

Quantum Chemistry for Surface Segregation in Metal Alloys
Final Technical Report

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Abstract

Metal alloys are vital materials for the fabrication of high-flux, high-selectivity hydrogen separation membranes. A phenomenon that occurs in alloys that does not arise in pure metals is surface segregation, where the composition of the surface differs from the bulk composition. Little is known about the strength of surface segregation in the alloys usually considered for hydrogen membranes. Despite this lack of knowledge, surface segregation may play a decisive role in the ability of appropriately chosen alloys to be resistant to chemical poisoning, since membrane poisoning is controlled by surface chemistry. The aim of this Phase I project is to develop quantum chemistry approaches to assess surface segregation in a prototypical hydrogen membrane alloy, fcc Pd₇₅Cu₂₅. This alloy is known experimentally to have favorable surface properties as a poison resistant H₂ purification membrane (Kamakoti et al., *Science* **307** (2005) 569-573), but previous efforts at modeling surfaces of this alloy have ignored the possible role of surface segregation (Alfonso et al., *Surf. Sci.* **546** (2003) 12-26).

Executive Summary

Quantum chemistry calculations were used to examine the relative energies of PdCu(111) surfaces under structures representative of potential surface segregation in these materials. To extend information from these calculations to finite temperatures, we have employed a cluster expansion approach (see, e.g., Blum and Zunger, *Phys. Rev. B* **72** (2005) 020104) to rigorously derive a lattice gas model that describes interactions between atoms. In conjunction with cluster expansions, we used the “Leave One Out” statistical approach to determine which interaction parameters are most significant. This description readily yields information at arbitrary temperatures when the equilibrium state of the lattice gas model is established via Kinetic Monte Carlo (KMC) simulations. Our KMC simulations show that strong anti-segregation of Cu out of the top surface layer occurs at the high temperatures relevant for coal gasification applications. At 700 °C, the surface is predicted to be more than 90 at.% Pd, and at lower temperatures the Pd content of this layer is even higher. This strongly suggests that earlier theoretical modeling of the surfaces of PdCu alloy. We have also performed some preliminary quantum chemistry calculations to examine the adsorption energy of atomic hydrogen on PdCu(111) surfaces that exhibit partial surface segregation.

The calculations used above were used as a basis to consider the resistances to hydrogen transport through PdCu membranes that arise from adsorption and desorption of hydrogen on membrane surfaces. Our approach follows the earlier modeling work of Ward and Dao (*J. Membrane Sci.*, **153** (1999) 211). That work examined pure Pd membranes and as a result could estimate surface resistance effects from prior surface science experimental data. In the case of alloy membranes of interest to us, information on surface kinetics is not currently available from experiment. We have used quantum chemistry calculations to estimate the hydrogen dissociation rates and recombinative desorption rates from the stable PdCu(111) surface structure determined from the calculations described above. Using these rates within the framework defined by Ward and Dao suggests that, similar to pure Pd membranes, desorption-related resistances are much more important than adsorption-related resistances. The latter resistances appear to be negligible under all conditions of practical membrane operation. At temperatures lower than 600 K, desorption resistances may be significant for membranes thinner than 10 microns.

Results and Discussion

We performed quantum chemistry calculations to examine the relative energies of PdCu(111) surfaces under structures representative of potential surface segregation in these materials. This alloy was chosen because of extensive previous experimental and theoretical work that suggests that membranes made from this alloy can have permeabilities for hydrogen similar to those of pure Pd but simultaneously perform in a robust way in the presence of sulfur-containing impurities.¹ Our calculations used well established density functional theory (DFT) methods suitable for metal surfaces.¹⁻³ The details of our DFT calculations were similar to those we have reported previously for the properties of H in the bulk of PdCu alloys and ordered intermetallics.⁴⁻⁷ We used DFT to compute the total energies of a series of realizations of a Pd₇₅Cu₂₅(111) surface that differed in the segregation of Cu and Pd between the upper two layers.

Our quantum chemistry calculations strictly only provide direct information on the energy of the surface at $T = 0$ K. Since we obviously need information on the state of the surface at finite temperatures, we have employed a cluster expansion approach.^{8,9} This approach rigorously derives a lattice gas model that describes the total energy of a collection of atoms located on the lattice sites defined by a fcc(111) surface. The CE formally defines a large number of possible models, so a parsimonious means to select the best model is required. We used the “Leave One Out” statistical approach, which formalizes the intuitive idea that on the one hand it is desirable to achieve the best possible fit to the available data set but on the other hand it is desirable to use models with small numbers of adjustable parameters. Screening a large number of two and three body interactions in this way, we developed a lattice gas model for the energy of the upper two surface layers of a Pd₇₅Cu₂₅(111) surface based on our collection of DFT data.

