Identifying the most stable accommodation mechanisms for Li in ZrO_2 fuel cladding

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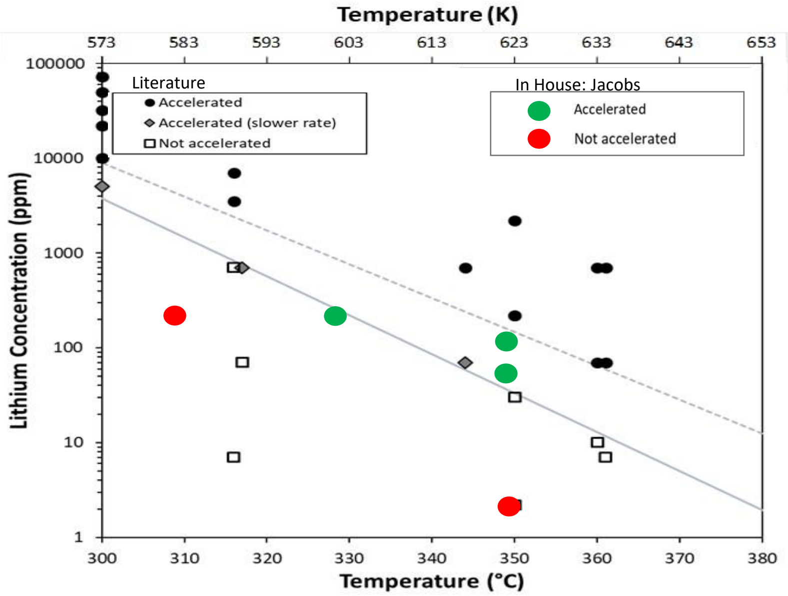
Aim: to predict the role of lithium in accelerated corrosion of zirconium alloys. This will enable:

- Design of preventative methods/alterations
- Prolong burnup and increase efficiency of PWRs
- Lower running cost and design simplification.

Figure 1 -Modified from: Hulme *et al.*, Investigating the Corrosion Behavior of Zircaloy-4 in LiOH under a Thermal Gradient and Two Phase Flow Regime, ASTM 2019. **Green points** highlight accelerated corrosion.



Previous experimental work by Jacobs has confirmed accelerated lithium corrosion due to higher Li concentrations and at higher temperatures

Method and results: Using density functional theory we found that for both monoclinic and tetragonal ZrO_2 :

- High Li concentrations (Blue) increase vacant O ($V_O^{\bullet\bullet}$) (Red) at the oxide's surface (zero partial pressure)
- Defects are predominantly unbound

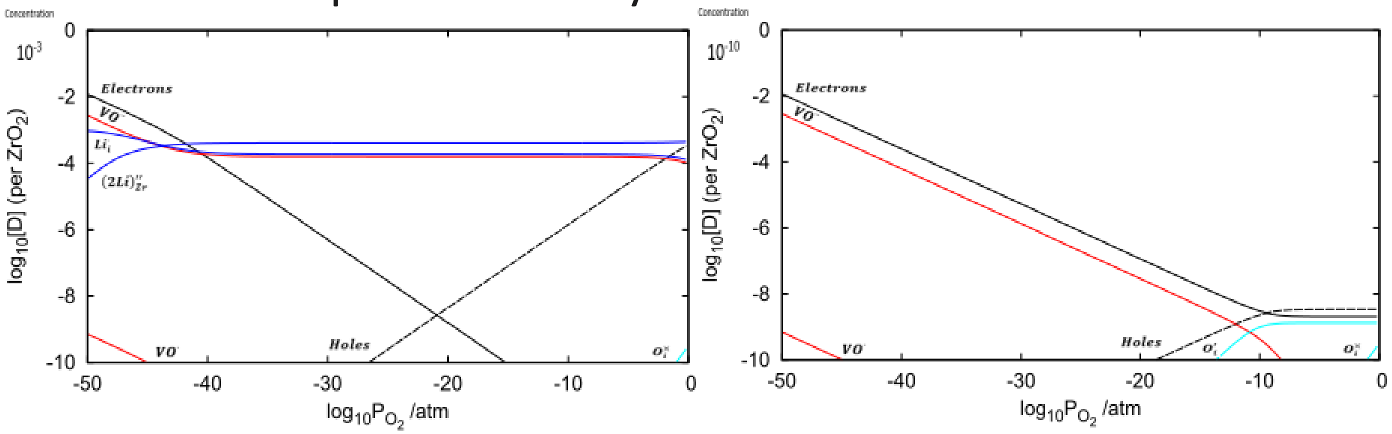


Figure 2 - Brouwer diagrams for monoclinic ZrO_2 at 700°C at constant volume. To the left 10^{-3} Li concentration. To the right 10^{-10} Li concentration. Li (Blue) VO (Red) O_i (Turquoise)

Summary: Diffusion rate of oxygen is largely determined by the concentration of oxygen vacancies (Yang, Yousef & Yildiz, 2018). It is observed that Li increases the O vacancy concentration and this could be a dominant mechanism to explain the experimental observations.

