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Mechanisms of helium accommodation in lithium metatitanate

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HIGHLIGHTS

- Determination of dominant modes for He accommodation in Li_2TiO_3.
- Identification of a mechanism by which He can increase tritium diffusivity.

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ABSTRACT

Helium is generated as a by-product of the transmutation of lithium in the breeder blanket region of a fusion reactor. The presence of helium in ceramic breeder materials, such as lithium metatitanate (Li_2TiO_3), can lead to pressure in the pebble and degradation of mechanical properties as well as influencing tritium retention in the matrix. Here, density functional theory is used to examine the mechanisms of helium accommodation in Li_2TiO_3 across a range of conditions relevant to a fusion reactor. The results show that the mechanism of helium accommodation depends on the availability of defect trap sites, which itself depends on the stoichiometry of the crystal. It is also shown that helium may displace tritium from lithium vacancy defects and may therefore increase the tritium extraction rate by increasing the fraction of mobile tritium ions.

1. Introduction

It is currently expected that future fusion power stations will employ the D–T reaction, whereby deuterium and tritium are fused together forming a helium atom and a high energy neutron. Deuterium can be extracted from sea water, however, due to its short half-life there is no natural source of tritium. Therefore, it is envisaged that tritium will be generated from the transmutation of lithium, induced by the high energy neutron released during the D–T reaction, via:

$$^{7}_{3}\mathrm{Li}+^{1}_{0}n\rightarrow^{3}_{1}\mathrm{T}+^{4}_{2}\mathrm{He}+^{1}_{0}n \tag{1}$$

or

$$^{6}_{3}\mathrm{Li}+^{1}_{0}n\rightarrow^{3}_{1}\mathrm{T}+^{4}_{2}\mathrm{He}. \tag{2}$$

Neutrons will be ejected from the D–T reaction in a random direction, therefore as much of the reactor chamber as possible will be surrounded with a breeder blanket that will contain the lithium breeder material. While the main role of this blanket region is the breeding of tritium, it is also where the kinetic energy of the high energy neutron will be converted into heat for use in electricity generation as well as providing some protection for the external structures.

Lithium ceramics, in particular Li_2TiO_3 and Li_4SiO_4, are under consideration for adoption as breeder materials due to their high lithium densities, high melting points and excellent chemical compatibility with structural and neutron multiplier materials [1]. In concepts, such as the EU's helium cooled pebble bed (HCPB), the ceramics will be in pebble form with a helium gas flowing between the pebbles acting as a coolant [2]. As the high energy neutron can easily penetrate the pebbles, transmutation will occur throughout the crystal and the resulting $^{3}_{1}$T and $^{4}_{2}$He will initially be accommodated in the bulk. There have been a number of studies that examine tritium accommodation and diffusion in ceramic breeders (see for example [3–6]) but there has been less effort to understand the behaviour of helium in the solid. Kulsartov et al. observed He release from Li_2TiO_3 at temperatures >1400 K using thermal desorption spectroscopy (TDS) after neutron irradiation [7]. This temperature is greater than the operating temperature of the breeder blanket, implying that the ceramic will maintain its helium inventory. More recent results on ^{3}He implanted samples suggested that desorption may occur at lower temperatures, beginning at 500 °C (773 K) with almost all He removed upon annealing for 5 min at 900 °C (1173 K) [8,9]. This discrepancy is important as Kobayashi et al. suggest that the presence of He in the matrix may improve the rate of tritium

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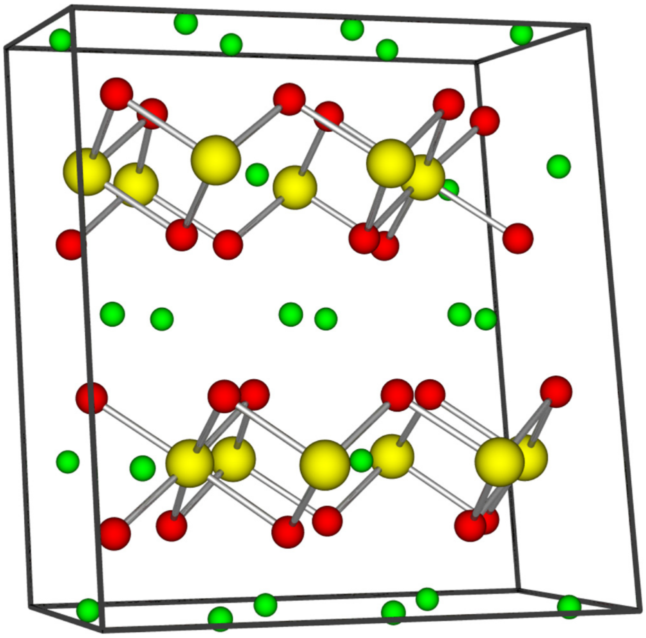

Fig. 1. The Li_2TiO_3 unitcell, where yellow, green and red spheres correspond to titanium, lithium and oxygen ions respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

extraction as the helium may displace tritium from defect trap sites or form bubbles which absorb many of the defects created by irradiation [10]. While these bubbles may lead to improved tritium extraction, they may also lead to significant swelling and a decrease in the thermal conductivity. Given that relatively little is known about the atomic processes governing the behaviour of helium in the Li_2TiO_3 matrix, and the important implications for tritium extraction, this study aims to examine mechanisms of He accommodation at defect trap sites using density functional theory.

