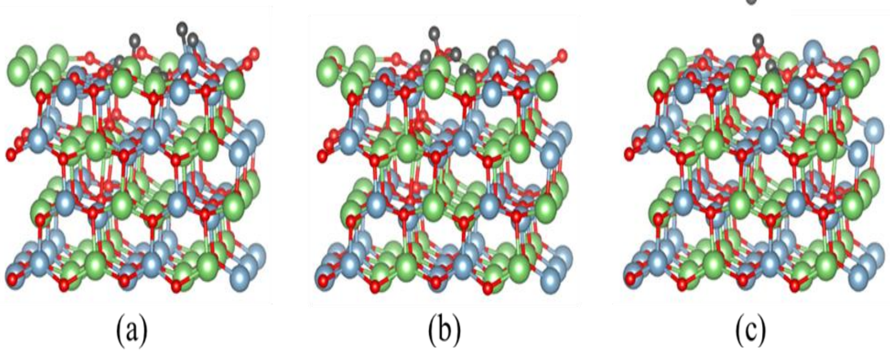
T. Jia, D. Sensor, Y. Duan, **J. Nucl. Mater. 540** (2020)152394.

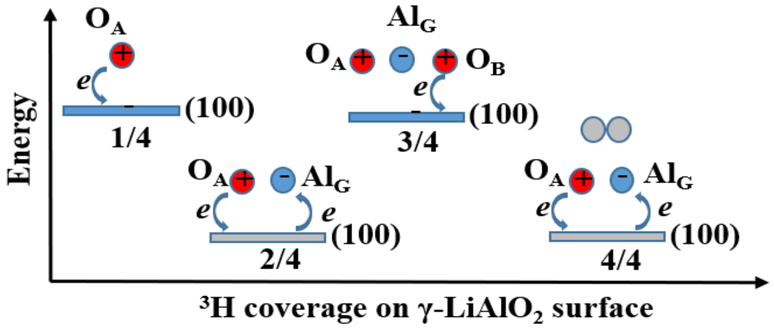
Configurations of More ^3H Binding on (100) Surface











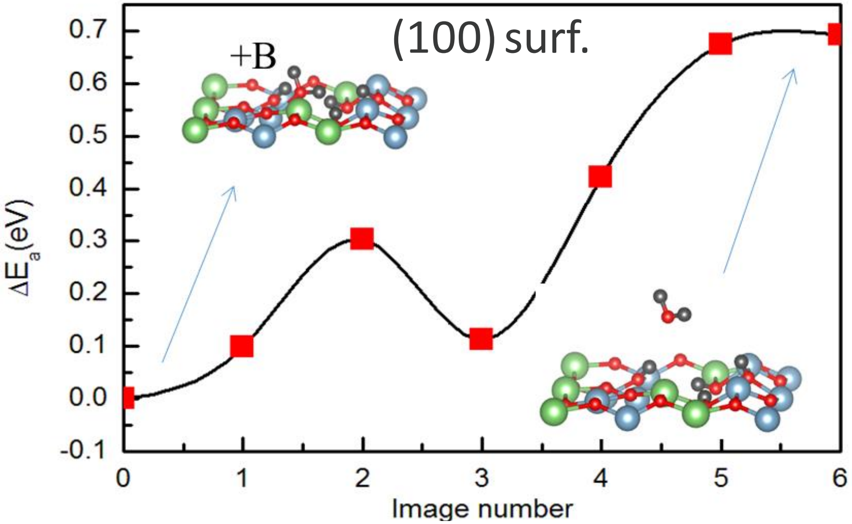
Major finding:

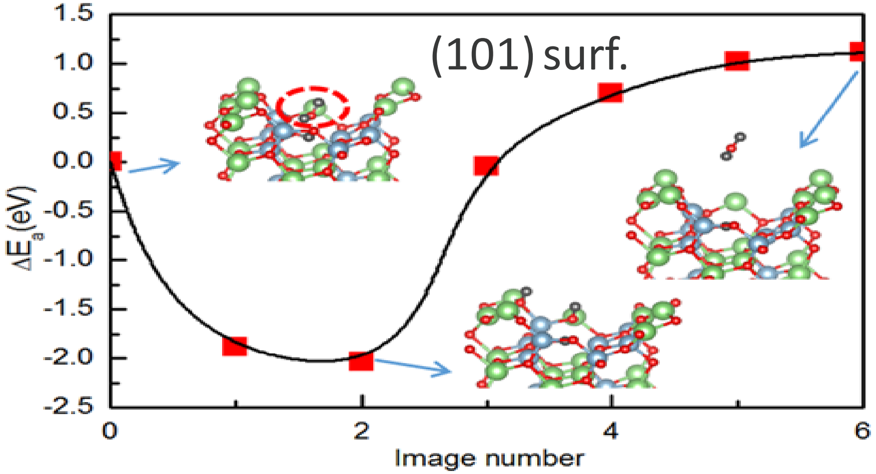
- Overall, the ^3H atoms produced in the bulk are firstly diffused toward surface and then accumulated in the V_{Li} of surface, due to the high energy barrier of ^3H desorption.
- With the increasing ^3H accumulation on the surface, it can be desorbed from the surface mainly in T_2 molecule form.

- T. Jia, *et al*, **Appl. Surf. Sci. Adv.** **5**(2021)100114; **J. Nucl. Mater.** **555**(2021)153111,**540**(2020)152394, **522**(2019)1-10.

Tritium trapping and recombination in V_{Li}

T trapping in the surface with two V_{Li}

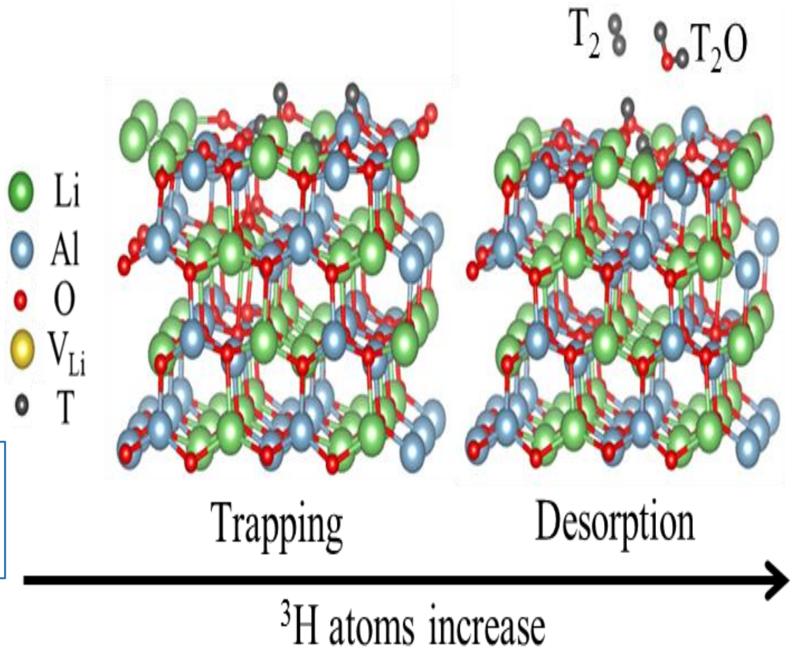




T_2O desorption energy is 0.69 eV.

O_B has only one coordination by two Li vacancies.

The more Li vacancies connected, the more T_2O produced.