The lattice model derived as described above readily yields information at arbitrary temperatures when the equilibrium state of the lattice gas model is established via Kinetic Monte Carlo (KMC) simulations.^{8,9} Our KMC simulations show that strong anti-segregation of Cu out of the top surface layer occurs at the high temperatures relevant for coal gasification applications. At 700 °C, the surface is predicted to be more than 90 at.% Pd, and at lower temperatures the Pd content of this layer is even higher. This strongly suggests that earlier theoretical modeling of the surfaces of PdCu alloy membranes that neglected surface segregation may require revision.

It is useful to note that the main prediction of these calculations, that Pd segregates to the surface of the alloy, is not sensitive to the details of the cluster expansion modeling. Rather, this prediction follows directly from the observation that in our DFT calculations the lowest energy structures are those for which the surface layer is entirely made up of Pd. The cluster expansion approach provides some additional quantitative information about the population of the top layer as a function of temperature, but the temperatures that are required for any substantial deviation from a pure Cu layer are high enough to be of little interest in practical settings. Because of these results, all the calculations described below that examined potential surface resistances in alloy membranes were made for a Pd₇₅Cu₂₅(111) surface where the upper surface was entirely made up of Pd atoms.

Several caveats related to the conclusions above must be noted. In the DFT calculations that formed the basis for the results, segregation of Cu and Pd atoms was

only allowed between the top two layers of the surface. In these calculations, a four layer slab was used with the bottom two layers constrained in their bulk positions and with a substitutionally random distribution of Cu and Pd atoms with the stoichiometry Pd₇₅Cu₂₅. It is possible that the true surface segregation profiles involve changes in the layer-by-layer stoichiometry over more than the top two layers of the surface. The calculation time required to examine this situation would be considerable, because the number of configurations required to examine the range of possibilities increases rapidly as the number of “active” layers is increased. Nevertheless, our calculations cannot exclude the possibility that the true surface segregation profile is more complex than the one we have reported because it involves more than two layers. A second caveat is that our surface segregation profiles were computed for a clean surface. It is well known that atomic or molecular adsorbates on surfaces can change the relative energies of surface states. The two principal atomic species that may be relevant in practical applications of these alloys for hydrogen purification are H and S. H adsorbs quite weakly on this metal surface, as on most metal surfaces (see below), so it is unlikely that the presence of H would significantly change the thermodynamic stability of the segregation profile. Adsorbed S is quite different, because S binds very favorably on many metal surfaces. In general, however, S binds more strongly to Pd atoms than to Cu atoms.¹⁰ This trend suggests that if S atoms are present on the alloy surface they will increase the relative stability of Pd atoms in the surface layer compared to Cu atoms. That is, adsorbed S appears likely to enhance the trend already predicted by our clean surface calculations that the alloy surface is likely to be rich in Pd in its top layer.

Models of hydrogen permeation through metal membranes typically assume that the only significant resistance to mass transport across the membrane arises from diffusion of H within the metal.^{1,11} When this is correct, the overall flux passing through a membrane can always be increased by making the membrane thinner. This fact drives much of the active research on metal membranes, which focuses on developing fabrication techniques for reducing film thicknesses. State of the art fabrication methods currently produce films with thicknesses from 1-10 μm. It is widely recognized, however, that transport of hydrogen through a metal film is a multi-step process that includes dissociation of H₂ on the upstream surface, diffusion of H from surface sites to subsurface interstitial sites, diffusion of interstitial H through the bulk of the membrane, hopping of H from subsurface sites onto the downstream membrane surface and finally recombinative desorption of H₂ from the downstream surface. Each of these steps can potentially create a resistance to mass transfer, so a complete description of hydrogen transport should include information on all of these processes. There are a number of experiments with ultrathin membranes that suggest that resistances associated with processes other than bulk interstitial diffusion can be important in practical devices.¹² The only detailed model that is currently available to describe these phenomenon is from the work by Ward and Dao on pure Pd films.¹³ In this work, experimental data from a broad range of surface science experiments was used to estimate the microscopic rates for all of the processes listed above and the overall resistance to H transport through Pd films was calculated on this basis. The principal conclusion from that work was that at high temperatures, interstitial diffusion was the dominant resistance to mass transfer even for films as thin as 1 μm. At temperatures below ~500 °C, the resistance to mass transfer associated with recombinative desorption of H₂ also was found to become important.

