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Predictions of H isotope separation using crystalline and amorphous metal membranes: A computational approach

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ABSTRACT

First-principles calculations offer a useful complement to experimental approaches for characterizing H_2, D_2 and T_2 permeance through dense metal membranes. In this study we performed calculations that combine *ab initio* density functional theory calculations and statistical mechanics to describe the properties of interstitial H and its isotopes in crystalline Pd-based binary alloys, crystalline Fe_3B and amorphous Fe_3B. We used Sieverts' law to calculate the solubility of each isotope in the Pd-based metal membranes and Grand Canonical Monte Carlo for the isotopic solubilities in Fe_3B membranes. A kinetic Monte Carlo (KMC) scheme was implemented to examine diffusion of H, D, and T at elevated temperatures. From these results we are able to predict the permeability of H_2, D_2 and T_2 in each material and consider which material would be best suited for membrane-based isotope separations at high temperatures.

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1. Introduction

Metal membranes have received much attention for the high temperature purification of hydrogen due to their high selectivity over other gases over a wide range of temperatures and pressures (Edlund *et al.*, 1994; Howard *et al.*, 2004; Ma *et al.*, 2003; Morreale *et al.*, 2003; Phair and Donelson, 2006; Sholl and Ma, 2006; Uemiya *et al.*, 2001). The most widely studied metal membranes are composed of Pd-based alloys. Palladium–hydrogen systems have been extensively studied because of the favorable H adsorption and the high mobility of the atom within Pd (Lässer and Klatt, 1983; Lässer, 1984; Lässer and Powell, 1986, 1987; Maeda *et al.*, 1994). The great majority of work on metal membranes has focused on the purification of hydrogen from mixed gas streams. There are applications, however, where the separation of isotopes of hydrogen is important, such as the design and operation of fusion reactors (Evans and Harris, 1983; Tosti and Violante, 1998). In this paper, we consider how metal membranes can be chosen to achieve effective separations of hydrogen isotopes at elevated temperatures.

Traditionally hydrogen isotope separation is based on principles of adsorption (Aoki *et al.*, 1998; Wang *et al.*, 1999) or cryogenic distillation (Aoki *et al.*, 1998; Evans and Harris, 1983). Methods involving infrared lasers for molecular separations (Polianski *et al.*, 2006) and magnetic field effects (Ito *et al.*, 2006) have also been explored. Membranes have also been used for the purification/storage of H, including dense polymers (Agrinier *et al.*, 2008), metal organic frameworks (Chen *et al.*, 2008), and dense metal membranes. Pure Pd membranes are known to separate H from its isotopes and are an attractive application for cost reduction of processes by developing a continuous operational mode (Tosti and Violante, 1998). The phase transition that exists between the α- and β-PdH phases at moderate temperatures complicates the use of pure Pd for membrane-based isotopic separations. Pd-based alloys can potentially offer improvements relative to pure Pd membranes (Paglieri and Way, 2002). By forming alloys with Pd, the temperature of hydride formation can be reduced, allowing for a wider range of operational temperatures for separation purposes (Alefeld and Völkl, 1978).

Pd and Pd-based membranes have been studied for the separation of hydrogen and its isotopes (Aoki *et al.*, 1998; Dudek, 2007; Evans and Harris, 1983; Matsuyama *et al.*, 2007) particularly at temperatures below 200 °C, yet interesting opportunities exist for using metal membranes for high temperature isotope separations (Serra *et al.*, 1998). Because of the challenges of examining the performance of metal membranes for isotope separation experimentally, quantitative modeling techniques can play a useful role in considering what materials are well suited for these separations. In recent years, first-principles calculations based on density functional theory (DFT) have been used to predict H permeation rates through a variety of metal membranes (Bhatia *et al.*, 2004; Bhatia and Sholl, 2005a; Hao and Sholl, 2008; Kamakoti *et al.*, 2005; Kamakoti and Sholl, 2006; Ling and Sholl, 2007; Semidey-Flecha and Sholl, 2008; Sholl, 2007; Sonwane *et al.*,

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Nomenclature

c_H	concentration of atom
D_s	self-diffusivity (or tracer diffusivity) (m^2/s)
D_t	transport (or Fickian) diffusivity (m^2/s)
D_0	Arrhenius diffusion pre-exponential factor (m^2/s)
E_a	activation energy (eV)
E_b	binding energies (eV)
$E_{host(/H)}$	total energy of metal system without (with) interstitial atoms (eV)
E_{H_2}	total energy of an isolated H_2 molecule (eV)
$E^{ZP}_{host/H(H_2)}$	zero point energy contribution of the interstitial (molecular) atom (eV)
h	Planck constant (J s)
k_i	permeability of atom ($mol/(m\,s\,Pa^{0.5})$)
$k_{A\rightarrow B}$	rate of hopping from site A to B (1/s)
k_B	Boltzmann constant (J/K)
k_0	Arrhenius permeability pre-exponential factor ($mol/(m\,s\,Pa^{0.5})$)
K_s	Sieverts' constant ($1/atm^{0.5}$)
N_{x_2}	flux of molecular species ($mol/(m^2/s)$)
P_{x_2}	pressure of molecular species (atm)
T	temperature (K)
v_i	vibrational frequency of atom (1/s)

Greek symbol

Θ_H	ratio of interstitial atom to metal atoms in the solid

2006a,b). DFT calculations are well suited for describing isotopic effects in the binding energy and site to site hopping energies for interstitial H in metals (Bhatia and Sholl, 2005b; Kamakoti and Sholl, 2003; Wimmer *et al.*, 2008).

