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## V.P.2 Ab-initio Screening of Alloys for Hydrogen Purification Membranes

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### Objectives

We are developing first-principles based methods for predicting the solubility and diffusivity of hydrogen in amorphous metal alloys. These methods are being used to seek new alloy compositions that will allow the fabrication of dense metal membranes for hydrogen purification that will exceed the performance limitations associated with well-known crystalline metal membranes.

### Technical Barriers

A number of experimental groups have demonstrated that it is possible to fabricate useful dense metal membranes from amorphous metals. Unfortunately, the large number of possible amorphous metal compositions makes experimental screening of these materials for membrane applications impractical. We are developing quantitative modeling methods that can aid in the discovery of new membrane materials by making predictions about membrane performance prior to experimental testing.

### Abstract and Future Directions

Within this project, we have demonstrated the development of methods to make quantitative predictions about the performance of amorphous metal films during use as hydrogen purification membranes. The modeling framework for the analogous problem with crystalline metals is relatively well developed, but the disordered nature of the interstitial sites in amorphous metals required extensive method development. In brief, our first-principles calculations for amorphous metals proceeds by (i) using *ab initio* Molecular Dynamics methods to create representative amorphous solid structures within a periodic supercell geometry, (ii) use efficient methods based on empirical forcefields to initialize first principles calculations to find the energy of H in *all* interstitial sites in the material, and (iii) use efficient methods to initialize first principles calculations to locate *all* transition states for H hopping

between adjacent interstitial sites. Once the binding sites and transition states are known, Grand Canonical Monte Carlo (GCMC) and Kinetic Monte Carlo (KMC) calculations are used to accurately describe the net solubility and diffusivity, respectively, of H in the amorphous material. These calculations include a characterization of the H-H repulsion that occurs at levels of interstitial H at which the interstitial species is not dilute. We have characterized this phenomenon via extensive first-principles calculations.

An important general property of amorphous metals is that the solubility of H in these materials is quite high due to the energetically favorable interstitial sites that are created by the amorphous material. At non-dilute concentrations, the differences that exist between various different diffusion coefficients (e.g. the self diffusion coefficient and the Fickian diffusion coefficient) become significant. Previous studies of H diffusion in crystalline metals had only examined the self diffusion coefficient. We have extended our KMC methods to allow the direct calculation of the Fickian diffusion coefficient. It is this diffusivity that is of the greatest physical interest in describing macroscopic mass transport through a membrane. In general, the Fickian diffusivity is larger than the self diffusivity at the same conditions. At high concentrations of interstitial H, the expansion of an amorphous alloy due to the interstitial H can also have a marked effect on the net solubility of H. We have developed efficient methods that allow us to quantify this effect.

We have demonstrated the validity of our modeling approach by comparing predictions from our models with experimental data that is available for permeation of hydrogen through amorphous ZrNi and ZrNiNb films. Once the effects of hydrogen-induced lattice expansion and concentration-dependent diffusion coefficients are taken into account, our model's predictions are in quantitative agreement with experimental data. Crucially, our approach does not require any experimental data, so it can be used in a truly predictive sense. We are currently using our method to screen a variety of binary and ternary alloys that are known to be good glass formers with high glass transition temperatures with the aim of identifying materials that will exhibit high permeability for hydrogen when used as membranes.

In addition to our work on amorphous metals for hydrogen purification, we have performed work on the related topic of understanding hydrogen diffusion in ionic hydrides. Specifically, we examined the diffusion mechanism of hydrogen in two prototypical ionic hydrides, MgH<sub>2</sub> and NaMgH<sub>3</sub>. An interesting conclusion from this work was that the relevant species that control

the mobility of H in these materials are charged, unlike the neutral species that control interstitial diffusion in metallic systems. Understanding the characteristics of H diffusion in these two materials opened the possibility of finding dopants that would accelerate H diffusion, and we used first-principles calculations to examine a larger range of possible dopants for this purpose. We also performed similar calculations for several light metal borohydrides, including  $\text{LiBH}_4$ . A surprising outcome from these calculations is that hydrogen diffusion in these materials appears to be mediated by formation of neutral molecular  $\text{H}_2$  within the solid.

### **Publications (including patents) acknowledging the grant or contract**

1. Comparison of first principles calculations and experiments for hydrogen permeation through amorphous ZrNi and ZrNiNb films, Shiqiang Hao and David S. Sholl, *Journal of Membrane Science*, **350** (2010) 402.
2. The role of interstitial  $\text{H}_2$  in hydrogen diffusion in light metal borohydrides, Shiqiang Hao and David S. Sholl, *Phys. Chem. Chem. Phys.*, **11** (2009) 11106.
3. Self diffusion and macroscopic diffusion of hydrogen in amorphous metals from first-principles calculations, Shiqiang Hao and David S. Sholl, *J. Chem. Phys.*, **130** (2009) 244705.
4. Selection of dopants to enhance hydrogen diffusion rates in  $\text{MgH}_2$  and  $\text{NaMgH}_3$ , Shiqiang Hao and David S. Sholl, *Applied Physics Letters*, **94** (2009) 171909.
5. Probing hydrogen interactions with amorphous metals using first-principles calculations, Shiqiang Hao, M. Widom, and David S. Sholl, *J. Phys. Condens. Matter*, **21** (2009) 115402.
6. Predictions of H isotope separation using crystalline and amorphous metal membranes: A computational approach, Lymarie Semidey-Flecha, Shiqiang Hao, and David S. Sholl, *J. Taiwan Inst. Chem. Eng.* **40** (2009) 246-252 (invited paper for Ed Ma Festschrift).
7. Hydrogen diffusion in  $\text{MgH}_2$  and  $\text{NaMgH}_3$  via concerted motions of charged defects, Shiqiang Hao and David S. Sholl, *Applied Physics Letters*, **93** (2008) 251901.
8. Using First-principles Calculations to Accelerate Materials Discovery for Hydrogen Purification Membranes by Modeling Amorphous Metals, Shiqiang Hao and David S. Sholl, *Energy and Environmental Science*, **1** (2008) 175-183.