Unfortunately, it is far from straightforward to extend Ward and Dao's approach to any material other than pure Pd, especially alloys. Their approach relies on the availability of a broad range of high quality surface science data for the interactions of H with Pd surfaces. Even with this compilation of data, several key parameters in their model had to be estimated rather than based on direct measurements. DFT calculations provide a useful avenue to extend Ward and Dao's approach to alloy materials, since in principal the activation energies, thermochemical energy differences, and microscopic reaction rates for each process of interest can be calculated directly. We have performed preliminary DFT calculations for the Pd₇₅Cu₂₅(111) surface to develop the information needed to assess possible surface resistances to mass transport for this surface. We focused our attention on the recombinative desorption of H₂ from the surface, since this was found by Ward and Dao to be the most important contribution to the net transport resistance (after interstitial diffusion) for pure Pd. A detailed description of bulk interstitial diffusion of H in PdCu alloys based on DFT data was already available from our previous work.^{1,7}

We initially calculated the binding energy (relative to gas phase H₂) of atomic H at low coverage in a large selection of possible three-fold sites on a Pd₇₅Cu₂₅(111) surface whose top layer was entirely comprised of Pd atoms. Because of the substitutional disorder in the atoms beneath the top layer, this results in a range of binding energies, as shown in Fig. 1.

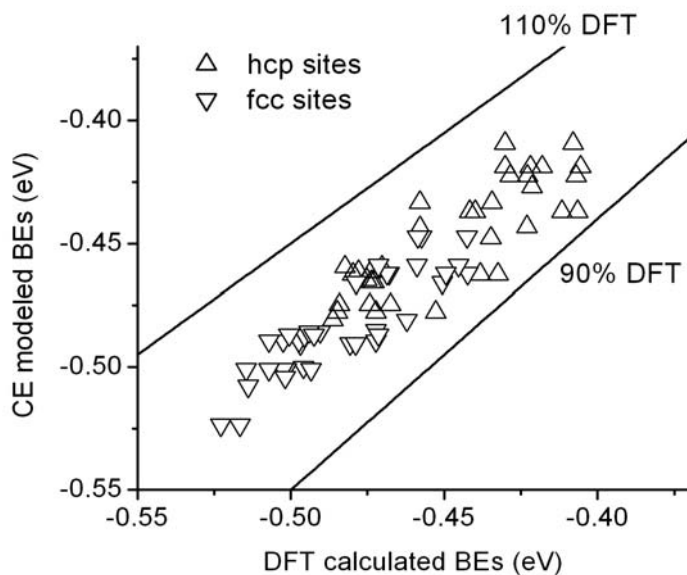


Figure 1: Binding energies of atomic H on three-fold sites of a Pd₇₅Cu₂₅(111) surface as computed with DFT (horizontal axis) and as modeled using a cluster expansion (CE) (vertical axis). The solid lines show the outcomes that would result from the CE having a systematic error of 10% in the binding energy.

Similar to our calculations with surface segregation, we developed a lattice model for the H binding energies using a combined cluster expansion/statistical approach. Figure 1 shows the correlation between the resulting lattice model and the DFT data. As might be hoped, the lattice model does an excellent job in describing the variation in the H binding energies between different types of sites on the surface. Our further

calculations for desorption resistances to mass transfer relied on this lattice model for the H binding energies.

The lattice model derived from our CE analysis is still somewhat awkward to use within a macroscopic model of mass transport across a membrane because it involves describing individual atoms. Following Ward and Dao, we converted our lattice model into a continuum form using the quasi-chemical approximation (QCA). The QCA is a well known closure approximation that incorporates interactions between particles on a lattice via a single interaction energy. We estimated this energy by performing a small number of DFT calculations for H atoms coadsorbed in adjacent sites on the $\text{Pd}_{75}\text{Cu}_{25}(111)$ surface. The interaction energy between nearby H atoms is weakly repulsive, as might be expected. It is possible to test the accuracy of the QCA by comparing its predictions for the adsorption isotherm of the surface with results from grand canonical Monte Carlo simulations of the full lattice model. The latter simulations can be regarded as being exact but are computationally expensive relative to the simplicity of the QCA. The results of this comparison are shown in Fig. 2. It can be seen from the figure that the QCA introduces only small errors under conditions of practical interest, that is, elevated temperatures and H_2 pressure of 1-10 atm. As a result, the QCA was used in all subsequent calculations.

