V.N.17 Ab Initio Screening of Ternary Alloys for Hydrogen Purification

David S. Sholl (Primary Contact),
Lymarie Semidey-Flecha, Chen Ling
Dept. of Chemical Engineering
Carnegie Mellon University
Pittsburgh, PA 15213, USA
Phone: (412) 268-4207; Fax: (412) 268-7139
E-mail: sholl@andrew.cmu.edu

DOE Program Officer: William Millman
Phone: (301) 903-5805
E-mail: william.millman@science.doe.gov

Objectives

We seek to develop accurate theoretical methods based on quantum chemistry calculations to predict the solubility and diffusivity of interstitial H in ternary Pd-based alloys. Using these methods, multiple ternary alloys will be examined with the objective of predicting alloy compositions that will yield high permeability metal membranes for hydrogen purification.

Technical Barriers

Significant amounts of experimental work on fabrication of thin membranes using metal alloys has shown that these membranes can be used reliably to produce high purity H_2. Using alloy films allows flexibility in terms of creating membranes that are robust in the presence of feed gas impurities and reducing the cost of membrane materials. Unfortunately, direct experimental screening of the large number of alloy materials that can be considered is challenging, especially for alloys with more than two components. Our work provides an avenue for guiding experiments in this area that could significantly advance the application of alloy membranes.

Abstract and Future Directions

Metal membranes are one of the most promising technologies for the large-scale production of high purity H_2. Considerable experimental work has taken place focusing on the fabrication of thin film membranes made from both pure metals such as Pd and metal alloys. The use of metal alloys has considerable advantages over pure metals, since alloys can reduce the negative effects of hydrogen embrittlement and membrane degradation due to contaminants such as S. An important unresolved challenge in this area is to identify alloy compositions that have particularly useful properties within the very large composition space of all alloys that might be considered.

We have previously demonstrated a theoretical approach to predicting the permeability of H_2 through binary Pd-based metal alloys that uses a combination of detailed quantum chemistry calculations and a rigorous coarse-graining strategy to connect these calculations with macroscopic observables. By comparing the predictions from this approach with extensive experimental results for Pd-Cu alloys, we have shown that out approach can give quantitatively accurate information [1]. Crucially, this theoretical approach can be used without input from experimental membrane data. That is, the approach is truly predictive.

We are currently extending our theoretical approach to screen ternary Pd-based alloys for use as H_2 purification membranes. The focus of our calculations is to predict the permeability of H_2 through defect-free membranes in the absence of contaminants in the feed stream to the membranes. We recognize that other factors such as the response of a membrane to contaminants are crucial in the long-term viability of a membrane technology, but achieving high pure gas permeability is a necessary prerequisite for considering a material's performance relative to these other factors. In other words, the pure gas permeability is a useful screening parameter.

We have already presented preliminary results from our calculations with ternary Pd-based alloys [2]. The most critical step in our modeling of these materials is to fit a lattice-based model of the energy of interstitial H in the octahedral sites(O), tetrahedral (T), and transition states separating O and T sites from Density Functional Theory (DFT) calculations for these energies in a representative sample of these sites in the substitutionally disordered alloy. This task is more challenging in ternary alloys than in binary alloys because of the greater diversity of distinct sites that can exist (as characterized, for example, by the number of Pd or non-Pd atoms in the shells defining the binding sites). Our previous work on binary alloys used relatively simple lattice models, but our preliminary results for ternary alloys motivated us to seek a more statistically reliable means of creating these models.

To create reliable lattice models for interstitial H in ternary alloys, we have developed an approach based on the concept of a cluster expansion (CE). A cluster expansion expresses a lattice model in terms of a formally infinite expansion of interaction terms involving one particle, two particle, three particle, four particle

energies and so on. Once a CE is truncated to create a model with a finite number of parameters, these parameters can be determined from a data set of DFT results via a standard least-squares fit. A procedure is then required to compare large numbers of distinct models with differing numbers of fitting parameters to select the model that gives the most parsimonious description of the underlying data. In our calculations, we have used the "Leave One Out" approach to make this model selection.

To initially explore the application of this CE-based method for describing interstitial H in metal alloys, we focused on three relatively simple binary Pd alloys, $Pd_{96}M$ with M = Ag, Cu, or Rh. For these dilute binary alloys, DFT calculations can be performed for almost the full range of site types that can exist, so the accuracy of the CE-based models can be tested in a detailed way. We have developed CE-based models for O sites, T sites, and the transition sites that control local diffusion of H between O and T sites in these alloys. In all cases we have demonstrated that we can determine well converged lattice models but that these lattice models need to include multi-body interactions that were neglected in our previous work. We have used our lattice models to characterize H solubility, diffusion, and permeability in these alloys.

We are now extending our CE-based approach to ternary Pd-based alloys. We have compiled an extensive DFT data set for the site energies and transition state energies of H in $Pd_{70}Cu_{26}M_4$ for M = Rh and Ag. These two data sets are being used as test cases for implementing CE-based model fitting for these ternary materials. We emphasize that once a lattice model for any material of this type is available, predicting the macroscopic permeance of H_2 through the material is straightforward. As soon as we have demonstrated the reliable derivation of our CE-based models we will extend our DFT calculations to a range of other ternary alloys, focusing initially on varying the Pd-Cu composition and the identity of the minority species M. It would be premature to collect DFT data on large numbers of materials prior to the completion of our work on $Pd_{70}Cu_{26}M_4$ for M = Rh and Ag because one of the key aspects of this work is to establish how to define what minimal set of DFT calculations can be used to achieve a reliable description of materials of this type.

We have also been using DFT-based calculations to address a separate issue that is of importance in the experimental fabrication of metal membranes, namely, the impact of surface processes in the overall permeation of H_2. It is well known that for sufficiently thick membranes that diffusion of interstitial H through the bulk material is the single rate-limiting process. When this is true, maximizing net H_2 permeability is achieved by reducing the thickness of the membrane. This simple observation has been the driving force behind much of the experimental work on metal membranes in recent years. It is also well known, however, that for sufficiently thin membranes processes associated with the surface of membranes such as recombinative desorption of H_2 from the downstream surface, must contribute to the overall permeation of H_2. A detailed model for these processes was introduced by Ward and Dao for pure Pd films[3], but this model relied on the availability of extensive surface science data for the interactions of H with Pd surfaces. Because this data is not available for metal alloys, there is currently no reliably means to estimate when surface resistances will begin to dominate the performance of alloy membranes as membrane film thicknesses are decreased. We have shown that DFT calculations can be used to calculate all of the information needed to extend Ward and Dao's model to metal alloys, using $Pd_{75}Cu_{25}$ as an example. The results of these calculations provide useful information about the physical regimes in which it is worthwhile to reduce membrane thicknesses beyond the range of 5-10 μm that can be routinely achieved with current methods.

References

1. *Prediction of hydrogen flux through sulfur tolerant binary alloy membranes,* Preeti Kamakoti, Bryan D. Morreale, Michael V. Ciocco, Bret H. Howard, Richard P. Killmeyer, Anthony V. Cugini, and David S. Sholl, Science, **307** (2005) 569-573.

2. *Towards Computational Screening of Ternary Metal Alloys for Hydrogen Purification Membranes,* Preeti Kamakoti and David S. Sholl, J. Membrane Sci., **279** (2006) 94-99.

3. *Model of hydrogen permeation behavior in palladium membranes,* T. L. Ward and J. Dao, T. J. Membrane. Sci., **153** (1999) 211.