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Rapid Ab-initio Screening of Ternary Alloys for Hydrogen Purification

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Work on this project examined two topics related to using DFT-based models to screen crystalline Pd-based alloys to find materials with high permeability for hydrogen These two topics are each described below

1 1 Surface Resistances in Ultra-thin Membranes

The transport of hydrogen through a metal membrane involves a series of distinct processes[1, 2] H_2 must dissociate on the membrane surface, H atoms must move from the membrane surface into the bulk of the membrane, interstitial diffusion must transport an H atom across the membrane, H atoms must move onto the downstream surface of the membrane, and finally recombinative desorption must take place to release H_2 For membranes that are sufficiently thick, transport across the bulk of the material dominates the overall rate of permeation, so permeability can be described using only information about the bulk material In this situation, improving membrane fabrication techniques to yield thinner membranes will increase the net flux of hydrogen through the membrane, a highly desirable situation For sufficiently thin membranes, on the other hand, surface processes dominate and reducing membrane thickness leads to no further increase in hydrogen flux Surface resistances of this kind can also be important in membrane applications with other kinds of membranes[3-7] In planning efforts to fabricate high performance membranes, it would of course be useful to understand where the transition between these two regimes occurs In principle this issue can be addressed experimentally by testing successively thinner films, but this procedure is, at best, resource intensive

The aim of our work was to develop quantitative methods for estimating the roles of surface processes in metal alloy membranes that were consistent with the DFT-based treatment described in section 2 for H transport in the bulk of these membranes A general framework for describing surface processes in metal membranes was given by Ward and Dao[8] In that work, the extensive surface science literature on Pd was used to provide kinetic parameters for each of the processes listed above for H_2 to pass through a membrane From the resulting kinetic model, the importance of surface processes for pure Pd membranes was estimated

The central difficulty in extending Ward and Dao's model to other membrane materials is that this model requires a large number of kinetic parameters that are unavailable for alloys For example, the

microscopic hopping rates of H atoms from the surface of an alloy into interstitial sites adjacent to the surface must be estimated. In our work[9], we showed that DFT calculations can be used to predict all of the kinetic parameters that are needed, therefore allowing an assessment of surface effects to be made without requiring an enormous investment of experimental resources.

To develop our methods, we examined fcc Pd-Cu alloys. Because the (111) surface has the highest density of surface atoms for fcc materials, we assumed that the external surfaces of a membrane are dominated by (111) surfaces. The surface stoichiometry of alloy surfaces is frequently different to the bulk material because of surface segregation[10-12]. We used DFT calculations of the bare surface for various possible surface stoichiometries to generate surface models that represented these effects. Because of the high temperature applications of interest to us and because Pd is an excellent catalyst for H_2 dissociation, we assumed that the dissociation process was barrierless. This assumption was motivated by extensive ab initio studies of H_2 dissociation on pure Pd surfaces[13, 14]. Under this assumption, the kinetics of dissociative adsorption and recombinative desorption of H_2 from the surface can be expressed in terms of the energies of H atoms on the surface[8]. We used extensive DFT calculations to calculate these energies, which vary from site to site on the surface because of the alloy's inherent disorder. A lattice model was derived from our DFT calculations to describe the occupancy of surface adsorption sites on the surface. A careful comparison between detailed MC simulations of this model and a numerically efficient but approximate approach for determining equilibrium states of the model based on the Quasi-Chemical Approximation[15] showed that the latter could be used to accurately describe the surface. DFT calculations were also used to estimate the net hopping rates of H between interstitial sites below the (111) surface and surface sites.

Using the kinetic parameters derived from the calculations just described, we examine the importance of surface processes as a function of operating parameters for a variety of Pd-Cu membranes. Qualitatively, our results are similar to those of Ward and Dao in predicting that the single surface process that is most relevant to controlling a membrane's performance is desorption of H_2 from the downstream membrane surface. Figure 1 shows an example of the kind of quantitative information that is accessible from our model. This figure shows the predicted flux for several different membranes based on the usual approach of neglecting surface processes (the solid curves) and more detailed calculations that include surface processes. A membrane that is 10 μm thick shows essentially no effect from surface processes at temperatures above 500 K. A membrane that is 1 μm thick, in contrast, exhibits a strong decrease in flux due to surface processes at 500 K.

