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Temperature- and concentration-dependent hydrogen diffusivity in palladium from statistically-averaged molecular dynamics simulations



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ABSTRACT

Solid-state hydrogen storage materials undergo complex phase transformations in which kinetics are often limited by hydrogen diffusion that significantly changes during hydrogen uptake and release. Here we perform robust statistically-averaged molecular dynamics simulations to obtain a well-converged analytical expression for hydrogen diffusivity in bulk palladium that is valid throughout all stages of the reaction. Our studies confirm the experimentally observed dependence of the diffusivity on concentration and temperature and elucidate the underlying physics. Whereas at low hydrogen concentrations, a single dilute hopping barrier dominates, at high hydrogen concentrations, diffusion exhibits multiple hopping barriers corresponding to hydrogen-rich and hydrogen-poor local environments.

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Solid-state hydrogen storage materials have the potential to replace current high-pressure storage solutions and accelerate the transition away from fossil fuels [1]. However, this technology transition has been slow to occur, in part because properties of existing hydrogen storage materials do not meet the necessary commercial targets. Improvement of the materials requires a better understanding of the kinetics of hydrogen uptake and release. Such kinetics are often limited by hydrogen diffusion. Unfortunately, hydrogen diffusivity changes continuously with concentration [2–7], and as a result remains poorly understood despite extensive past experimental studies.

Palladium hydride (PdH_x) is ideal for developing a fundamental understanding of hydrogen diffusion because PdH_x exhibits a diffusional phase transformation on a fixed face-centered-cubic (fcc) crystal lattice, and features hydrogen diffusion across varying concentration. Practically, PdH_x also has many hydrogen-related applications [8,9], including hydrogen or hydrogen isotope storage, separation membranes, chemical sensing, and hydrogen-based catalytic reactions. Interestingly, many groups [2–7] have discovered that the hydrogen diffusion energy barrier in palladium is constant at low hydrogen concentration but becomes concentration and temperature dependent when hydrogen concentration is high. Nevertheless, these experiments exhibit no clear consensus, and are unable to isolate the specific mechanisms accounting for the observations. As a result, experimental data of hydrogen diffusivity in palladium continues to be controversial, particularly as a function of temperature and concentration. An analytical expression

for these dependencies would be extraordinarily valuable for understanding PdH_x hydrogen uptake and release in the entire processes.

Molecular dynamics (MD) methods provide a powerful and fundamental approach to study diffusive phenomena, accounting for both concentration and thermal effects that may directly influence diffusion kinetics. Here we use PdH_x as a prototypical metal hydride material to achieve three major objectives: (i) develop robust molecular dynamics methods capable of predicting diffusivity at any concentration and temperature; (ii) apply these methods to construct an analytical expression for hydrogen diffusivity as a function of both concentration and temperature; and (iii) obtain mechanistic insights that can help clarify the existing experimental data on diffusivity.

Diffusion energy barriers are frequently calculated at 0 K for distinct atomic jumps using a nudged elastic band method [10–12] based on molecular statics (MS) simulations. However, for PdH_x alloys the number of possible atomic jumps with respect to local composition and atomic configuration is exceedingly high. Even if these jumps could be exhaustively studied, it is still unclear how they could be combined to represent the overall diffusion behavior seen in experiments. To overcome this problem, we performed MD simulations to calculate statistically-averaged diffusivities from the mean-square displacement of hydrogen atoms [13], and then fit these diffusivities obtained at different temperatures to the Arrhenius equation to obtain effective diffusion energy barrier and pre-exponential factor. This approach has not been widely used in the past because it is associated with significant statistical errors from either the diffusivity or the Arrhenius fits [13]. We perform extremely long simulations at multiple temperatures to minimize such errors.

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Our computational cells contained $8 \times 8 \times 8$ unit cells of an fcc palladium lattice aligned in the three $\langle 100 \rangle$ coordinate directions. The relatively small systems (2048 Pd atoms) helped to minimize phase separation, which is important as the objective is to study diffusion over the entire concentration range, including those that cannot be accessed when phase separation occurs. Using a previously reported Pd-H embedded-atom method (EAM) potential [14], a total of 130 MD simulations with a zero-pressure NPT ensemble (i.e., constant number of atoms, pressure, and temperature) were performed for a matrix of 10 PdH_x concentrations ($x = 0.1, 0.2, \dots, 1.0$) at 13 temperatures ($T = 300.0, 325.0, 350.0, \dots, 600.0$ K), for a total period of 2.3 ns using a time step size of $dt = 0.5$ fs. After the first 0.1 ns was discarded for equilibrating the velocity distribution, the hydrogen positions were recorded at every $\Delta t = 2.2$ ps for the remaining $t_{MD} = 2.2$ ns of simulation time. The resulting hydrogen positions were used to calculate the mean-square displacements as a function of time t . The time derivative of the mean-square displacements, δ , averaged over a short period $t \leq 0.0132$ ns, was used to calculate diffusivities, D , according to $D = \delta / 6$. This translates to $t_{MD} / t \sim 166$ sampling data points for the calculation of each value of D , which minimizes the associated statistical errors [13].

