

Powered by DFT: Screening Methods That Accelerate Materials Development for Hydrogen in Metals Applications

Kelly M. Nicholson, Nita Chandrasekhar, and David S. Sholl*

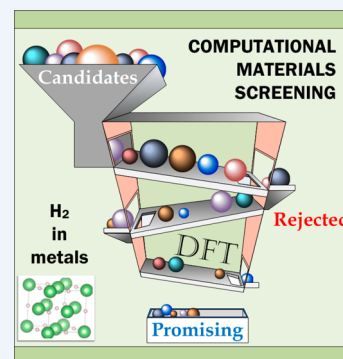
School of Chemical & Biomolecular Engineering Georgia Institute of Technology 311 Ferst Drive Atlanta, Georgia 30332-0100, United States

CONSPECTUS: Not only is hydrogen critical for current chemical and refining processes, it is also projected to be an important energy carrier for future green energy systems such as fuel cell vehicles. Scientists have examined light metal hydrides for this purpose, which need to have both good thermodynamic properties and fast charging/discharging kinetics. The properties of hydrogen in metals are also important in the development of membranes for hydrogen purification. In this Account, we highlight our recent work aimed at the large scale screening of metal-based systems with either favorable hydrogen capacities and thermodynamics for hydrogen storage in metal hydrides for use in onboard fuel cell vehicles or promising hydrogen permeabilities relative to pure Pd for hydrogen separation from high temperature mixed gas streams using dense metal membranes.

Previously, chemists have found that the metal hydrides need to hit a stability sweet spot: if the compound is too stable, it will not release enough hydrogen under low temperatures; if the compound is too unstable, the reaction may not be reversible under practical conditions.

Fortunately, we can use DFT-based methods to assess this stability via prediction of thermodynamic properties, equilibrium reaction pathways, and phase diagrams for candidate metal hydride systems with reasonable accuracy using only proposed crystal structures and compositions as inputs. We have efficiently screened millions of mixtures of pure metals, metal hydrides, and alloys to identify promising reaction schemes via the grand canonical linear programming method.

Pure Pd and Pd-based membranes have ideal hydrogen selectivities over other gases but suffer shortcomings such as sensitivity to sulfur poisoning and hydrogen embrittlement. Using a combination of detailed DFT, Monte Carlo techniques, and simplified models, we are able to accurately predict hydrogen permeabilities of metal membranes and screen large libraries of candidate alloys, selections of which are described in this Account. To further increase the number of membrane materials that can be studied with DFT, computational costs need to be reduced either through methods development to break bottlenecks in the performance prediction algorithm, particularly related to transition state identification, or through screening techniques that take advantage of correlations to bypass constraints.



1. INTRODUCTION

Computational methods can be very useful in applied science problems, particularly when a substantial set of materials is to be evaluated for an application. Previously, Hao et al. have argued that computational screening efforts should meet five target criteria in order to be useful.¹ Theoretical predictions should (1) characterize multiple materials faster than is possible experimentally, (2) require few inputs from experimental data, (3) predict quantities relevant to the final application rather than phenomena that are experimentally unobservable, (4) be quantitatively accurate enough to help identify promising materials or to eliminate poor performers, and (5) clearly state assumptions, caveats, and limitations so that users can judge how these factors will affect “real world” performance of the materials. In this Account we highlight selections of our recent efforts to screen materials for the storage (separation) of gaseous hydrogen using metal hydrides (dense metal membranes) where density functional theory (DFT) has been useful in driving materials development by identifying materials with promising properties or by helping to describe the characteristics of materials that should be targeted in future screenings.

Although the degree of computational effort strongly limits the system size that can be studied, DFT often provides sufficient quantitative accuracy to describe interesting metal–hydrogen properties of interest. For example, two properties that we care about that can be measured both theoretically and experimentally are the diffusivities of H in metal films and the heats of reaction for metal hydride systems. Fitting DFT-predicted diffusivities of H in pure Pd membrane films to an Arrhenius form $D = D_0 \exp(-E_d/(kT))$ between 400 and 700 K gives a diffusion coefficient of $D_0 = 3.1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and activation energy $E_d = 0.21 \text{ eV}$,² in excellent agreement with the experimental result $D_0 = 2.9 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and $E_d = 0.24 \text{ eV}$ from Volkl and Alefield for an assembly of low and moderate temperature data.³ Comparing a set of 21 metal hydride dehydrogenation reaction enthalpies compiled from plane wave GGA DFT calculations by Wolverton et al.⁴ and Alapati et al.⁵ gives average values of $\Delta H_{\text{DFT}} - \Delta H_{\text{expt}} = -6.3 \text{ kJ mol}^{-1} \text{ H}_2$