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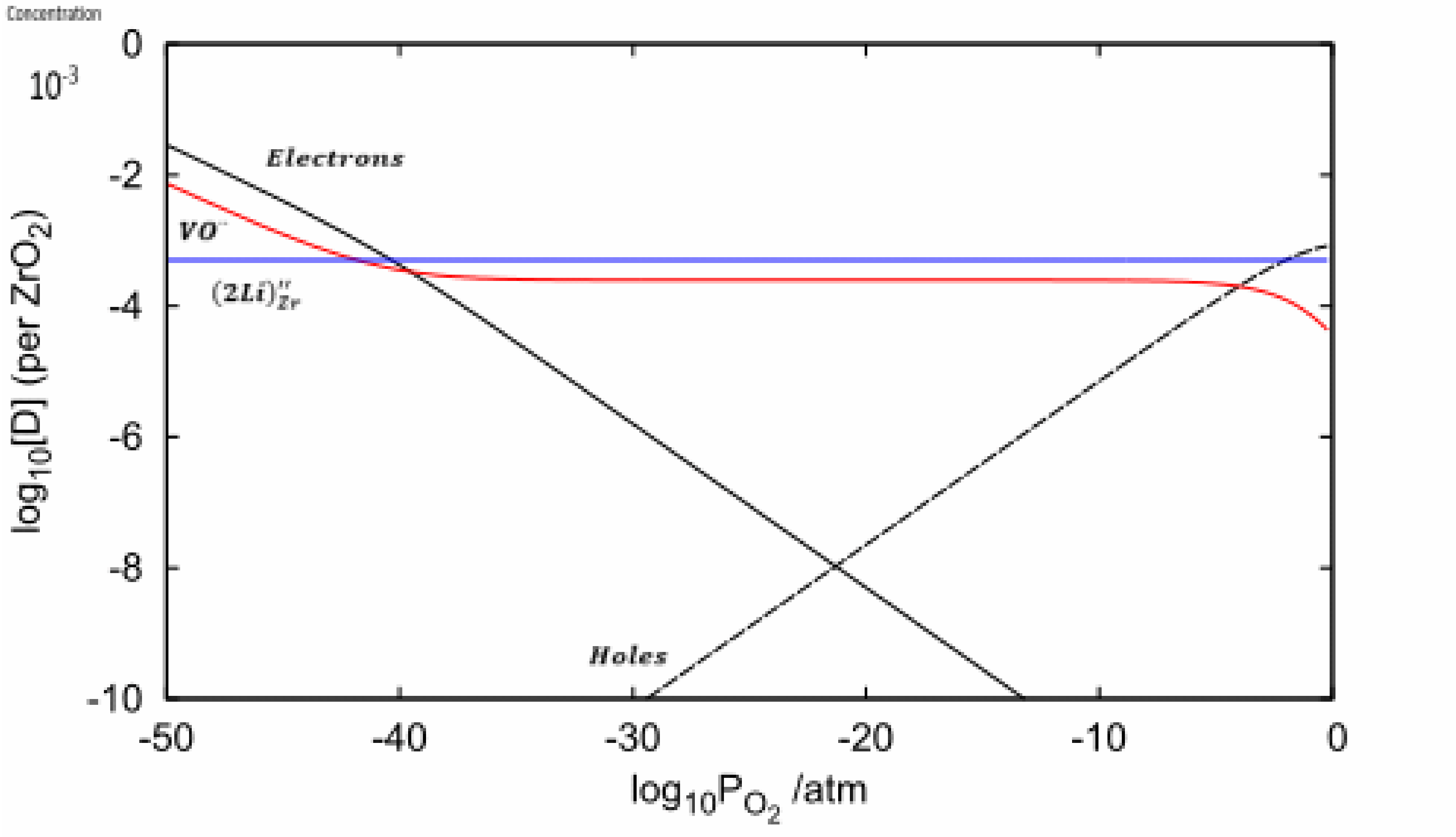
Monoclinic 700°C $(2Li)''_{Zr}$ concentrations



- Diffusion rate of oxygen is determined by concentration of oxygen vacancies:

$$D_{oxygen} = \sum_q [V_O^q] D_{V_O^q} + \sum_q [O_i^q] D_{O_i^q}$$