Journal of Membrane Science 329 (2009) 153–159

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

First principles investigation of metal sulfides as membranes in hydrogen purification

Chen Ling, David S. Sholl*

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

ARTICLE INFO

Article history:
Received 17 September 2008
Received in revised form 17 December 2008
Accepted 17 December 2008
Available online 27 December 2008

Keywords:
Hydrogen
Metal sulfides
Solubility
Diffusivity
Permeability

ABSTRACT

Degradation of metal membranes by sulfur in high temperature hydrogen purification is an important challenge in practical use of these membranes. If metal sulfides could be identified with high hydrogen permeabilities, they could potentially sidestep the difficulties faced by metal membranes. We have used first principles calculations to predict the permeability of hydrogen through eight metal sulfides in their defect-free, crystalline form. Although the solubility of H in some of these materials is considerable, H diffusion is extremely slow in every case. Our calculations indicate that films of any of the sulfides we considered will have extremely low permeabilities for hydrogen.

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1. Introduction

Dense metal membranes are well established to be good candidates for high temperature hydrogen purification, in part because of the high selectivity that can be achieved with these membranes [1–5]. One application for these membranes has been the treatment of syngas streams from gasification processes. Trace gases such as hydrogen sulfide in these streams can dramatically affect the application of metal membranes [6–9]. For example, H_2S severely reduces the performance of Pd membranes, the most studied metal membranes for hydrogen purification [8,9]. Recent experiments on the poisoning of Pd membranes by H_2S revealed that the sulfur containing gas reacts with the membrane surface to produce a thick Pd_4S layer on the membrane [10]. These experiments were used to estimate the permeability of hydrogen through a Pd_4S scale by considering the contaminated device as a multi-layered membrane. The permeability of Pd_4S was thus estimated to be approximately 20 times less than that of pure palladium from 600 to 900 K. This permeability was in reasonable agreement with an independent prediction of this quantity made using first principles Density Functional Theory (DFT) calculations [10].

It is widely thought that the observations listed above for Pd_4S are likely to apply to other sulfides as well, meaning that the formation of sulfide layer on a metal membrane will lead to strong decreases in hydrogen permeability [8]. If, on the other hand, dense sulfides show appreciable permeability for hydrogen, they could potentially be used as membranes suitable for sulfur-containing environments. The motivation of our work is thus to examine a novel approach to the challenge of sulfur poisoning of metal membranes, namely the use of metal sulfides rather than metals as membrane materials. The crystal structures of numerous metal sulfides are already known. However, we know of no experimental efforts to measure H permeability through metal sulfides.

In situations where experimental examination of dense membrane materials is challenging, first principles calculations based on DFT can be a useful complementary tool. DFT calculations have been shown to be useful for predicting H diffusion and permeability in numerous dense materials, including pure metals [11], metal alloys [12,13], amorphous metals [14], intermetallic compounds [15,16] and, as mentioned above, Pd_4S [10]. For instance, DFT gives a prefactor of $2.93 \times 10^{-7}\ m^2/s$ and an activation energy barrier of 0.23 eV for H diffusion in Pd. The results of experiments by Wicke and Brodowsky gave a fit of $5.33 \times 10^{-7}\ m^2/s$ and 0.24 eV, respectively which is in good agreement with DFT results [17]. Previous DFT results also showed that DFT is a useful approach to explore the crystal and electronic structures of metal sulfides [18–20]. It can also accurately describe the diffusion of metal atoms in metal sulfides [21]. This body of previous work with DFT calculations indicates that these methods may be useful for examining the permeation of H through metal sulfides.

In this paper, we apply DFT calculations to predict the permeation characteristics of H in five metal sulfides with $B8_1$ structure (NiAs-type), two with C2 structure and one with B1 structure. One reason to choose these materials is that previous reports showed

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* Corresponding author.
E-mail address: david.sholl@chbe.gatech.edu (D.S. Sholl).

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doi:10.1016/j.memsci.2008.12.034

that DFT can accurately predict these material's crystal structures and their cohesive and electronic properties. This idea excludes MoS_2, for example, because DFT does not accurately characterize the weak interactions between layers in this layered material [22].

The paper is structured as follows. In Section 2, we discuss the computational details of using theoretical models to predict H permeability in metal sulfides. In Section 3, we discuss the binding and diffusion characteristics of interstitial hydrogen, and calculate H solubility and diffusivity through metal sulfides. In Section 4 we summarize the results we have obtained and discuss possible improvements to our method.

2. Computational details

DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) using the generalized gradient approximation (GGA) with the PW91 functional to describe electron exchange-correlation effects. Ion–electron interactions were described by ultrasoft pseudopotentials. A plane-wave expansion with a cutoff of 250 eV is used in all calculations [23]. Geometry relaxations were performed with a conjugate gradient method algorithm until the forces on all unconstrained atoms were less than 0.03 eV/Å. A Monkhorst–Pack mesh with 4 × 4 × 4 *k*-points was used for all calculations. Spin effects were considered in materials involving Fe and Ni.