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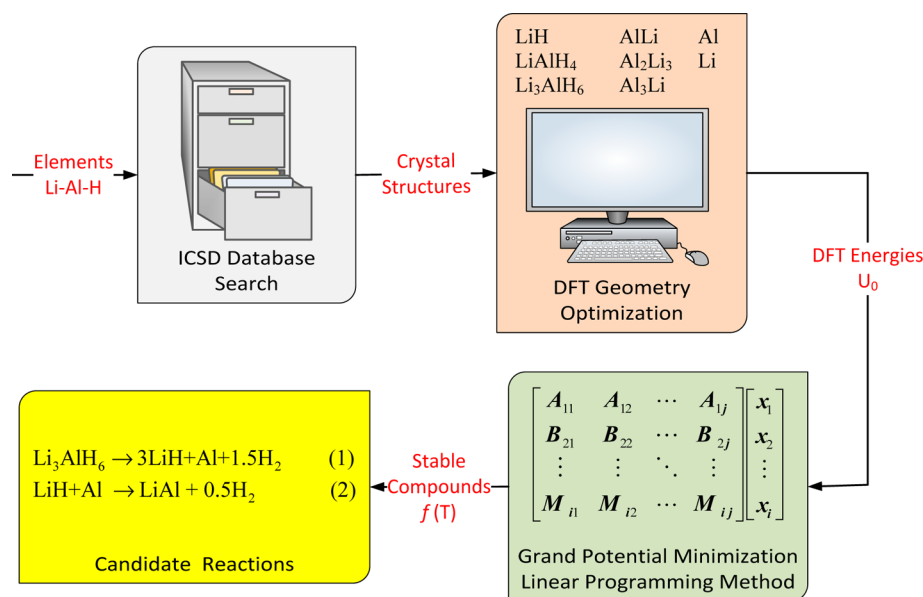


Figure 1. Illustration of computational methods to predict thermodynamically interesting metal hydride destabilization reactions for the Li–Al–H system for $P_{\text{H}_2} = 1$ bar of H_2 .

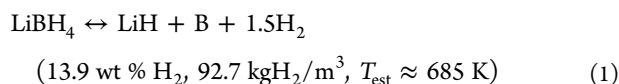
with a standard deviation of $14.9 \text{ kJ mol}^{-1} \text{ H}_2$. In general, reaction enthalpies can be reliably determined to an accuracy of $\sim 10 \text{ kJ mol}^{-1} \text{ H}_2$ using DFT energies. This provides sufficient accuracy for most screening applications since we are primarily interested in identifying real systems where $30 \leq \Delta H \leq 60 \text{ kJ mol}^{-1} \text{ H}_2$, and DFT uncertainties can be accounted for by relaxing these bounds slightly.

2. METAL HYDRIDES

2.1. Background

Currently, either high pressure or low temperature conditions are required to store and deliver hydrogen for onboard fuel cell vehicle applications. Reversible metal hydrides and in particular, complex light metal hydride systems have been extensively investigated as a materials-based alternative that offer potential improvements in safety, handling, and equipment costs.^{6,7} Desirable materials that meet U.S. DOE targets for the ultimate full-fleet automobile onboard hydrogen storage system will release more than 7.5 wt % H_2 and store $70 \text{ kg H}_2 \text{ m}^{-3}$ at ambient pressures relatively inexpensively.⁸ To be useful in this application, metal hydrides should have good thermodynamics and fast charging/discharging kinetics. While kinetics can be somewhat engineered through catalysis and particle size control,⁷ thermodynamics is the more critical constraint.⁹ If a metal hydride is too thermodynamically stable, it will not release appreciable hydrogen until heated to high temperature. Conversely, if not stable enough, the system may not be easily reversible.¹⁰ Thus, for 1 bar H_2 partial pressure, P_{H_2} , the hydrogen desorption temperature, T_{est} , should ideally fall between 273 and 373 K.

Hydrogen release from LiBH_4 offers a good example of a well-studied complex light metal hydride system:^{10,11}



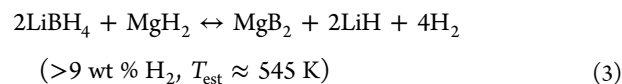
The van't Hoff relation can be used to compare predicted and experimental metal hydride performance

$$\frac{P_{\text{H}_2}}{1 \text{ bar}} = \exp\left(\frac{-\Delta G}{RT}\right) \quad (2)$$

where ΔG is the hydrogen release reaction free energy predicted using DFT and R is the universal gas constant.¹² Thus, DFT provides a useful method to assess the thermodynamics of proposed metal hydride systems prior to expensive experimental testing.

2.2. Large Scale Screening of Metal Hydrides

Many metal hydrides are too thermodynamically stable for onboard storage applications. For example, LiBH_4 does not release appreciable hydrogen until heated to $T_{\text{est}} \approx 685 \text{ K}$.^{10,11} A method to lower T_{est} is to find mixtures of materials that meet the DOE targets through destabilization reactions, for example,^{10,11}



This reaction stores $96 \text{ kg H}_2 \text{ m}^{-3}$ but suffers kinetic limitations.^{11,13} DFT has been used to systematically screen orders of magnitude more mixtures of metal hydrides and related compounds than possible experimentally.^{10,14} Alapati et al. first used a library of 212 materials composed of 13 elements and hydrogen to evaluate stable mixtures for 715 combinations of up to four elements and hydrogen and then to compute decomposition reactions using DFT. To complete each phase space, calculations were repeated at 0.02 mol fraction increments for non-H elements, resulting in several million distinct mixtures.¹⁰ Kim et al. later extended this database to 359 compounds and searched for both single-step and multistep reactions.¹⁴ Both studies identified promising destabilization reactions, but we will discuss only the more recent work by Kim et al.