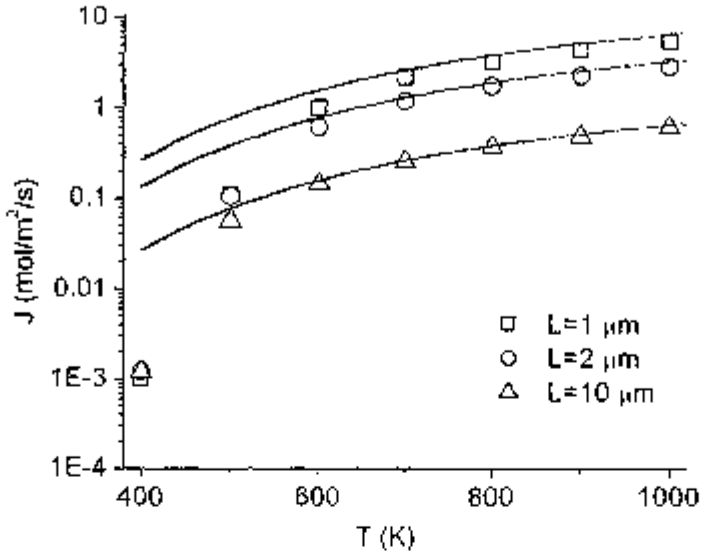

Figure 1: Hydrogen flux as a function of temperature for $Cu_{25}Pd_{75}$ membranes of different thicknesses, L. The solid line shows the diffusion limited flux for each thickness. The feed and permeate pressure are fixed to be 1 atm and 0, respectively.

A useful feature of our approach is that it can be used to rapidly understand the role of surface processes under a wide range of operating conditions once the underlying kinetic parameters are determined. Figure 2 is one example of this kind of calculation. This figure indicates the desorption resistance ratio, a useful quantity for concisely describing how large the contribution of desorption processes is to the net transport of H_2 through a membrane[9]. When this ratio is close to 0, surface processes can be neglected; when it is close to 1 surface processes dominate the membrane performance. The figure shows the behavior of this ratio for membranes with thicknesses from 1-100 μm as a function of the operating temperature and H_2 feed pressure.

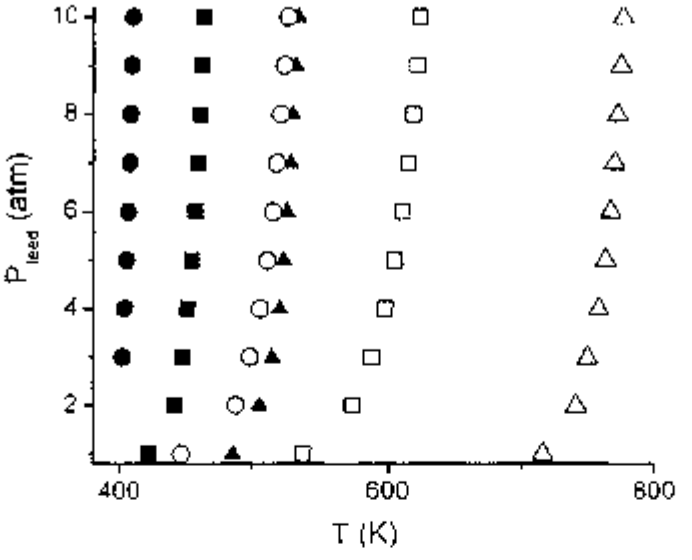

Figure 2: The desorption resistance ratio as a function of temperature for $Cu_{25}Pd_{75}$ membranes of different thicknesses. Solid symbols correspond to R_{des}/R_{tot}= 0.9 and open symbols correspond to R_{des}/R_{tot}= 0.1. Circles, squares, and triangles show the result for 100 μm, 10 μm and 1 μm membranes, respectively.

1.2 Cluster Expansions for Crystalline Alloy Membranes

In a disordered crystalline alloy such as fcc Pd-Cu alloys, a large number of different interstitial sites exist if these sites are characterized by the number and location of atoms of each metal species around the site. A key step in the approach we have used to describe the macroscopic properties of H in materials of this kind is to derive a lattice model for the site energies and transition state energies in terms of the atoms defining each possible kind of site from an ensemble of DFT calculations for individual sites. In our earlier work, we used relatively simple approaches for deriving these models. For example, the binding site of H atoms in octahedral sites in Pd Cu alloys was fitted using a linear relation involving the number of Pd atoms in the nearest neighbor and next nearest neighbor shell around the site[16, 17]. Based on this kind of approach, we examined a series of additives to Pd-Cu alloys to test whether small amounts of a third metal might create a ternary alloy with a higher permeability than the original Pd-Cu alloy[18].

