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First-principles calculations on sulfur interacting with ternary Pd–Ag-transition metal alloy membrane alloys

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ABSTRACT

Pd-alloy membranes are promising for use in fossil-fueled power plants with integrated carbon capture, but for some applications this requires resistance to performance degradation in the presence of sulfur containing gases like H_2S. By use of atomistic modeling based on density functional theory, the role of transition metals (TMs) in ternary Pd–Ag–TM alloys was in the current article used to identify new Pd-alloys with potentially less performance degradation in contact with H_2S. A number of slab models were created, giving a wide and representative span of compositions of the two upper atomic layers of the Pd-alloys. All TMs in the 4th, 5th and 6th rows of the periodic table were included, as well as some of the poor metals. By comparing energies of pure alloy slabs, the tendency of different TMs to segregate to the surface in vacuum was quantified; this turned out to depend only weakly on the presence of silver. In order for the TM to be of any benefit for the surface properties of the membrane, the segregation energy towards the bulk should not be too large. The free energy of different compositions was then calculated for two systems: a clean surface in a gas mixture of H_2 containing a fraction of 20×10^{-6} H_2S, and a slab with adsorbed sulfur in pure H_2 atmosphere. This was used to calculate a typical release temperature for sulfur from the surface and a maximal H_2S concentration before the membrane surface can be expected to be blocked by adsorbed S. When using a tentative threshold for the segregation energy (0.2 eV) and the release temperature (600 °C), we arrived at the following list of potential TM additives to sulfur-resistant Pd–Ag membranes: Cu, Zn, Ga, Cd, In, Sn, Pt, Au, Hg, Tl, Pb, and Bi.

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1. Introduction

Palladium (Pd) membranes are promising in a range of technologies where hydrogen separation is involved, due to extremely high selectivity of hydrogen gas (H_2) diffusion through Pd-based alloys and due to very high H_2 fluxes. One such technology is fossil-fuel power plants with integrated carbon capture, where resistance to H_2S is a particularly important – H_2S from the fossil fuel may lead to severely reduced performance and in some cases breakdown of the membrane. Membranes consisting of the fcc phase of Pd–Cu and Pd–Au alloys exhibit apparently good resistance to bulk sulfidation, but they still exhibit a sharp decrease of the H_2 flux upon H_2S exposure even when bulk sulfidation is not thermodynamically expected [1]. In the latter case, a significant flux decrease has been observed for H_2S concentrations as low as a fraction of 2×10^{-6} for 2 μm thick membranes at 450 °C. The H_2 flux penalty due to H_2S is significant, illustrated by the large reduction in permeability compared to that of the more conventional $Pd_{77}Ag_{23}$ in the absence of H_2S. The ideal Pd-based alloy for such membranes would thus display both sulfide tolerance and a reasonable H_2 permeability in the presence of H_2S. Such a solution could lead to economically viable applications of Pd-based membranes in integrated gasification combined cycle power plants.

Density functional theory (DFT) calculations have shown to be an important tool for predicting and understanding Pd-based membrane properties. Previous modeling studies on sulfur tolerance based on atomic-scale density functional theory (DFT) calculations have focused on pure metals or binary alloys [2–5], comparing the surface reactivity between various alloys and gases. Much of the work has been dedicated to increasing the hydrogen permeability of Pd–Cu alloys, which exhibit quite good sulfidation tolerance but have low hydrogen permeability [6–11]. It was shown that sulfur forms strong bonds with the surfaces and favors hollow sites in the case of densely packed surfaces of Pd, Cu, Ag, Au as well as some of their alloys [2–4]. The bonds were strongest on Pd, followed by Cu, Au and Ag. It was further shown that dissociative adsorption of H_2S is exothermic on a number of (111) transition metal surfaces (pure Ag, Au, Cu, Ir, Ni, Pd, Pt), but with rather high kinetic barriers on the Ag(111) and Au(111) surfaces [3,12,13]. A few studies also investigated formation of sulfides, which is an additional hindrance to sulfur-tolerant membranes. DFT calculated formation energies of various binary sulfides have

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been used to assess the tendency of different Pd-based alloys to form bulk sulfide phases which cannot be easily removed [8], while Pd_4S-similar clusters at alloy slabs were seen as a precursor to sulfide formation and thus membrane collapse [4].

Our approach in this study is to investigate the adsorption strength of sulfur on the surface of various ternary Pd–Ag-based alloys. The aim is to enhance sulfur tolerance of Pd_3Ag while maintaining the high hydrogen permeability of this alloy. We have thus used theoretical modeling of ternary Pd–Ag–TM alloys with the aim to improve their sulfur tolerance. This should provide theoretical support for the choice of transition metals improving the sulfur resistance of Pd–Ag-based membranes. We have first investigated the segregation behavior of various ternary Pd-based alloy materials with and without sulfur adsorbed. This was needed to properly calculate the strength of sulfur adsorption on alloy surfaces, which is a measure of how easily active sites are blocked from hydrogen adsorption and penetration. The adsorption strength was quantified by calculating the temperature at which adsorbed S will be released to S in the form of H_2S in the gas phase, given a certain S surface coverage. A higher release temperature means that sulfur adsorbs more strongly on the surface, and may be trapped there at the working temperatures of the membrane. The main hypothesis of this work was that the sulfur adsorption energy thus can serve to rank and exclude elements from the pool of potential additives.