Wolverton, Ozolins, and colleagues have made important contributions to the computational characterization of metal hydride systems. In particular, they developed a grand canonical linear programming (GCLP) methodology for predicting phase diagrams and multistep governing reactions at a fixed ratio of

non-hydrogen elements open to a hydrogen atmosphere.^{9,15} They used this approach to describe the thermodynamics of metal hydride mixtures in the Li–Mg–Ca–B–H, Li–B–N–H, Li–Mg–N–H, and Li–Mg–Al–H element systems.^{13,15,16,17} The GCLP method finds the combination of compounds that minimizes the hydrogen grand potential for a particular hydrogen chemical potential, μ_{H_2} (i.e., fixed T and P_{H_2}), given a library of free energies for compounds that can form in a targeted element space (e.g., Li, Mg, LiBH_4 , MgB_2 , LiH, MgH_2 , etc., for the Li–Mg–B–H space). Crystal structures for this library of compounds are pulled from a database such as the ICSD,¹⁸ published literature, or theoretical structures. If changes in the equilibrium mix are tracked as a function of temperature, both individual and overall reaction steps can be identified and enthalpies or heats of reaction at the given pressure computed from the stable compounds. This procedure can be repeated for different non-H elemental ratios to rigorously survey all possible mixtures and to search for reactions that meet the target T_{est} and capacity criteria. An important caveat with this method is that it cannot make predictions about compounds not present in the initial library. This might include compounds without solved crystal structures, amorphous or disordered solids, or structures too large to be studied readily with DFT.¹⁰ Typically, it is assumed that free energy differences due to vibrational contributions from all solids are approximately zero and that temperature effects are controlled through the μ_{H_2} for a given P_{H_2} . This allows the free energies of solid compounds to be determined through computationally accessible ground state DFT energies, U_0 . For additional precision, the vibrational density of states for each solid phase can be computed (within the harmonic approximation).¹⁶

The Kim et al.¹⁴ and Alapati et al.¹⁰ DFT studies relaxed geometries and computed energies for 359 crystalline compounds containing $X = \text{Al, B, C, Ca, K, Li, Mg, N, Na, Sc, Si, Ti, V, and H}$. The GCLP method was used to analyze element spaces with up to four non-H elements open to a hydrogen atmosphere at $P_{\text{H}_2} = 1$ bar between $0 \leq T \leq 1000$ K, identifying interesting metal hydride decomposition reactions that met their initial screening criteria. Figure 1 shows this process schematically. In the Li–Al–H system, a library of known compounds is generated that can form from the elements, and crystal structures are relaxed using DFT to obtain U_0 . The U_0 library is fed to the GCLP algorithm, which loops over the desired μ_{H_2} range and elemental ratios in small incremental steps to predict stable states. If changes to this stable mixture are tracked with temperature, equilibrium reactions can be written as shown for Li_3AlH_6 .

Figure 2 describes a key result from the large scale computational screening by Kim et al. that identified 74 promising single-step reactions that met initial gravimetric (>6 wt % H_2) and enthalpic targets ($15 \leq \Delta H \leq 75$ kJ mol⁻¹ H_2).¹⁴ Crucially, 57 of the reactions were not previously predicted in the earlier work by Alapati et al.¹⁰ because they involved intermediates such as $\text{B}_{12}\text{H}_{12}$ species not then known to exist. The accuracy of these predictions depends heavily on the completeness of available materials databases with solved crystal structures. Noted in Figure 2 are reactions that proceed via a $\text{B}_{12}\text{H}_{12}$ intermediate, involve refractory materials, or contain carbon, which may have kinetic limitations or form CH_4 at low temperatures. Three interesting single-step reactions are highlighted including a previously analyzed 2:1

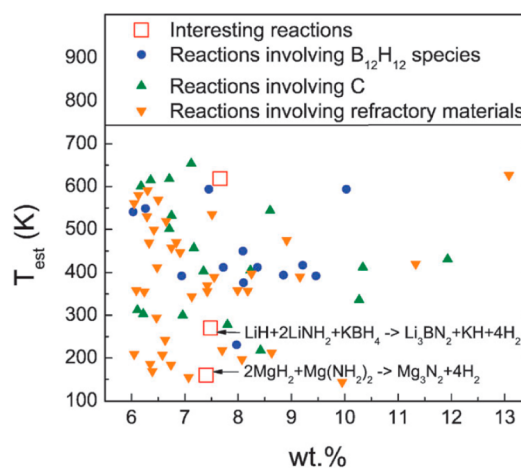


Figure 2. Temperature to release 1 bar of H_2 as a function of H_2 capacity (wt %) for 74 promising single step reactions identified in large scale first-principles screening calculation. Adapted from ref 14. Reproduced by permission of the PCCP Owner Societies.