2. Crystallography

The lithium metatitanate phase displays a wide stoichiometric range from 47% to 51.5% TiO_2, which may be exploited for improved tritium breeding by increasing lithium content. At intermediate temperatures (300–1215 °C), the Li_2TiO_3 structure can be thought of as a disordered rocksalt structure with alternating Li and $LiTi_2$ (1 1 1) planes. Within the mixed cation layer the Ti^{4+} ions form hexagons centered on Li^{1+} ions. These hexagonal layers can be stacked upon each other in different ways leading to the assignment of a number of different space groups i.e. *C*2/*m*, *C*2/*c* and $P3_112$ [11], although the monoclinic *C*2/*c* is most frequently quoted [12,13]. This complex layered structure leads to highly anisotropic properties, such as conductivity, and thus the calculation of fully converged defect energies requires care. A graphical representation of monoclinic *C*2/*c* Li_2TiO_3 studied in this work is presented in Fig. 1.

3. Methodology

3.1. Defect formalism

Considering only point and electronic defects (i.e. electrons and holes) the condition of charge neutrality in a crystal may be expressed as:

$$\sum_i q_i c_i - N_c \exp\left(-\frac{E_g-\varepsilon_F}{k_BT}\right) + N_v \exp\left(-\frac{\varepsilon_F}{k_BT}\right) = 0 \tag{3}$$

where the first term is simply the sum of the charges (q_i) of the ionic defects multiplied by their concentration (c_i) and the second and third terms correspond to the electron and hole concentrations respectively. N_c and N_v are the effective conduction band and valence band density of states and E_g is the bandgap, ε_F is the position of the Fermi level, k_B is Boltzmann's constant and T is the temperature. Within a simple point defect model, the concentration of a defect i is related to the formation energy of the defect, that is:

$$c_i \propto m_i \exp\left(\frac{-\Delta G_f^i}{k_BT}\right) \tag{4}$$

where, m_i is the multiplicity of equivalent sites. At the temperatures relevant to solids, the difference in vibrational contributions to the free energy between perfect and defect simulation supercells are expected to be relatively small. Consequently, ΔG_f^i can be approximated with ΔE_f^i, which is calculated from the differences in total energies between perfect and defective simulation supercells according to the formalism of Zhang and Northrup [14]. At higher temperatures vibrational contributions can become significant so the defect formation energies presented here should be considered a lower bound [15]. Following Zhang and Northrup, the defect formation energy can then given by:

$$\Delta E_f^i = E^T_{\text{defect}} - E^T_{\text{perf}} + \sum_\alpha n_\alpha \mu_\alpha + q_i\mu_e + dE, \tag{5}$$

where, E^T_{defect} is the DFT energy of the defect containing supercell, E^T_{perf} is the energy of the perfect supercell, n_α is the number of atoms added or removed, μ_α is the chemical potential of the species α that is added/removed and $\mu_e = E_{\text{VBM}} + \varepsilon_F$ (with E_{VBM} given as the energy of the valence band maximum). The dE term in Eq. (5) is a correction applied to the final defect formation energies to correct for finite size effects arising due to the use of relatively small supercells and will be discussed in more detail in Section 3.3.

3.2. Chemical potentials

Under any given conditions, the sum of the chemical potentials per formula unit of the constituent species must equal the chemical potential of Li_2TiO_3, i.e.

$$\mu_{\text{TiO}_2}(p_{\text{O}_2},T) + \mu_{\text{Li}_2\text{O}}(p_{\text{O}_2},T) = \mu_{\text{Li}_2\text{TiO}_{3(s)}}, \tag{6}$$

where $\mu_{\text{TiO}_2}(p_{\text{O}_2},T)$ and $\mu_{\text{Li}_2\text{O}}(p_{\text{O}_2},T)$ are the chemical potentials of TiO_2 and Li_2O as a function of the oxygen partial pressure and temperature and $\mu_{\text{Li}_2\text{TiO}_{3(s)}}$ is the chemical potential of solid Li_2TiO_3. For a solid, $\mu(p^\circ_{\text{O}_2},T^\circ) \approx \mu(0,0)$, therefore the temperature and pressure dependencies have been dropped.

At equilibrium, the chemical potentials of the constituents in a crystal have an upper bound that is the chemical potential of the relevant constituent in its natural state; for example, the chemical potential of Li_2O in Li_2TiO_3 cannot exceed that of solid Li_2O, otherwise a Li_2O would form [14]. The chemical potentials can be used to represent different stoichiometric regimes: i.e. for growth conditions with excess Li_2O (referred to here as Li_2O-rich), $\mu_{\text{Li}_2\text{O}}\left(p_{\text{O}_2},T\right) = \mu_{\text{Li}_2\text{O}_{(s)}}$ and $\mu_{\text{TiO}_2}\left(p_{\text{O}_2},T\right) = \mu_{\text{Li}_2\text{TiO}_{3(s)}} - \mu_{\text{Li}_2\text{O}_{(s)}}$. Similarly, for growth conditions with excess TiO_2 (i.e. TiO_2-rich conditions), we have $\mu_{\text{TiO}_2}\left(p_{\text{O}_2},T\right) = \mu_{\text{TiO}_{2(s)}}$.

$\mu_{\text{Li}_2\text{O}_{(s)}}$ may be further decomposed as follows:

$$\mu_{\text{Li}_2\text{O}_{(s)}} = 2\mu_{\text{Li}}(p_{\text{O}_2},T) + \mu_{\frac{1}{2}\text{O}_{2(g)}}(p_{\text{O}_2},T) \tag{7}$$

where, $\mu_{\text{Li}}(p_{\text{O}_2},T)$ and $\mu_{\frac{1}{2}\text{O}_{2(g)}}(p_{\text{O}_2},T)$ are the respective chemical potentials of lithium and oxygen atoms in $\mu_{\text{Li}_2\text{O}_{(s)}}$ in equilibrium