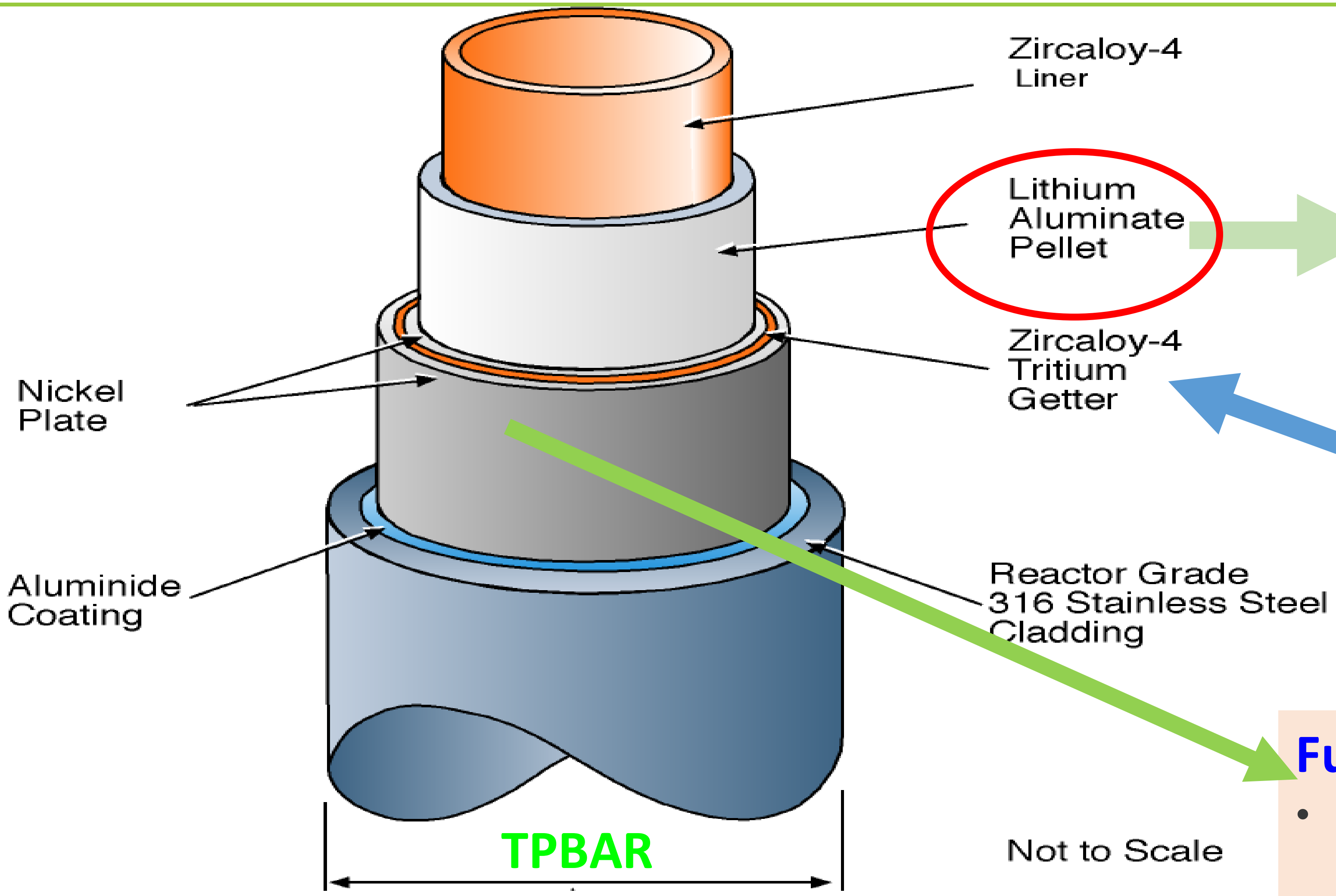


Main findings:

- **The ^3H atoms are combined into T_2 or T_2O molecules after over-accumulation. T_2 should be the main product at beginning. As the number of V_{Li} increases under irradiation, T_2O could be increased.**

- H. P. Paudel, *et al*, **Comput. Mater. Sci. 181**(2020)109748 ; **193**(2021)110419; **J. Phys. Chem. C 122**(2018)9755-9765, 28447-28459
- T. Jia, *et al*, **J. Nucl. Mater. 555**(2021)153111,**540**(2020)152394, **522**(2019)1-10; **Appl. Surf. Sci. Adv. 5**(2021)100114

Conclusion: Tritium production from r-LiAlO$_2$ Pellet



In Conclusion,

$$^{6}_{3}\mathrm{Li} + \mathrm{n} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H} + 4.8\ \mathrm{MeV}$$

Main product

T_2, T_2O

Further work:

- T_2 & T_2O diffusion on Nickel plate & across Ni-Zircalcoy-4 to form metal hydrides.

- H. P. Paudel, *et al*, **Comput. Mater. Sci. 181**(2020)109748 ; **193**(2021)110419; **J. Phys. Chem. C 122**(2018)9755-9765, 28447-28459
- T. Jia, *et al*, **J. Nucl. Mater. 555**(2021)153111; **540**(2020)152394, **522**(2019)1-10; **Appl. Surf. Sci. Adv. 5**(2021)100114

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Thank You !