mixture of $\text{MgH}_2/\text{Mg}(\text{NH}_2)$ with ~ 7.4 wt % H_2 and $T_{\text{est}} = 160$ K and an unexplored 2:1:1 mixture of $\text{LiNH}_2/\text{LiH}/\text{KBH}_4$ with ~ 7.4 wt % H_2 and $T_{\text{est}} = 300$ K. The direct decomposition reaction of MgH_2 is also identified, but it is known that this material has slow kinetics and high T_{est} . Further filtering and tightening of constraints to parse the large number of possible reactions enabled Kim et al. to additionally identify 23 promising multistep reactions.¹⁴

2.3. Limitations of the GCLP Method and DFT for Predicting Useful Metal Hydride Systems

There are several caveats and limitations associated with the grand potential approach to screening for interesting metal hydride reactions in addition to those usually mentioned in conjunction with DFT or numerical calculations (i.e., the exchange–correlation functional, convergence, etc.). A key limitation highlighted earlier is that the methods cannot make predictions about reactions that include compounds missing from the materials library. As new compounds are identified, the calculations will need to be updated, but this should be straightforward because the algorithms for doing so are well-developed. Additionally, we are typically limited to studying compounds with complete crystal structures and atomic positions resolved, no partial site occupancies, and unit cells less than about 400 atoms. Current DFT methods that examine these excluded materials individually or that predict new materials are, at present, too costly for rapid screening applications.^{14,19}

A key assumption of the GCLP method is that it finds mixtures of compounds that minimize the overall system free energy, that is, the compounds that lie on a so-called convex hull. Interesting element systems can be studied at higher levels of theory,²⁰ but the errors for low to moderate temperature systems are still about ± 10 kJ mol⁻¹ H_2 compared with experiments. Uncertainty in the calculations arises primarily from the inexactness of the exchange–correlation functional and is unavoidable with DFT-based methods.¹²

The GCLP method as originally developed cannot detect metastable reaction paths that have free energies similar to those of the ground state system. Kim et al. developed a method for incorporating uncertainties inherent in DFT data to identify thermodynamically plausible alternate reaction path-

ways.¹² To give one example, the 2:1:1 mixture of LiNH₂/LiH/KBH₄ identified in Figure 2 has a GCLP-predicted reaction path¹⁴

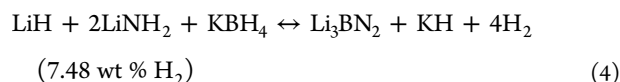


Figure 3 shows van't Hoff plots and reaction free energies relative to the lowest energy path, $\Delta\Delta G$, for eight possible

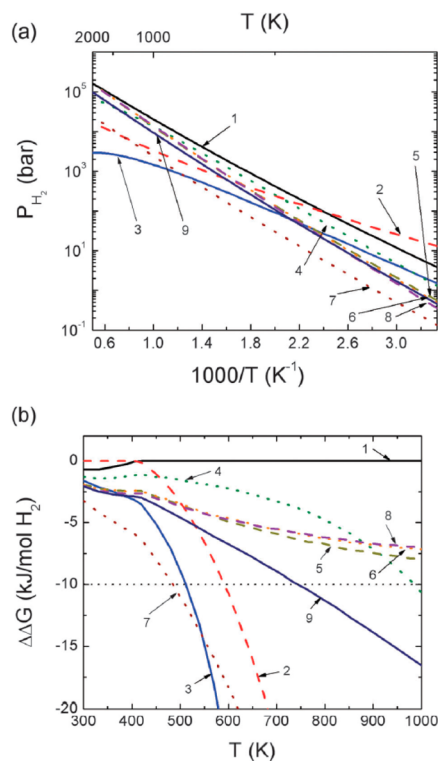
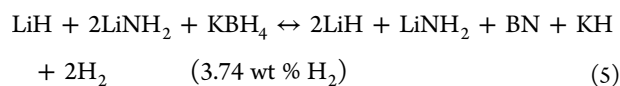


Figure 3. (a) van't Hoff plots for the eight (labeled) possible decomposition reactions predicted using metastability analysis in 2:1:1 LiNH₂/LiH/KBH₄ mixture. (b) Reaction free energies relative to low energy path. Adapted from ref 12. Reproduced by permission of the PCCP Owner Societies.

metastable reaction paths (labeled 1–8) for these reactants. An analysis that accounted for zero point and vibrational free energy corrections to the DFT ground state energies indicated that for high temperatures or pressures, the reactants decompose via eq 4 (labeled as 1 in Figure 3b), but for low temperatures or pressures, the predicted reaction pathway is



(labeled as 2 in Figure 3b), which has a much lower hydrogen capacity. For these two reactions, $\Delta\Delta G \leq \pm 10$ kJ mol⁻¹ H₂, across the T, P spectrum. Kim et al. concluded that DFT does not give absolute predictions of thermodynamically preferred decomposition reactions for this system since the competing paths are too close in energy. Including this kind of assessment of uncertainty in DFT-based predictions is valuable, especially in systems like metal hydrides where kinetic limitations may influence experimental observations.