Typical Arrhenius plots constructed from the MD data shown in Fig. 1(a)–(d) for four representative concentrations: $x = 0.4, 0.7, 0.8$, and 0.9 demonstrate that all MD data points fall on smooth trend lines, confirming that statistical errors are indeed negligible. We note that the deviation of data points from the trend lines in Fig. 1 is even smaller than that achieved previously [13] despite our shorter simulation time (2.2 ns vs. 13.2 ns). This is because the previous work modeled the diffusion of a single hydrogen atom in Al [13], whereas in Fig. 1, the system contains many hydrogen atoms ($x = 0.4$ or above) that reduce the statistical error. In addition, diffusion of hydrogen in Pd is significantly faster than in Al, which accelerates statistical convergence.

Fig. 1(a) and (b) shows that below $x = 0.8$, the plots are highly linear, indicating that at dilute hydrogen concentrations, a single diffusion energy barrier is operative. However, the plots become non-linear at concentrations $x = 0.8$ or $x = 0.9$ in Fig. 1(c) and (d). Thus, the effective

energy barrier becomes a continuous function of temperature, preventing a single energy barrier from being determined for higher hydrogen content.

Experimental activation energies and pre-exponential factors of hydrogen diffusion in α ($x \sim 0.2$) and β ($x \sim 0.65$) phases of PdH_x have been reported in prior studies [2–7]. For convenience, we summarize these experimental values in Table 1, along with the corresponding results from MD simulations. As shown in the table, our predicted activation energies and pre-exponential factors are comparable to the experimental measurements. Interestingly, for the α (low-concentration) phase, each group reported only a single experimental diffusion energy barrier (and pre-exponential factor) over a wide range of temperatures. This implies that Arrhenius plots should be ideally linear, in good agreement with the simulation results shown in Fig. 1(a) and (b). On the other hand, for the β (high-concentration) phase, Arons et al. [2,3], Cornell and Seymour [4], Mazzolai and Zuchner [5], Burger et al. [6], and Torrey [7] independently reported two experimental diffusion energy barriers in two different temperature ranges. Specifically, the higher barrier occurred at high temperatures and the lower barrier occurred at low temperatures, in agreement with Fig. 1(c) and (d).

The nonlinear behavior at higher concentrations in Fig. 1(c) and (d) can be understood. First, consider that hydrogen atoms typically diffuse through palladium via alternating octahedral \rightarrow tetrahedral \rightarrow octahedral hops. In the limit of dilute solution, this should consistently give the same overall energy barrier, since there are always available jumping pathways that are unperturbed by any additional local background hydrogen content. On the other hand, at higher hydrogen concentrations, the system exhibits a distribution of local hydrogen compositions that impact site energies in different ways. This results in a multiplicity of different local energy barriers. According to our results, the transition between the single-barrier and multi-barrier regimes occurs beyond $x = 0.7$. Nonetheless, for a given concentration in the high concentration region, the multiple barriers can be effectively replaced by two barriers, one that becomes increasingly dominant at high temperatures and another at low temperatures. A continuous

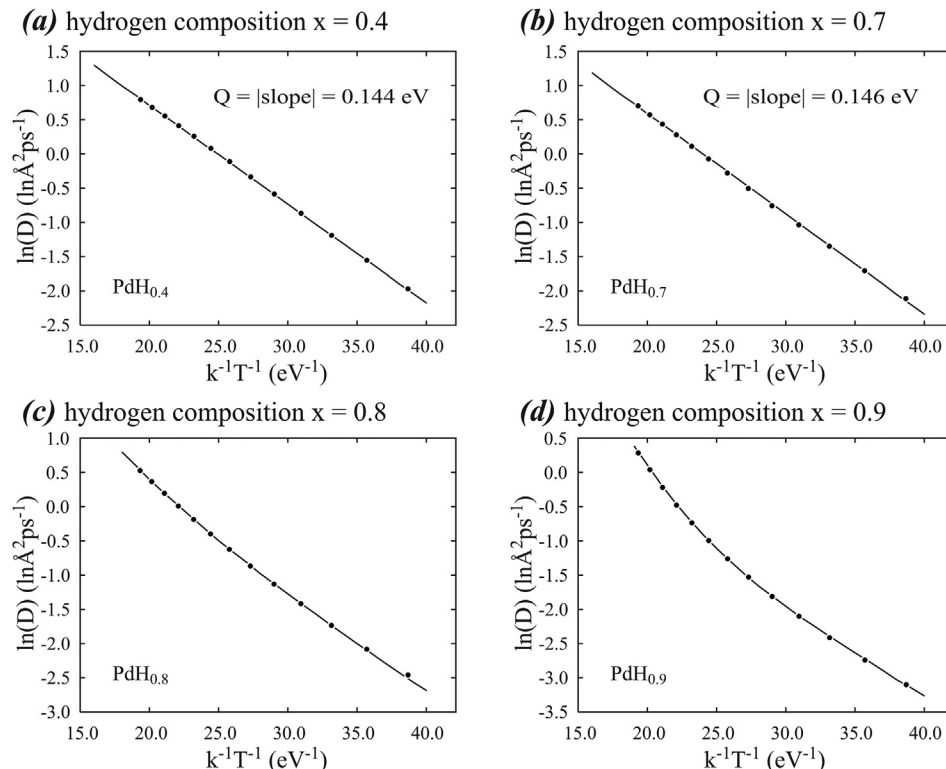


Fig. 1. Arrhenius plots at different hydrogen concentrations of (a) $x = 0.4$; (b) $x = 0.7$; (c) $x = 0.8$; and (d) $x = 0.9$. Lines are fitted to Eqs. (1)–(5).

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