Bi-Arrhenius diffusion and surface trapping of $^{8}\text{Li}^{+}$ in rutile TiO$_{2}$

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We report measurements of the diffusion rate of isolated ion-implanted $^{8}\text{Li}^{+}$ within ~120 nm of the surface of oriented single-crystal rutile TiO$_{2}$ using a radiotracer technique. The $\alpha$-particles from the $^{8}\text{Li}$ decay provide a sensitive monitor of the distance from the surface and how the depth profile of $^{8}\text{Li}$ evolves with time. The main findings are that the implanted Li$^{+}$ diffuses and traps at the (001) surface. The $T$-dependence of the diffusivity is described by a bi-Arrhenius expression with activation energies of 0.3341(21) eV above 200 K, whereas at lower temperatures it has a much smaller barrier of 0.0313(15) eV. We consider possible origins for the surface trapping, as well the nature of the low-$T$ barrier.

It is well known [1, 2] that Li$^{+}$ diffusion in rutile TiO$_{2}$ through the c-axis channels is extremely fast, greatly surpassing all other interstitial cations [3], with a room temperature diffusion coefficient exceeding many modern solid-state Li electrolytes [4]. A major limitation to its use as an electrode material in Li-ion batteries is its limited Li uptake at room temperature [5, 6]; however, the discovery that using nanosized material in Li-ion batteries is its limited Li uptake, as well as why reported Li diffusion rates differ by orders of magnitude, even under the same experimental conditions [1, 9–13]. Theoretical studies (see e.g., [14–20]) have been unable to reproduce the characteristics of Li$^{+}$ migration found in experiments [1, 11, 13]. A direct technique applicable to the nanoscale could help resolve these issues. To this end, we developed a variation to the classical radiotracer method, the $^{8}\text{Li}$ $\alpha$-radiotracer method, which uses the attenuation of the progeny $\alpha$-particles from the radioactive decay of $^{8}\text{Li}$, to study nanoscale Li diffusion. This method differs from conventional radiotracer diffusion experiments in several key aspects: (a) it is non-destructive (b) it is sensitive to motions on the nanometer scale [21] (c) it can be applied to thin films and heterostructures and (d) it is amenable for the use of short-lived isotopes ($\tau_{1/2} \sim 1$ s).

In this study, we employ the $\alpha$-radiotracer method to extract the diffusion coefficient and its activation energy for isolated Li in rutile TiO$_{2}$ and show that Li$^{+}$ traps at the (001) rutile surface. In addition, we report that the nanoscale Li diffusion exhibits bi-Arrhenius behavior. The high-$T$ (above ~200 K) activation energy and diffusion rate are in agreement with previous studies. The low-$T$ behavior is discussed in the context of the recently reported Li-Ti$^{3+}$ polaron complex [13]; here we suggest that part of that signal is also connected to Li hopping/diffusion. The experiment was performed using the ISAC facility at TRIUMF [22], in Vancouver, Canada. The samples were commercial chemo-mechanically polished (roughness $<0.5$ nm) single crystal rutile TiO$_{2}$ substrates (CRYSTAL GmbH) with typical dimensions of $7$ mm $\times$ $7$ mm $\times$ $0.5$ mm. The surfaces were free of macroscopic defects under 50x magnification.

In the experiment, a short beam pulse of low energy ($0.1 – 30$ keV) $^{8}\text{Li}$ ions is implanted close to the surface of the rutile targets (at an average depth of ~100 nm) housed in an ultra-high vacuum cold finger cryostat [22, 23]. The energy of the beam defines the initial Li$^{+}$ implantation profile. Upon arrival, the $^{8}\text{Li}$ starts to diffuse through the sample and undergoes $\beta$-decay to $^{8}\text{Be}$ which then decays (immediately) into two energetic $\alpha$-particles, each with a mean energy of 1.6 MeV. Due to their rapid attenuation inside the sample, the highest energy $\alpha$-particles escaping the sample originate from $^{8}\text{Li}^{+}$ that have diffused back closer to the surface.