2.4. Additional Considerations

We have described a few examples of our large scale screening computational studies to identify promising metal hydride systems based on thermodynamic principles of pure compounds. Additional DFT work has been done to tune thermodynamic properties using dopants.^{21–23} While thermodynamic considerations are critical, they are not sufficient to ensure that reversible metal hydride systems perform adequately in real systems. For example, almost all metal hydride systems release H₂ more slowly than desired for onboard vehicle applications,²⁴ but there are methods to improve kinetics such as reducing particle size,²⁵ incorporating metal hydride additives into nanocomposites,^{26,27} or using catalysts.²⁸ We have previously employed DFT-based methods to screen dopants for use in MgH₂ and NaMgH₃ and identified several elements that may contribute to enhanced hydrogen diffusion in the materials.^{24,29,30} DFT-based thermodynamics can also be used to assess the evolution of impurity gases from metal hydrides.³¹ Interested readers are referred to these references for further information on kinetic or diffusion-based DFT studies for metal hydride systems.

3. DENSE METAL MEMBRANES

3.1. Background

Hydrogen is critical for current refining and chemical processes and is expected to play a significant role as an energy carrier in clean energy applications. Typical industrial hydrogen production proceeds via the high temperature gasification of hydrocarbons and requires cost-competitive purification schemes to separate H₂ from syngas components such as CO, CO₂, CH₄, and H₂S.^{1,32} Dense metal membranes are being investigated for this application due to the stability of many metals at high temperatures and the potential for perfect H₂ selectivity over the other syngas species.³³ Candidate metal membranes must have good stability at high temperatures and pressures, high H₂ flux, strong resistance to poisoning, and long operational life times to be cost-effective.^{32,33}

Pd membranes are the current standard metal membrane, with permeability $k \approx 10^{-8}$ mol·m⁻¹·s⁻¹·Pa^{-0.5} at 600 K for pure Pd with a pure H₂ feed.³² Pd-based membrane systems are expensive and highly sensitive to poisoning by sulfur species. Thus, there are incentives to identify alternate materials with similar or better H₂ permeabilities with greater resistance to surface contamination.^{32,33} Detailed DFT-based methods have been developed to compute permeabilities of both crystalline^{34–39} and amorphous metal membranes^{1,32,40} to screen materials for the H₂ separation application and to provide mechanistic insights that guide the rational selection of alloying elements and compositions that further improve membrane H₂ flux and robustness.

A complete description of membrane transport would include the dissociation of molecular H₂ into atomic H at the feed-side membrane surface, uptake of H into the bulk, diffusion through the membrane via bulk interstitial sites, recombination of atomic H into molecular H₂ at the permeate side, and subsequent desorption of H₂. However, for dense metal membranes, it is often a good approximation to ignore surface effects and consider net transport of hydrogen through the membrane to be limited by bulk diffusion via interstitial site hopping.³⁸

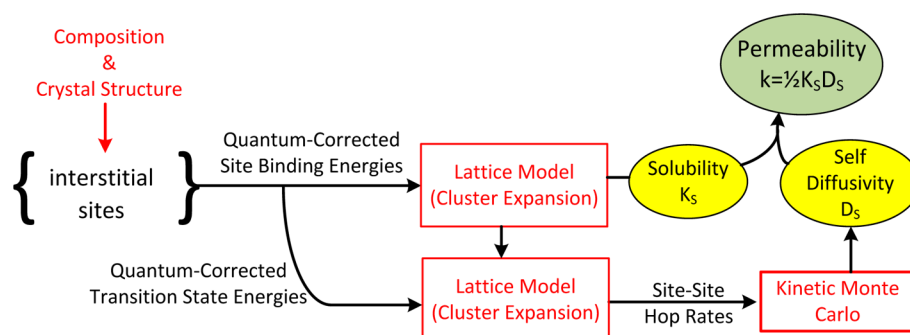


Figure 4. Illustration of detailed first-principles model to compute hydrogen permeability through crystalline metal membranes.

3.2. Crystalline Alloys

Figure 4 illustrates key steps for computing the permeability of hydrogen through a candidate dense metal membrane using DFT calculations.^{36,39,41,42} DFT calculations typically recover qualitative permeability trends with respect to composition and temperature and can be expected to perform well for screening purposes when membrane transport resistances are dominated by bulk properties. The primary challenge for describing hydrogen solubilities and diffusivities in crystalline alloys is the frequent substitutional disorder of the metal atoms. This leads to a large library of local interstitial environments that H can encounter for which binding energies must be computed. Cluster expansion (CE) methods have been developed to help resolve this.³⁹ Providing reasonable quantitative accuracy, these methods use large libraries of interstitial site binding and transition-state energies to develop a lattice model. Once the lattice model is determined, hydrogen solubility and site hop rates are computed. These rates are then fed to a kinetic Monte Carlo calculation to predict the self-diffusivity of hydrogen through the metal lattice. The identification of transition states is the most computationally intensive bottleneck in Figure 4 when computed using methods such as the nudged elastic band approach. However, the computational cost can be greatly reduced if transition states can be located based on geometric or symmetry considerations.⁴¹ Only an initial alloy crystal structure is required to predict the permeability of hydrogen in metal alloys with these methods.