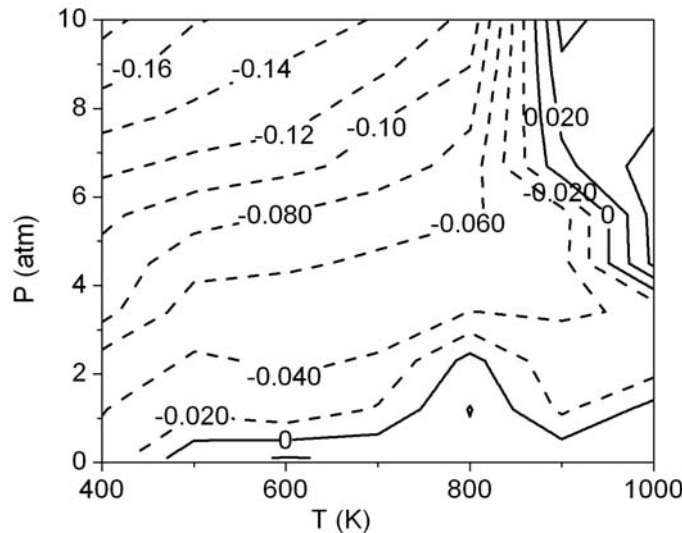


Figure 2: The fractional deviation between the adsorbed amount of H on a $\text{Pd}_{75}\text{Cu}_{25}(111)$ surface as predicted by the QCA and using grand canonical Monte Carlo simulations of the full lattice model. The vertical axis corresponds to the bulk pressure of H_2 .

The final stage in our work was to modify the model introduced by Ward and Dao to include only bulk interstitial diffusion and recombinative desorption of H_2 from the downstream surface of the membrane. All other processes were assumed to not be rate limiting. In particular, this assumption meant that the surface coverage on the upstream surface of the membrane was computed by establishing an equilibrium between the bulk gas phase and the surface.¹ The steady-state flux through each membrane of interest was

then calculated by finding a self-consistent solution to the combined fluxes from interstitial bulk diffusion and recombinative desorption.

Figure 3 shows results from our calculations for three membranes of differing thicknesses. In each case the solid line show the result that is obtained if desorption resistances are neglected. As expected, the effects of this approximation are most severe for the thinner membranes and at the lowest temperatures. These calculations suggest that at temperatures below ~ 600 K, surface resistances might become a dominant factor in the performance of PdCu alloy membranes that are significantly thinner than $10 \mu\text{m}$.

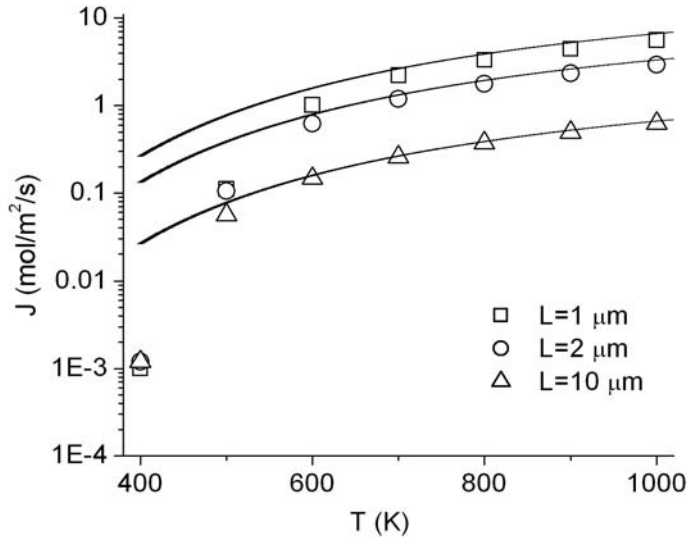


Figure 3. Hydrogen flux as a function of temperature for $\text{Cu}_{25}\text{Pd}_{75}$ membranes of different thicknesses, L . The solid line shows the diffusion limited flux for each thickness. The feed and permeate pressure are fixed to be 1 atm and 0 atm, respectively.

An alternative way to view the data from Fig. 4 is in terms of the permeability of the membranes, k . The data is plotted in terms of permeability in Fig. 4. When bulk interstitial transport is the only process included, the permeability of a membrane is independent of membrane thickness.