To further amplify the sensitivity to $^{8}\text{Li}$ near the surface, the $\alpha$-detector is placed at a grazing angle, $\theta \leq 4.4^\circ$, relative to the surface, as shown in Fig. 1. The $\alpha$-detector in our setup is an Al ring, whose inside surface is cut at ~45$^\circ$ and coated with a thin layer of Ag-doped ZnS, a well known scintillator sensitive to $\alpha$-particles [24]. The light from the ZnS:Ag scintillator is collected in the forward direction using two 5 cm $\varnothing$ lenses which focus the light onto the photo-cathode of a fast photomultiplier (PMT). The second lens and the PMT are positioned outside the vacuum chamber, behind a transparent viewport. The PMT pulses have a large signal to noise ratio ($> 10$) and pass through a timing filter amplifier to be discriminated, so that only the top 1/3 of pulses above the noise level are counted.

The diffusion rate of Li inside the sample is directly related to the time it takes to reach the surface, which in turn relates to the $\alpha$-rate as a function of time. This method has intrinsic time- and length-scales of $\tau_{1/2} \sim 1$ s and $d \sim 100$ nm, respectively, which leads to a theoretical sensitivity to the diffusion rate...
$D$ from $10^{-12}$ to $10^{-8}$ cm$^2$/s$^{-1}$. This technique thus covers an optimal range of $D$ for battery materials. However, our effective sensitivity limit is closer to $10^{-11}$ cm$^2$/s$^{-1}$, determined by experimental factors such as the finite counting statistics and the existence of small distortions due to pileup in the detector response. In addition, the experimental sensitivity is somewhat higher for a lower implantation energy (see insert of Fig. 4).

In situations where Li$^+$ is immobile, the probability of detecting an $\alpha$ for any given decay event is time-independent and the measured $\alpha$-counts follow the decay rate of $^8$Li. This can be monitored conveniently using the high energy $\beta$-particles from the $^8$Li decay, which are weakly attenuated over these distances. Thus, the ratio of counts $Y_\alpha = N_\alpha / N_\beta$ is constant in time. On the other hand, when Li$^+$ is mobile, the ratio is time-dependent when the mean diffusion length in the $^8$Li lifetime is comparable to the mean depth of implantation, reflecting the fact that the $^8$Li$^+$ depth distribution is evolving in time. The information on Li diffusion comes from the time evolution of the $\alpha$-signal. The absolute $\alpha$-to-$\beta$ ratio, i.e., the baseline ratio of $Y_\alpha$, in the absence of diffusion, depends on experimental factors such as detector efficiencies, therefore in order to account for these systematics, each $\alpha$-spectrum is self-normalized to start from unity at time zero, i.e., $Y_\alpha^n(t) = Y_\alpha(t) / Y_\alpha(0)$ [26].

In order to extract the Li diffusion rate, the experimentally acquired normalized $Y_\alpha^n(t)$ was compared to a library of simulated $Y_\alpha^n(t)$ signals. To this end, we performed numerical solutions to Fick's laws in 1D to generate the time-evolved depth distribution of $^8$Li$^+$, accounting for the boundary conditions of the crystal surface and the initial $^8$Li$^+$ stopping profile as simulated by the SRIM Monte Carlo package [27]. $Y_\alpha^n(t; D)$ is then obtained by multiplying each bin of the depth profile of $^8$Li with the probability of detecting an $\alpha$ emitted at that depth. The $\alpha$-detection probability versus depth was extracted using the Geant4 [28] simulation package. The qualitative characteristics of $Y_\alpha^n(t; D)$ were found to depend heavily on whether the diffusing Li$^+$ ions accumulate or reflect upon reaching the sample surface (see Fig. 2), implying that one can unambiguously infer the $^8$Li$^+$ behavior at the surface, i.e., whether it is trapped or reflected. Furthermore, $Y_\alpha^n(t; D)$ deviates significantly from the simple exponential decay of $^8$Li ($\propto \exp[-t/\tau]$) with increasing diffusion rate.