CE methods have been applied to predict pure hydrogen permeabilities in Pd_{96}M_4 alloys ($M = \text{Ag}, \text{Cu}, \text{and Rh}$) relative to that of pure Pd.³⁹ Experimental evidence indicates k/k_{Pd} is reduced in Pd–Cu membranes and increased in Pd–Ag alloys, and the DFT method recovers these trends although quantitative comparisons of predicted, and experimental k indicate only reasonable agreement. For pure Pd, the computational method predicts $k = 3.25 \times 10^{-8} \text{ mol}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$ at 623 K compared with an experimental value by McKinley of $1.24 \times 10^{-8} \text{ mol}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$ at 623 K.⁴³ For $\text{Pd}_{96}\text{Cu}_4$ at 623 K, the computational method predicts $k = 2.47 \times 10^{-8} \text{ mol}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$ compared with available experimental data for $\text{Pd}_{84}\text{Cu}_{16}$ at the same temperature of $6.78 \times 10^{-8} \text{ mol}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$. For a $\text{Pd}_{90}\text{Ag}_{10}$ membrane at 773 K, Gryaznov gives an experimental $k/k_{\text{Pd}} \approx 1.5$, while a detailed CE model reports $k/k_{\text{Pd}} \approx 1.5$ for $\text{Pd}_{96}\text{Ag}_4$ at 773 K.⁴⁴

Predictions of permeability via the approach shown in Figure 4 are computationally intensive in terms of the number of alloys that can be characterized quickly. In order to study a large number of materials, Kang et al. used lessons learned from previous binary Pd-alloy calculations to derive simplified lattice models with binding and transition state energies parametrized

from a limited number of DFT calculations.⁴⁵ Figure 5 displays the predicted hydrogen permeabilities using this simplified approach for all Pd-rich face-centered cubic binary alloys with atomic composition Pd_{96}M_4 at $T = 600 \text{ K}$ where M is the set of 50 elements that form solid solutions with Pd at that temperature.⁴⁵ Typical rigorous calculations based on the CE approach required ~ 600 DFT calculations per material, but the simplified model reduced this to 12 geometry optimizations on a 27-atom supercell. A comparison of performance results from

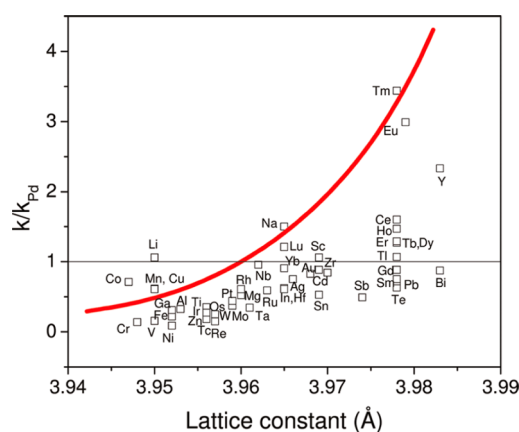


Figure 5. DFT-predicted permeability of Pd_{96}M_4 fcc alloys at 600 K normalized by the permeability of pure Pd as a function of simulated lattice constant. The solid black line indicates the permeability of pure Pd. Reprinted with permission from ref 45. Copyright 2011 American Chemical Society.

12 diversified alloys computed using both the rigorous and simplified approach shows good general agreement and highlights the utility of simplified models that balance computational expense with quantitative accuracy.

Figure 5 shows several alloys that are predicted to have normalized permeabilities greater than one, i.e., larger than that of pure Pd at 600 K. For example, DFT predicts that Pd_{96}Y_4 films have permeabilities for hydrogen ~ 2.3 times larger than pure Pd at 600 K. Experimentally, similar compositions have produced films with ~ 4.5 times enhanced performance for 573–623 K.⁴⁵ Interestingly, the screening calculations identify $\text{Pd}_{96}\text{Tm}_4$ (a previously untested material) as a significant improvement over pure Pd for hydrogen permeance. Fabrication and testing of a $\text{Pd}_{95.5}\text{Tm}_{4.5}$ film between 673 and 773 K showed that the Pd–Tm film had higher permeability than either pure Pd or the industry standard $\text{Pd}_{80}\text{Ag}_{20}$.⁴⁵ Though absolute agreement with experimental permeabilities is not guaranteed, this work illustrates that DFT-based character-