We studied H binding in VS, CrS, FeS, NiS and NbS, all of which have a $B8_1$ (NiAs-type) crystal structure, FeS_2 and NiS_2, both with a C2 structure and ScS with a B1 (NaCl-type) structure. A computational supercell containing 2 × 2 × 2 primitive unit cells was used in all calculations. We note that the International Crystal Structure Database (ICSD) does not list any crystal structures that simultaneously include any of these metals, sulfur, and hydrogen [24]. To find the energy minima for interstitial H in these materials, we applied a method based on using empirical Lennard–Jones pair potentials to create initial states for DFT calculations using interaction parameters from previous reports [25–27]. All atoms were relaxed during the DFT geometry optimization, although the unit cell size and shape was fixed at the DFT-optimized structure for the sulfide.

Transition states for diffusion of H were determined using the Nudged Elastic Band (NEB) method [28]. The vibrational frequencies of local minima and transition states were calculated in the harmonic approximation by assuming that localized vibrations of H atoms are decoupled from vibrations of the metal atoms. This procedure gives three real frequencies at a local energy minimum and two real frequencies and one imaginary frequency at a transition state.

3. Results and discussion

3.1. Optimization of the crystal structure

Table 1 lists the DFT optimized lattice constants of the metal sulfides we studied, as well as experimental data for these quantities. We also list the difference of unit cell volume between the DFT optimized structure and experimental measurements. For all the sulfides we considered, the DFT optimized structures were in good agreement with experimental data, which confirmed that DFT is a good tool to study these systems, consistent with previous reports [18].

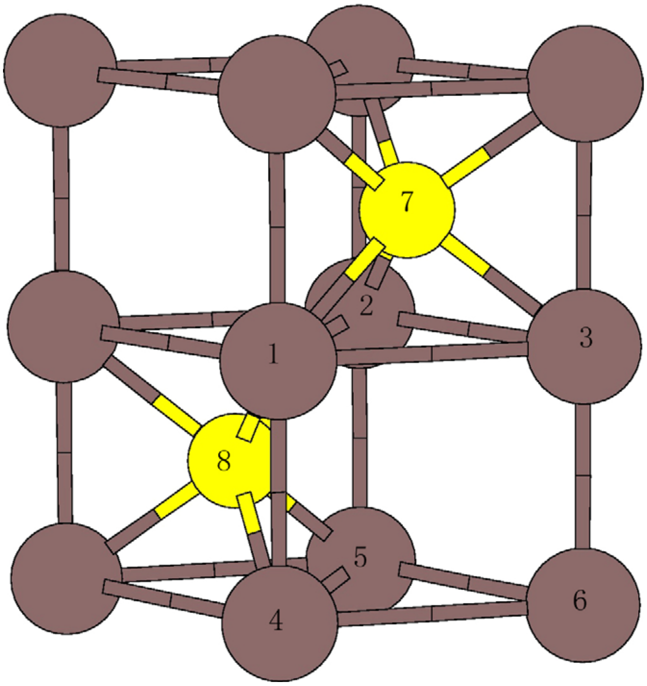

Fig. 1. Illustration of the unit cell of metal sulfides with $B8_1$ structure, with metal (sulfur) atoms colored brown (yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.2. Interstitial H properties in metal sulfides

Our calculations examining interstitial H in metal sulfides placed one H atom in a supercell containing 2 × 2 × 2 unit cells of the solid. Except where otherwise noted, the lattice constant of each material was fixed at the DFT-optimized value listed in Table 1.

For VS, CrS, FeS, NiS and NbS in the $B8_1$ crystal structure, the metal atoms (M) form a hexagonal lattice and sulfur atoms occupy half of the M_6 prisms, as shown in Fig. 1. DFT optimizations revealed that there are three types of interstitial sites for H in these sulfides. Site A is a site located in the empty M_6 prism (atoms labeled 1–6 in Fig. 1) and close to a M_3 plane (atoms labeled 1–3 in Fig. 1). Site B is located in the middle of two metal atoms and two sulfur atoms (atoms 1, 2, 7, and 8 in Fig. 1). Site C is located in the same empty prism with site A, but close to M_4 plane defined, for example, by atoms 1, 2, 4, and 5 in Fig. 1.

Both FeS_2 and NiS_2 have a C2 crystal structure. DFT optimizations gave two possible binding sites for interstitial H. Site A is located in

Table 1
Crystallographic data for metal sulfides, with experimental data from Raybaud et al. [18].

	Bravais class	Space group	DFT optimized lattice constants (Å)		Measured lattice constants (Å)		ΔV (%)
VS	Hexagonal	$P6_3/mmc$	$a = 3.327$	$c = 5.717$	$a = 3.340$	$c = 5.785$	−2.0
CrS	Hexagonal	$P6_3/mmc$	$a = 3.360$	$c = 5.374$	$a = 3.329$	$c = 5.324$	2.9
FeS	Hexagonal	$P6_3/mmc$	$a = 3.432$	$c = 5.581$	$a = 3.445$	$c = 5.763$	−3.9
NiS	Hexagonal	$P6_3/mmc$	$a = 3.436$	$c = 5.318$	$a = 3.439$	$c = 5.323$	−0.3
NbS	Hexagonal	$P6_3/mmc$	$a = 3.347$	$c = 6.512$	$a = 3.320$	$c = 6.460$	2.5
FeS_2	Cubic	$Pa\bar{3}$	$a = 5.527$		$a = 5.428$		5.6
NiS_2	Cubic	$Pa\bar{3}$	$a = 5.529$		$a = 5.620$		−4.8
ScS	Cubic	$Fm\bar{3}m$	$a = 5.245$		$a = 5.190$		3.2

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