With an accumulating boundary condition at the surface, faster diffusion results in a monotonically increasing $Y_\alpha^n(t; D)$, while a reflecting boundary condition leads to $Y_\alpha^n(t; D)$ that decreases with time, since the overall mean distance from the surface will then increase with time as the Li migrates away from the surface back to the bulk of the sample, towards the uniform depth distribution. Between these two ideal cases, there could be a non-zero trapping probability $P_{tr}$ at the sample's surface. For a fixed diffusivity $D$, $Y_\alpha^n(t; D, P_{tr})$ gradually evolves from looking reflective-like ($P_{tr} < 20\%$), towards resembling the
accumulating condition (for \( P_{tr} \geq 50\% \)). Note that after each reflection, the Li\(^{+}\) will continue their random walk, so for any non-zero value of \( P_{tr} \), most Li ions will eventually (after several reflections) get trapped at the surface if the diffusion is fast enough.

A technique similar to the one discussed here has been developed by Jeong et al. [29] for Li\(^{+}\) diffusion on micrometer and, recently, by Ishiyama et al. [21] on a nanometer length scales; however, the experiment reported here differs in a few key ways. In particular, the \( ^8\)Li implantation rates accessible at TRIUMF (typically \( 10^{-7} - 10^{-8} \) Li\(^{+}\)/s) are 1-2 orders of magnitude larger [21], which allows the \( \alpha \)-detector to be placed at a grazing angle \( \theta \) (\( \leq 4.4^\circ \) versus \( 10(1)^\circ \) [26]). This detector configuration significantly decreases the \( \alpha \)-counts, but greatly enhances the sensitivity to the near-surface region. In addition, the ZnS:Ag ring detector used in the present setup is much simpler and easier to install close to the sample in UHV compared to a Si detector [26], although it has less energy resolution.

Using this technique, we performed \( \alpha \)-radionuclide measurements on rutile TiO\(_2\) at various temperatures with two beam energies (10 and 25 keV) and two sample orientations. As Li\(^{+}\) is known to diffuse primarily along the \( c \)-axis of rutile, if the \( c \)-axis is oriented parallel to the surface (perpendicular to the beam), then the \( ^8\)Li\(^{+}\) motion should not change the initial implantation profile. Since the \( ab \)-plane diffusivity \( D_{ab} \ll 10^{-12} \) cm\(^2\) s\(^{-1}\), \( Y_n(\alpha)(t) \) is expected to be time-independent. On the other hand, if the \( c \)-axis is perpendicular to the surface, then the depth distribution of lithium should be evolving with time, since \( D_c \gg 10^{-12} \) cm\(^2\) s\(^{-1}\).

In Fig. 3 we compare the measured normalized \( \alpha \)-yield \( Y_n^\alpha(t; D, P_{tr}) \) for the (110)- and (001)-oriented rutile TiO\(_2\) and fits (orange lines) for a beam energy of 25 keV and a surface trapping probability \( P_{tr} = 1 \). The increasing signal with time in the (001) crystal is consistent with the anisotropy of the Li diffusion coefficient [1] and indicates that Li diffuses fast along the \( c \)-axis and gets trapped upon reaching the sample surface. For increasing temperature, \( Y_n^\alpha(t; D) \) saturates more rapidly, indicating that above room temperature, most of Li gets trapped at the (001)-surface during its lifetime. In contrast, the diffusion coefficient along the \( ab \)-plane is smaller than the theoretical detection limit of \( \sim 10^{-12} \) cm\(^2\) s\(^{-1}\), yielding \( Y_n^\alpha = 1 \) independent of time. Above room temperature, the \( c \)-axis normalized spectra \( Y_n^\alpha(t; T) \) get progressively suppressed, as the normalization factor \( Y_n(t = 0; T) \) increases substantially due to fast diffusion.