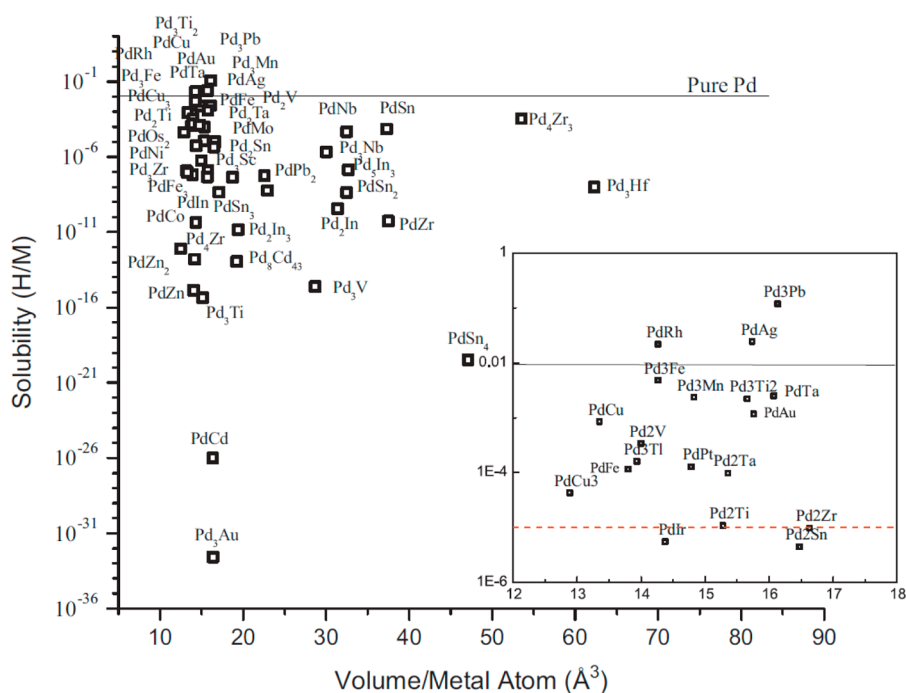


Figure 6. DFT-predicted solubilities (H/M hydrogen/metal atom) at 600 K for 57 intermetallics. The volume per metal atom for pure Pd is 15.9 \AA^3 . The inset shows an expanded view of the solubility for volumes between 12 and 18 \AA^3 . The black solid line and the red dashed line in the inset show the favorable solubility range used to screen candidates (10^{-1} – 10^{-5} H/M). Adapted from ref 46. Reprinted with permission of Elsevier.

ization of dense metal membrane hydrogen transport can be accessible from a computational intensity perspective and, critically, can identify new materials with enhanced properties.

DFT-based methodologies have also been used to screen Pd-based intermetallics with discrete, ordered compositions. Intermetallics have potential to exhibit improved resistance to contaminants due to the enhanced thermodynamic stabilities of these materials relative to the disordered solid solutions discussed previously. Chandrasekhar et al. predicted hydrogen permeabilities for 78 binary Pd-based intermetallics and also identified those intermetallics with the tendency to form hydrides with implications for hydrogen embrittlement.⁴⁶ Figure 6 displays the computed solubilities for 57 intermetallics. Solubility was used as a first screening parameter to identify interesting materials at the target temperature. The solubility of pure Pd is shown as a reference.

The models developed to predict H permeabilities through these intermetallics are similar to those used for pure Pd, for which the predictions are in reasonable quantitative agreement with experiments.³⁶ Based on this, Chandrasekhar et al. conclude that the predictions made for the intermetallics are sufficiently accurate to eliminate unfavorable materials, despite lack of experimental corroboration. The screening criteria account for DFT-induced uncertainties in calculated values, making the predictions useful for identification of materials with enhanced H permeabilities.

3.3. Amorphous Alloys

Recent efforts have extended the computational methods for crystalline metal membranes to amorphous materials.^{1,32,40} Amorphous membranes lack the long-range ordering of crystalline materials and have several advantages such as increased resistance to hydrogen embrittlement or sintering and potential lower costs relative to Pd-based materials. Several systems have demonstrated H_2 permeabilities on par with pure Pd.³²

Transport of H through amorphous materials is challenging to model because the identification of interstitial sites and transition states is no longer straightforward. A crucial deviation from crystalline behavior is that the solubility of hydrogen in amorphous materials can no longer be considered dilute due to very stable binding sites.^{24,47} Thus, we must correct the diffusivity for hydrogen concentration dependence, taking into account repulsive H–H interactions. Detailed methods that address these issues with DFT for amorphous membranes have been described¹ and validated using experimental data for amorphous $\text{Zr}_{36}\text{Ni}_{64}$ and $\text{Zr}_{30}(\text{Ni}_{0.6}\text{Nb}_{0.4})_{70}$.⁴⁰

The original methods of Hao and Sholl are computationally expensive and not easily adapted for large scale screening.¹ As with the calculations for crystalline materials, much computational effort is expended in locating the transition states and computing binding energies. Hao and Sholl describe a phenomenological model in which a Gaussian distribution is used for interstitial binding energies and a correlated saddle point model accounts for interstitial hop transition state energies.³² This approach means that only the distribution of interstitial binding energies has to be determined with DFT to qualitatively predict a membrane's performance, a large reduction in computational effort.

