

**Support of Advanced Coal Research at U.S. Colleges and Universities: IC Phase I
Program: Computational Efforts in Support of Advanced Coal Research
(DE-FG26-05NT42538)**

Pd-based metallic membranes for hydrogen separation: First principles studies of separation mechanisms aimed at knowledge-based rational formulations of improved materials.

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Period: 09/2005 – 04/2006

Objective

As we gear towards hydrogen economy, the efficient purification and storage of hydrogen are becoming increasingly important. In order to separate hydrogen from various impurities, such as CO, sulfur compounds, hydrocarbons, and various trace elements produced during coal gasification, different methods have been proposed. A very appealing concept is to utilize Pd or Pd-based alloy metal membranes which have been shown to be selectively permeable for hydrogen molecules. Even though, the Pd-based membranes represent a promising class of materials, the molecular level understanding of hydrogen interactions with these membranes is lacking. Furthermore, there are a number of operational problems that need to be addressed before these membranes become technologically viable. These problems are associated with damaging effects of various contaminants (sulfur compounds and CO), membrane embrittlement, Pd-material oxidation, and the costs of Pd materials.

We have employed quantum chemical density functional theory (DFT) calculations, and state-of-the-art thermodynamic and kinetic simulations to investigate the molecular level mechanism of hydrogen separations over Pd and Pd-alloy membranes. Pd-based membranes operate by dissociative adsorption of molecular hydrogen on membrane surfaces. The dissociated atomic hydrogen diffuses through the membranes and is recombined into molecular hydrogen which desorbs on the other side of the membranes. Rationale for the proposed work stems from the fact that DFT can be used to accurately and efficiently analyze chemical pathways and molecular transformations in solids, which can not be easily accomplished by other means. Also, the DFT calculations, when coupled with kinetic and thermodynamic simulations, have significant predictive powers towards the formulation of novel solid state materials. Our ultimate objective is to use these molecular level insights to develop a knowledge-base in support of bottom-up rational (as opposed to traditional Edisonian trial and error approaches) formulations of

new materials with higher hydrogen storage capacity, and the materials that have higher hydrogen separation fluxes.

Accomplishments to date

We have performed DFT calculations, and ab initio thermodynamic and kinetic simulations to investigate the molecular level mechanism of hydrogen separations over Pd. The key results of our investigations are highlighted below:

- We have evaluated employed DFT calculations to calculate the adsorption energies of hydrogen on Pd surfaces in the presence and absence of membrane fouling agents like sulfur and carbon monoxide (CO). We have calculated adsorption energies of hydrogen on clean Pd(111)-(2x2) surface to be -0.70 eV (-70 kJ/mol), on sulfur poisoned Pd(111)-(2x2) +0.5 eV endothermic, and on CO-poisoned Pd(111)-(2x2) -0.58 eV. It is observed that the presence of sulfur severely affects the dissociative adsorption of hydrogen on Pd surface, making it an endothermic process. The effect of CO is comparatively less dramatic. The calculations show that sulfur adsorbs much more strongly on Pd surface compared to CO.
- Extensive analysis of hydrogen binding at interstitial sites of Pd lattice has also been performed. It is observed that hydrogen binds more strongly at the octahedral sites (-0.35 eV) as compared to tetrahedral (-0.22 eV) sites and the migration energy barrier from octahedral site to tetrahedral site is estimated to be 0.15 eV above the octahedral site energy. These studies also demonstrate that the kinetically slow rate-determining step in hydrogen diffusion through a pure Pd membrane is the penetration of hydrogen atoms from the Pd surface into the subsurface interstitial sites between the top and the second layer of Pd membrane.
- We have developed an efficient lattice-based Kinetic Monte Carlo (KMC) simulation code based on “n-fold way” algorithm proposed by Bortz, Kalos and Lebowitz [1] to model hydrogen diffusion through the Pd membrane. The kinetic parameters for the KMC simulations (binding energies, vibrational frequencies, energy barriers of hydrogen hopping from one lattice site to another) were obtained from first principles DFT calculations as mentioned above. The KMC simulations allow us to relate the DFT calculations to macroscopic observables such as tracer diffusivities and fluxes. We find that the hydrogen diffusivity of obtained through our KMC simulations is in an excellent agreement with the experimental data [2].

Future Work

We will further employ our methodology to explore the effect of CO and S-containing compounds on the H₂ flux and the diffusivity. These studies will allow us to identify the underlying physical factors that govern a membrane performance. We will also utilize our approach to investigate the separation potential (rates of hydrogen diffusion,

hydrogen selectivity, resistance to sulfur, carbon, and CO) of Pd/Cu and Pd/Ag alloy materials. Aside from extending our computational work we will further contrast our results with experimental findings.

Students Supported

Teresa Misiti, 3rd year undergraduate

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[1] A.B. Bortz, M.H. Kalos, and J.L. Lebowitz, "A New Algorithm for Monte Carlo Simulation of Ising Spin Systems," *J. Computational Physics*, Vol. 17, 1975, pp. 10-18.

[2] J. Volkl and G. Alefeld, "Hydrogen in Metals", Vol 28, ed. by G. Alefeld and J. Volkl (Springer-Verlag, Berlin) (1978).