![Figure 3: Comparison of the measured normalized \( \alpha \)-yield \( Y_n^\alpha(t; D, P_{tr}) \) for the (110)- and (001)-oriented rutile TiO\(_2\) and fits (orange lines) for a beam energy of 25 keV and a surface trapping probability \( P_{tr} = 1 \). The increasing signal with time in the (001) crystal is consistent with the anisotropy of the Li diffusion coefficient [1] and indicates that Li diffuses fast along the \( c \)-axis and gets trapped upon reaching the sample surface. For increasing temperature, \( Y_n^\alpha(t; D) \) saturates more rapidly, indicating that above room temperature, most of Li gets trapped at the (001)-surface during its lifetime. In contrast, the diffusion coefficient along the \( ab \)-plane is smaller than the theoretical detection limit of \( \sim 10^{-12} \) cm\(^2\) s\(^{-1}\), yielding \( Y_n^\alpha = 1 \) independent of time. Above room temperature, the \( c \)-axis normalized spectra \( Y_n^\alpha(t; T) \) get progressively suppressed, as the normalization factor \( Y_n(t = 0; T) \) increases substantially due to fast diffusion.](https://example.com/figure3.png)

To fit the data, we used a custom C++ code applying the MINUIT [30] minimization functionalities of ROOT [31] to compare the \( Y_n^\alpha \) signals to the library of calculated spectra. The free parameters of the fit were \( D \) and \( P_{tr} \). All \( Y_n^\alpha(t; D, P_{tr}) \) spectra at both implantation energies (10 keV and 25 keV) were fitted simultaneously with a shared \( P_{tr} \) value. For the (001) orientation \( Y_n^\alpha \) increases rapidly with time, approaching saturation, indicating that lithium diffuses fast along the \( c \)-axis and gets trapped at (or within few nm of) the surface (see Fig. 2). For \( P_{tr} \geq 50\% \), the global \( \chi^2 \) value is completely insensitive to \( P_{tr} \), but for \( P_{tr} < 50\% \), the quality of the fits deteriorates rapidly. This is the first unambiguous evidence for Li trapping (with at least 50\% probability) at the (001) surface. There is no evidence of Li de-trapping up to 370 K, since at that temperature \( Y_n^\alpha(t; T) \) reaches saturation after \( \sim 2 \) s and any Li surface de-trapping would lead to an observable decrease of \( Y_n^\alpha(t; T) \) at later times. The non-zero trapping probability is most likely related to the reported difficulty of intercalating Li into rutile, as the Li ions would tend to stick at or near the surface rather than diffusing into the bulk.

It is not clear whether the Li\(^{+}\) surface trapping is caused by an electrostatic potential well (similar to H in Pd [32]), a partially reconstructed surface [33], or by a chemical sink either due to an adsorbate, or a solid state reaction at the surface (e.g., forming cubic LiTiO\(_2\)). Subsequent measurements of an adsorbate-free rutile sample, as well as samples capped with thin layers of materials capable of altering the surface chemistry are needed to resolve this question.

Turning to the values of \( D(T) \) extracted using the above analysis (see Fig. 4), they reveal a bi-Arrhenius relationship of the form:

\[
D(T) = D_H \exp[-E_H/(k_B T)] + D_L \exp[-E_L/(k_B T)],
\]