Illustrating this approach, Hao and Sholl performed detailed calculations for amorphous $\text{Zr}_{30}\text{Cu}_{60}\text{T}_{10}$ ($T = 13$ elements) and for $\text{Zr}_x\text{Cu}_y\text{T}_{100-x-y}$ as a function of composition. Figure 7 shows the mean value and standard deviation of the Gaussian distribution for each material and highlights the values that correspond to the most desirable membrane performance. The black circles correspond to parameters with permeabilities more than twice that of $\text{Zr}_{54}\text{Cu}_{46}$ at 600 K, which could be targeted for materials development. Figure 7 predicts that $\text{Zr}_{30}\text{Cu}_{60}\text{T}_{10}$ ($T = \text{Sc}, \text{Ta}, \text{Y}, \text{Ti}$) have the best permeabilities for H_2 and that materials outside the rectangle in Figure 7 will have highly unfavorable performance. An interesting feature of Figure 7 is

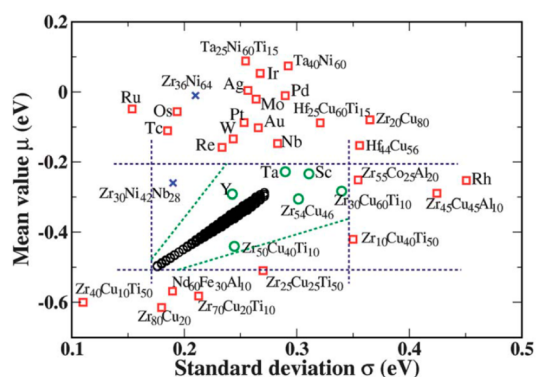


Figure 7. Gaussian model parameters for H binding energy from detailed DFT calculations (blue, red, and green symbols) and the optimized parameters from fitted results for $Zr_xCu_yTi_{100-x-y}$ (black circles). Element labels indicate the T element in samples of $Zr_{30}Cu_{60}Ti_{10}$. Blue crosses indicate previous DFT results for $Zr_{36}Ni_{64}$ and $Zr_{30}Ni_{42}Nb_{28}$ from ref 40. Adapted from ref 32. Reproduced by permission of The Royal Society of Chemistry (RSC).

that it suggests that amorphous materials with optimized Gaussian distributions of binding energies will have permeabilities ~ 3 times that of pure Pd. This is likely to define an upper limit for H_2 permeability in amorphous metals.

4. CONCLUSIONS

DFT is useful for predicting the performance of metal-based materials for hydrogen applications because it describes key quantities like binding energies and heats of formation with sufficient accuracy and, critically, with no experimental input. Predictions of materials performance can be made for materials with compositions that span the periodic table provided that the DFT-based method meets the four other criteria for useful theoretical predictions presented in the Introduction. We have discussed several examples of our efforts to computationally screen either libraries of existing materials or proposed materials to identify systems with enhanced properties. Examples included substitutionally disordered metal alloys, ordered stoichiometric compounds, and amorphous metals. Often in these screening studies, only a handful of many materials tested show potential for a given application. Without guiding principles to facilitate this down-selection, it would be a daunting task to pick winners *a priori*.

Tools that enable large scale DFT-based screening methods include easily navigable experimental crystal structure databases that are continually updated with completely solved structures and information on synthesis temperatures and pressures.¹⁸ Also, databases such as the Materials Project based on common DFT calculations that can be mined quickly to obtain DFT-optimized structures, ground state energies, electronic properties, or convex hulls will become important for efficiently evaluating materials for novel applications.⁴⁸ Open source codes such as Pymatgen or AFlow that allow for automating property prediction algorithms also play an enabling role in increasing the number of calculations that can be completed using existing resources.^{49,50} Great strides are being made in the area of computational materials discovery⁵¹ and experimental-computational structure refinement⁵² that expand, complete, and improve current databases of both stable and metastable states. However, for continued acceleration in materials discovery and property prediction, we need methods that overcome DFT simulation size restrictions and rapidly explore

potential energy surfaces to isolate stable structures of complex materials⁵³ and transition states.

DFT-based methods have unavoidable limitations with regards to accuracy stemming from available exchange–correlation functionals. Improving these functionals is fundamentally important, but it is clear that the current functionals provide sufficient balance of accuracy and speed in H–metals applications. The examples reviewed in this Account illustrate how DFT-based methods are being used to significantly accelerate materials development for several practical applications.

■ AUTHOR INFORMATION

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The authors declare no competing financial interest.

Biographies

Kelly Nicholson is pursuing her Ph.D. in Chemical & Biomolecular Engineering at the Georgia Institute of Technology in 2014. Her research primarily focused on large scale material screening of metal hydrides for a high temperature nuclear application.

Nita Chandrasekhar completed her Ph.D. in Chemical & Biomolecular Engineering at the Georgia Institute of Technology in 2014. Her work examined intermetallics as candidates for dense H_2 membranes and the effects of hydrogen heat treatment on dense metal membranes.

David Sholl is Chair of the School of Chemical & Biomolecular Engineering at the Georgia Institute of Technology, where he is also the Michael Tennenbaum Family Chair and GRA Eminent Scholar in Energy Sustainability. He is active in using quantum chemistry and atomistic calculations for materials screening in a range of applications, including gas capture and storage and membrane-based separations.

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