We anticipate that a publication describing the details of this modeling will be prepared and submitted in the future. Prior to submitting this publication there are several topics that deserve further attention. In particular, we are extending the description above to include DFT-based information on the rates of hopping of H between surface and subsurface sites. In Ward and Dao's analysis of pure Pd, this was the process whose rates involved the greatest uncertainty. We feel that by providing definite information on these processes using DFT, the importance of these processes in a range of metal membranes will be clarified.

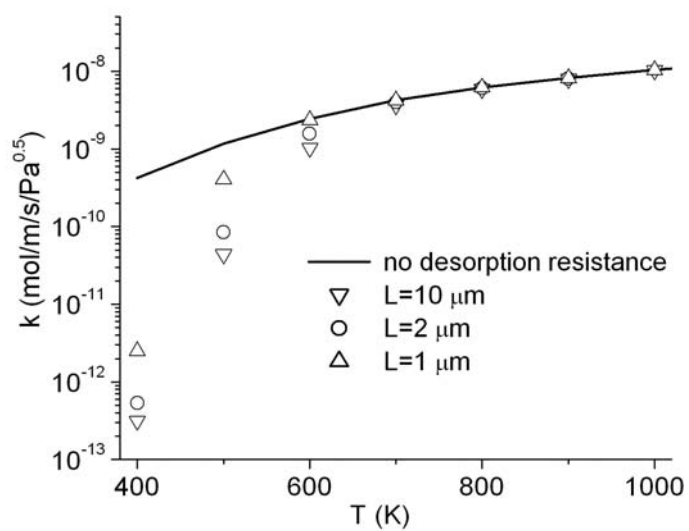


Figure 4: The same data as in Fig. 3 but shown in terms of membrane permeability, k .

References Cited

1. Kamakoti, P. et al. Prediction of Hydrogen Flux through Sulfur-Tolerant Binary Alloy Membranes. *Science* **307**, 569-573 (2005).
2. Shah, V., Li, T., Baumert, K.L., Cheng, H., Sholl, D.S. A Comparative Study of CO Chemisorption on Flat and Stepped Ni Surfaces using Density Functional Theory. *Surf. Sci* **537**, 217-227 (2003).
3. Asthagiri, A., Feibelman, P. J. & Sholl, D. S. Thermal Fluctuations in the Structure of Naturally Chiral Pt Surfaces. *Tops Appl Phys* **18**, 193-200 (2002).
4. Bhatia, B., Luo, X., Sholl, C. A. & Sholl, D. S. Diffusion of hydrogen in cubic Laves phase HfTi_2H_x . *J. Phys. Cond. Mat.* **16**, 8891-8903 (2004).
5. Bhatia, B. & Sholl, D. S. Quantitative Assessment of Hydrogen Diffusion by Activated Hopping and Quantum Tunneling in Ordered Intermetallics. *Phys. Rev. B* **72**, 224302 (2005).
6. Kamakoti, P. & Sholl, D. S. A comparison of hydrogen diffusivities in Pd and CuPd alloys using Density Functional Theory. *J. Membrane. Sci* **225**, 145-154 (2003).
7. Kamakoti, P. & Sholl, D. S. Ab initio based lattice gas modeling of interstitial hydrogen diffusion in CuPd alloys. *Phys. Rev. B* **71**, 045415 (2005).
8. Blum, V. & Zunger, A. Prediction of ordered structures in the bcc binary systems of Mo, Nb, Ta, and W from first-principles search of approximately 3,000,000 possible configurations. *Phys. Rev. B* **72**, 020104 (2005).
9. Muller, S. Bulk and Surface Ordering Phenomena in Binary Metal Alloys. *J. Phys. Condens. Mat* **15**, R1429-R1500 (2002).
10. Alfonso, D. R., Cugini, A. V. & Sholl, D. S. Density functional theory studies of sulfur binding on Pd, Cu, Ag and their alloys. *Surf. Sci* **546**, 12-26 (2003).
11. Paglieri, S. N. & Way, J. D. Innovations in palladium membrane research. *Sep. Purif. Methods* **31**, 1-169 (2002).
12. McCool, B. A., Lin, Y.S. Nanostructured Thin Palladium-Silver Membranes: Effects of Grain Size on Permeation Properties. *J. Mater. Sci* **36**, 3221-3227 (2001).
13. Ward, T. L. & Dao, T. Model of hydrogen permeation behavior in palladium membranes. *J. Membrane. Sci* **153**, 211-231 (1999).