where \( E_i \) is the activation energy and \( D_i \) is the prefactor of each component. These were found to be \( E_H = 0.3341(21) \) eV and \( D_H = 2.31(18) \times 10^{-4} \) cm\(^2\) s\(^{-1}\) for the high-\( T \) component and \( E_L = 0.0313(15) \) eV and \( D_L = 7.7(7) \times 10^{-10} \) cm\(^2\) s\(^{-1}\) for the low-\( T \) component, respectively. This extracted \( E_H \) is in excellent agreement with values deduced by other techniques [1, 11, 13] and the diffusion rates at high temperatures are very...
Arrhenius components can’t be the same as above. While we would become irrelevant at fast diffusivities, explaining the \( \beta \)-NMR measurements really shows that there is some long range diffusion of \(^8\text{Li}^+\) at low-\( T \), with a barrier significantly different than high-\( T \). While our \( E_f \) is of a similar magnitude to that found with \( \beta \)-NMR, it is also compatible with the diffusion barrier predicted from theory for isolated \( \text{Li}^+ \) in rutile \([14–20,38]\). The \( \alpha \)-radiotracer cannot distinguish whether \( \text{Li}^+ \) moves either as a simple interstitial, or as part of a \( \text{Li}_2 \)-polaron complex, it would only identify their weighted average contribution to the motion of \(^8\text{Li}^+\). The similarity of the observed activation energy at low temperatures to the theoretical value suggests that a small fraction of the \( \text{Li}^+ \) interstitials does not combine with a polaron, but rather diffuses as a simple ion. If this fraction is small, that would explain why the low-\( T \) prefactor is so much smaller than the high-\( T \).

It seems possible that the larger activation energy observed above 200 K may involve diffusion of a more complex object, possibly a \( \text{Li}_2 \)-polaron complex, or it could be related to a dissociation energy of \( \text{Li}^+ \) with the polarons, which are known to form Coulomb bond defect complexes. Indeed, theory predicts a diffusion barrier of 0.29 eV for the \( \text{Li}_2 \)-polaron complex and a dissociation energy of 0.45 eV \([36]\), both comparable to the high-\( T \) barrier found here. The \( \text{Li}_2 \)-polaron complex is overall electrically neutral, so its movement should contribute to the diffusivity of \( \text{Li}^+ \) but not to the ionic conductivity in terms of charge transport. An electric field would not cause it to move - unless it was strong enough to destabilize the complex (strong potential gradient). Thus, if it is a neutral \( \text{Li}_2 \)-polaron complex moving at high-\( T \), one would expect the impedance measurement to yield a very different Arrhenius slope.

The much larger prefactor above 200 K, compared to low-\( T \), is also quite intriguing and is further evidence that these are two very different mechanisms for diffusion of \( \text{Li}^+ \) in rutile. Indeed, \( D_H \) when written in terms of frequency, yields \( \tau_H^{-1} \sim 2 \times 10^{12} \text{ s}^{-1} \), which is in the \( 10^{12} - 10^{13} \text{ s}^{-1} \) range one would normally expect from phonons driving a thermally activated motion. Note that this frequency is \(~5000\) times smaller than what was found with \( \beta \)-NMR \([13]\), as well as with optical absorption \([1]\), which infer \( D \) indirectly, whereas this is a direct measurement.

In summary, we used the radioactive \( \alpha \)-decay of \(^8\text{Li} \) to study \( \text{Li}^+ \) diffusion in a single crystal rutile \( \text{TiO}_2 \) in the range of 60 K to 370 K. The nanoscale \( \text{Li}^+ \) diffusion rate was found to exhibit bi-Arrhenius behavior. We report a high-\( T \) activation energy of \( E_H = 0.334(21) \text{ eV} \), in agreement with measurements carried out with different techniques \([1,11,13]\). At low temperatures, a second Arrhenius component was revealed, with an activation energy of \( E_L = 0.0313(15) \text{ eV} \). We suggest that this might be related to a small fraction of the \( \text{Li}^+ \) that does not bind to a
Li-polaron complex but rather hops as a simple interstitial with an activation energy near theoretical calculations. In addition, we found evidence that Li traps at the (001) surface, which could contribute to the reduced Li uptake at room temperature. We believe that this technique can shed new light on the Li motion in Li-ion battery materials and across their interfaces.

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