In this paper we use DFT-based calculations to predict isotope properties within the bulk of several disordered binary Pd-based alloys with the aim of understanding whether particular binary alloys have useful properties for isotopic separations using membranes. Although most experimental studies of metal membranes have focused on crystalline materials, interest in using amorphous metals as membranes for hydrogen separations is growing rapidly (Nenoff *et al.*, 2006; Sholl, 2007). No experimental information on isotopic separations using any amorphous metal membrane is currently available. We have recently introduced quantitative modeling methods suitable for treating the solubility and mobility of interstitial H in amorphous metals (Hao and Sholl, 2008). To explore whether the characteristics of isotopic separations in amorphous metal membranes may hold some advantages over crystalline materials, we use DFT-based calculations to explore this topic in crystalline and amorphous Fe_3B membranes.

2. Calculation methods

2.1. DFT calculations for interstitial atoms

We performed plane wave density functional theory calculations with the PW91 GGA exchange-correlation functional using the Vienna *Ab-initio* Simulation Package (VASP) (Kresse and Furthmuller, 1996) to characterize interstitial H in substitutionally disordered fcc $Pd_{96}M_4$ alloys (M = Ag, Cu, and Rh), amorphous Fe_3B (a-Fe_3B) and crystalline Fe_3B (c-Fe_3B) with Pearson symbol oP16. Further details on these calculations can be found in our previous publications (Hao and Sholl, 2008; Semidey-Flecha and Sholl, 2008).

In fcc crystals H can be located in two distinct interstitial sites, the octahedral (O) and tetrahedral (T) sites. In the c-Fe_3B material we examined, H can reside in three types of interstitial sites that include O sites composed of six Fe atoms, T sites composed of four Fe atoms, and T sites composed of one B and three Fe atoms. The majority of the interstitial sites in the a-Fe_3B structure can be described as distorted versions of the interstitial sites found in the c-Fe_3B structure. The binding energy of interstitial H found in the various possible interstitial sites, based on DFT calculations can be characterized using (Kamakoti *et al.*, 2005; Ke and Kramer, 2002; Løvvik and Olsen, 2003):

$$E_b = E_{host/H} - E_{host} - \tfrac{1}{2}E_{H_2} + E^{ZP}_{host/H} - \tfrac{1}{2}E^{ZP}_{H_2} \quad (1)$$

where E_{host} ($E_{host/H}$) is the total energy of the system without (with) atomic H in an interstitial site of the host metal membrane, E_{H_2} is the total energy of an isolated H_2 molecule, and $E^{ZP}_{host/H}$ ($E^{ZP}_{H_2}$) is the zero point energy (ZPE) contribution of interstitial (molecular) H. Including ZPE contributions is crucial to capturing isotopic effects. For interstitial H, ZPEs were computed within the harmonic approximation by assuming that the vibrational modes of interstitial H are decoupled from lattice phonons (Ackland, 2002). Within the harmonic approximation, the ZPE for H isotopes are related to the result obtained for H by

$$E^{ZP}_{host/D} = \frac{E^{ZP}_{host/H}}{\sqrt{2}}, \qquad E^{ZP}_{host/T} = \frac{E^{ZP}_{host/H}}{\sqrt{3}} \quad (2)$$

Our results for the isotopic ZPE in an O site of pure Pd and the ZPE for the molecular gas phase species have been compared with experimental results in Table 1. There is good agreement between the experimental results and our calculated values. By comparing the ZPE between the atomic and the molecular state of each isotope to H, it can be observed that heavier isotopes have a deeper zero point level in the gas state than in the interstitial state (Fukai, 2005; Sicking, 1984; Wicke and Brodowsky, 1978). This effect means that the isotopic solubility is ordered as T < D < H. This can also be seen from our calculated binding energies in the Pd O site; for H, D, T our calculations give $E_{b,H}$ = −0.176 eV, $E_{b,D}$ = −0.166 eV, and $E_{b,T}$ = −0.161 eV respectively. This ordering is known as a reverse isotope effect (Alefeld and Völkl, 1978; Sicking, 1984).

2.2. Solubility

For the crystalline materials we studied, the concentration of interstitial H is low at elevated temperatures, so the solubility of H can be calculated using Sieverts' law (Ward and Dao, 1999): $\Theta_H = K_s\sqrt{P_{H_2}}$. Here, Θ_H is the ratio of atomic H to metal atoms in the solid and K_s is the Sieverts' constant. K_s can be defined using the partition function of the gas phase molecule, the vibrational modes of the interstitial and molecular forms of the H and E_b of the interstitial atom (Kamakoti and Sholl, 2003; Morreale *et al.*, 2004). This approach can be applied independently to each H isotope. These calculations include all vibrational energy levels of the molecular and interstitial H, not just the ground state that is characterized by the ZPE described above. We calculated the Sieverts' constants for H, D, and T in c-Fe_3B by using this approach

Table 1
Zero point energy values for isotopes in an octahedral site of pure Pd (molecular gas phase) compared to experimental values (Alefeld and Völkl, 1978).

Isotope	DFT calculated results (eV)	Experimental results (eV)
H (H_2)	0.100(0.270)	0.102(0.269)
D (D_2)	0.071(0.191)	0.072(0.192)
T (T_2)	0.058(0.156)	–

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