A complication that is more serious for ternary alloys than for binary alloys is that it is difficult to demonstrate that simple relations such as the one mentioned above are sufficient to accurately describe the full range of sites that can exist in these materials. To address this issue, we spent a considerable amount of time developing a more rigorous method based on Cluster Expansions (CE). CEs are a well known statistical technique that has been applied to problems such as the prediction of binary alloy

phase diagrams[19-27] that had not, to the best of our knowledge, been applied to describing interstitial H in metals The idea underlying a CE is that the energy of a state of interest, for example, the energy of H in an interstitial site, can be written as a formally infinite expansion of one-body, two-body, three-body etc energies By truncating this expansion, the parameters of the resulting model can be fitted to an appropriate data set In our case, this data set is a collection of energies from DFT calculations Because many possible truncations of the infinite expansion can be considered, it is important to be able to select the most relevant one In our work, we used the Leave One Out (LOO) method, a simple technique that determines the "best" model among a collection of models with differing numbers of parameters[26]

As an example of the CE approach, we examined several simple binary alloys of the form $Pd_{96}M_4$, where M is a transition metal Considering fourteen possible two-, three-, and four-body interactions in our description of the octahedral sites defined > 16,000 possible truncated CEs The models found by testing each of these expansions with the LOO method were found to fit the underlying DFT data sets with much better precision than the simpler correlations used in our earlier work[28] To derive a lattice model for the transition states for H hopping in these alloys, we examined > 500 million possible truncated expansions defined in terms of the properties of the octahedral and tetrahedral sites that define the transition state Not surprisingly, this approach yields results that are more statistically reliable than our earlier simple correlations The best lattice models defined in this way typically contain substantially fewer parameters than were considered in the overall CE treatment This is a good indication (although not a rigorous proof) that the set of interactions that was considered is sufficient to describe the data set used in the model determination

The procedure of examining many millions of possible models may sound daunting, but it only involves the numerical solution of a large number of linear least squares problems, so it can be performed very efficiently The DFT calculations that form the data set from which the CE model can be derived are far more time consuming than the numerical calculations required to assign the best CE Moreover, once the best CE models for the interstitial sites and transition states are defined, the statistical mechanics and Kinetic Monte Carlo simulations needed to describe H solubility and diffusion are no more involved than they were when using simple correlations Because the DFT calculations remain the most time consuming part of this approach, it is important to perform these calculations in the most efficient possible way In our ongoing calculations with ternary alloys, we have developed techniques that allow us to rigorously find transition states between interstitial sites using far less

computational effort than a traditional chain-of-states calculation[29, 30] As described in section 3 1, these methods will play a key role in our proposed work on describing H diffusion in amorphous alloys

We are now using these CE-based methods to screen ternary crystalline alloys based on adding a third metal to Pd-Cu alloys As described in section 1, this continuing work is occurring within a multi-institution effort funded by the National Energy Technology Laboratory in which the other partners are fabricating and testing thin film membranes based on ternary alloy compositions suggested by our calculations

2. *List of Publications From Previous Period*

Publications arising from the work in the current period of funding were

- Kamakoti, P and D S Sholl, *Towards first principle-based identification of ternary alloys for hydrogen purification membranes* J Membrane Sci , 2006 279 p 94
- Sholl, D S and Y H Ma, *Dense Metal Membranes for the Production of High-Purity Hydrogen* MRS Bulletin, 2006 31 p 770
- Ling, C and D S Sholl, *Using first-principle calculations to predict surface resistances to H_2 transport through metal alloy membranes* J Membr Sci , 2007 303(1) p 162
- Semidey-Flecha, L and D S Sholl, *Combining Density Functional Theory and Cluster Expansion Methods to Predict H_2 Permeance Through Pd-based Binary Alloy Membranes* J Chem Phys , 2008 Submitted
- Sholl, D S , *Using density functional theory to study hydrogen diffusion in metals A brief overview* J Alloys Compounds, 2007 446 p 462

Numerous invited and contributed presentations were made based on this work at national and international conferences Notable invited presentations by the PI included Metal-Hydrogen 2006, the Gordon Conference on Physical Metallurgy 2006, and the Gordon Conference on Hydrogen in Metals 2007

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