It is important to be aware that other effects may also govern the sulfur tolerance of Pd-based membranes. One is the formation of Pd_4S in the surface region, which is not possible to remove for certain membrane materials [4]. This means that, even if a compound cannot be excluded by the present study, it does not necessarily mean that it will be a good material for Pd membranes; the main aim of the present work is to exclude non-promising alloy elements through the screening procedure.

2. Methodology

Atomistic simulations of Pd-based materials for membrane applications were performed applying the generalized gradient approximation (GGA) of density functional theory (DFT). The calculations were performed utilizing the Vienna ab initio Simulation Package (VASP) [14,15] which employs plane waves as basis functions and has implemented the projector augmented wave method [16] to represent the core regions. The Perdew–Burke–Ernzerhof (PBE) functional [17] was used to express the exchange correlation contributions. All numerical parameters were thoroughly checked for convergence, and most reported energies are accurate to within approximately 1 meV per unit cell with respect to these parameters. The cut-off energy of the plane wave expansion was 410 eV and the density of k points in the reciprocal space numerical integrations was higher than 25 points/Å^{-1} in all directions. Spin polarization was allowed. When a vacuum layer was inserted to generate a slab geometry, only the Γ point was used in that direction. Temperature was included by using free energies of the gases from standard tables. It was not included explicitly in the slab calculations, since the solid state entropy contributions are normally much smaller than those of the gases.

An appropriate representation of realistic membrane materials using periodic models with a limited size requires some care. The surface properties of these materials have been the primary focus of this study, and slab models were used to represent alloy surfaces of various compositions. The densely packed (111) surface of fcc unit cells was used in all the calculations, since this has previously been demonstrated to give quite reliable results for the catalytic properties of alloy surfaces [18]. In addition, it has been found that this is also the preferred orientation in magnetron sputtered films [10]. A surface unit cell of 2 × 2 was used; this contains four metal atoms, which are sufficient to provide a relatively large range of surface compositions. The thickness of the unit cell was four or five layers, which yield 16 or 20 atoms in the unit cell. One of the sides (the ‘bottom’ layer) was fixed to the bulk crystal structure, representing continuation of the structure into the bulk. Due to the three-dimensional periodicity used in VASP, a vacuum layer was inserted between the slabs to create the surfaces. The thickness of this layer was at least 10 Å, which was enough to avoid interaction between the periodic slabs. Fig. 1 shows an example of a four-layer slab with the composition $Pd_{11}Ag_3TM_2$, where TM = Au. The layers of this particular slab have the compositions Pd_3Au–Pd_2AgAu–Pd_3Ag–Pd_3Ag; this is given the name 301-211 (see Table 1 for definition of these names). A number of such different slab compositions were investigated, in order to probe the effect of different surface compositions, and to calculate the tendency of segregation to and from the surface layer. The different slab compositions are summarized in Table 1.

Slabs with slightly different TM content (with stoichiometry $Pd_{12}Ag_3TM$) were checked, and the results were very similar to those presented here. It thus seems that the conclusions are not very sensitive to the choice of unit cell composition. Note that the

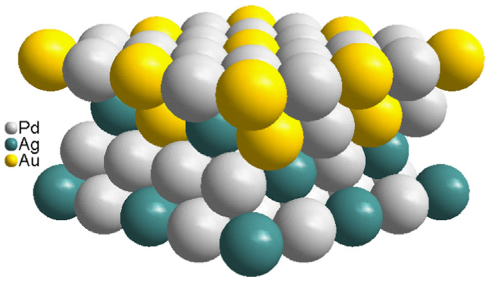

Fig. 1. An example of a slab model with four layers having the stoichiometry $Pd_{11}Ag_3Au_2$. The unit cell consists of four metal atoms per layer, and the atoms are represented as gray (Pd), green (Ag), and yellow (Au) balls. This model is designated 301-211 (see Table 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
The different models used for the $Pd_{11}Ag_3TM_2$ (upper 12) and $Pd_{19}TM$ (lower 3) compositions. The model names are generated by listing the number of atoms of the different types (Pd, Ag, or other transition metal (TM)) for the uppermost two layers. In the case of $Pd_{11}Ag_3TM_2$, the 4th (bottom) layer always consisted of 3 Pd atoms and one Ag atom, and the 3rd layer contained the remaining atoms to achieve the stoichiometry. For $Pd_{19}TM$, the 4th and 5th (bottom) layers always consisted of Pd_4, while the 3rd layer contained the remaining atoms.

Model name	1st layer			2nd layer		
	Pd	Ag	TM	Pd	Ag	TM
400-211	4	0	0	2	1	1
301-310	3	0	1	3	1	0
310-211	3	1	0	2	1	1
301-211	3	0	1	2	1	1
220-301	2	2	0	3	0	1
211-310	2	1	1	3	1	0
202-310	2	0	2	3	1	0
211-211	2	1	1	2	1	1
121-400	1	2	1	4	0	0
112-310	1	1	2	3	1	0
121-301	1	2	1	3	0	1
022-400	0	2	2	4	0	0
400-400	4	0	0	4	0	0
400-301	4	0	0	3	0	1
301-400	3	0	1	4	0	0

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