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

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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 H2S. 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 H2S. 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 H2 containing a fraction of 10−6 H2S, and a slab with adsorbed sulfur in pure H2 atmosphere. This was used to calculate a typical release temperature for sulfur from the surface and a maximal H2S 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, Ti, 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 (H2) diffusion through Pd-based alloys and due to very high H2 fluxes. One such technology is fossil-fuel power plants with integrated carbon capture, where resistance to H2S is a particularly important – H2S 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 H2 flux upon H2S exposure even when bulk sulfidation is not thermodynamically expected [1]. In the latter case, a significant flux decrease has been observed for H2S concentrations as low as a fraction of 2×10−6 for 2 μm thick membranes at 450°C. The H2 flux penalty due to H2S is significant, illustrated by the large reduction in permeability compared to that of the more conventional Pd77Ag23 in the absence of H2S. The ideal Pd-based alloy for such membranes would thus display both sulfide tolerance and a reasonable H2 permeability in the presence of H2S. 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 H2S 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 Pd₄S-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–TM alloys. The aim is to enhance sulfur tolerance of PdAg 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 H₂S 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 Pd₄S 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 Pd₁₁Ag₂TM₂, where TM = Au. The layers of this particular slab have the compositions Pd₄Au–Pd₃AgAu–Pd₃Ag–Pd₃Ag; 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 Pd₁₂Ag₂TM) 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 Pd₁₁Ag₂Au₂. 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>
<thead>
<tr>
<th>Model name</th>
<th>1st layer</th>
<th>2nd layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Ag</td>
<td>TM</td>
</tr>
<tr>
<td>400-211</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>301-310</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>310-211</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>301-211</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>220-301</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>211-310</td>
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</tr>
<tr>
<td>202-310</td>
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<td>0</td>
</tr>
<tr>
<td>211-211</td>
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<td>1</td>
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<tr>
<td>121-400</td>
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<td>112-310</td>
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<tr>
<td>121-301</td>
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</tr>
<tr>
<td>022-400</td>
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<tr>
<td>400-400</td>
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<td>4</td>
<td>0</td>
</tr>
<tr>
<td>301-400</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>
stoichiometry of the slab models does not necessarily reflect the overall bulk composition of the alloy; there will always be segregation effects, and the slab compositions only represent the situation that enough TM is present to decorate up to 50% of the upper atomic layer. How an alloy stabilizes the surface composition during operation depends on a number of factors like kinetics, defects, and impurities, and to discuss this is far beyond the scope of this work.

3. Results and discussion

We would like to know how addition of sulfur affects the segregation behavior of the various alloys in our study. This has relevance for the local atomic arrangements and thus for the surface reactivity. It can also influence on the mechanical stability of membranes, since large segregation energies can potentially lead to weakening of the membrane caused by diffusion and phase separation. In order to clarify the effect of sulfur additions, we first calculate segregation of the slab models in vacuum, then with sulfur adsorbed at the surface.

3.1. Segregation of transition metals in binary Pd–TM slabs

As a reference for the ternary slab calculations, computations involving only binary Pd–TM slabs in vacuum were first performed. This is an extension of the work in [19]. These slabs consisted of five layers and a surface unit cell of $2 \times 2$. The stoichiometry of these slabs was Pd$_{15}$TM; thus only one transition metal was included in an otherwise pure Pd slab. The segregation tendency of TM in Pd was assessed by the segregation energies $E_{\text{seg1}}$, which were defined as

$$E_{\text{seg1}} = E(301 - 400) - E(400 - 400) \quad (1a)$$

$$E_{\text{seg2}} = E(400 - 301) - E(400 - 400) \quad (1b)$$

Here $E$ is the total electronic energy as calculated by VASP, and the numbers refer to the model names defined in Table 1. Thus, $E_{\text{seg1}}$ ($E_{\text{seg2}}$) quantifies the tendency to move from the 3rd or middle layer of the slab to the surface (subsurface) layer. If we assume that the middle layer of the slab is representative of the bulk, this means that a positive segregation energy implies the tendency of a TM atom to move away from the surface or subsurface layer, towards the bulk. A negative segregation energy means segregation towards the surface or subsurface layer. The calculated segregation energies have been plotted in Fig. 2.

We see that there is a similar trend across the periodic table for the 3d, 4d, and 5d transition metals. $E_{\text{seg1}}$ first increases with increasing atomic number, then it decreases. This must be a trade-off between the surface energy of the metals and the size of the atoms. A large atom gains more energy when going to the surface simply due to geometry; on the other hand, the surface energy of a metal decreases approximately with the cube of the atomic size [20]. Segregation to the uppermost layer is seen to be beneficial only for the largest atoms – to the right of Zn, Pd, and Pt in the periodic table. It is not surprising that the balance between size and surface energy appears approximately at the same column in the periodic table, since the relationship in [20] does not depend on the row. This is consistent with experimental findings; e.g. in Pd–Ag alloys it is seen that the outermost atomic layer consists of pure Ag in vacuum, see e.g. [21].

The segregation to the subsurface layer follows a quite similar trend, first increasing and then decreasing as we move to the right in the periodic table. In this case, however, $E_{\text{seg2}}$ is negative or only slightly positive in all the cases, which means that segregation towards the subsurface layer is thermodynamically much more favorable than towards the surface layer. Here this can be explained by the geometric effect being much more important than the surface energy, since atoms in the subsurface layer do not contribute directly to the surface energy. Only when the curve of $E_{\text{seg1}}$ is below that of $E_{\text{seg2}}$, segregation to the surface layer can be expected; this is the case to the right of Pd and Pt for the 4d and 5d metals only. This means that an oscillatory behavior of the TM content can be expected when plotted against the layer number. This has been seen previously for similar systems, both experimentally and theoretically (see, e.g. [22] and references therein).

It is now interesting to see whether the presence of Ag influences the segregation tendency of TM additives. Since the ternary models only contained four layers in order to save computational resources, a segregation energy similar to that defined in Eq. (1) cannot be defined in this case. Instead, we now use the difference in energy between layers 1 and 2 as our segregation energy; $E_{\text{seg12}} = E_{\text{seg1}} - E_{\text{seg2}}$ for the binary models. This provides the tendency to move from layer 2 to 1, and does not give direct information about segregation from the bulk to the surface layer; we use it here in order to compare directly the binary and ternary alloys. In the case of the ternary models, this was calculated as

$$E_{\text{seg12}} = E(211 - 310) - E(310 - 211) \quad (2)$$

A positive (negative) $E_{\text{seg12}}$ implies a tendency to segregate from (to) the uppermost surface layer, relative to the subsurface layer. This has been plotted for the binary and ternary models in Fig. 3. It is encouraging to see how closely the curves follow each other for the binary and ternary models. This means that the presence of Ag does not mean much for the qualitative surface segregation behavior of the TM atoms, despite increased segregation energies for the most positive energies. It also means that the four-layer models are of similar quality as the models with five layers for the study of atomistic segregation of these surfaces. An important conclusion from these observations is that a surface which only has been into contact with vacuum will primarily consist of pure Pd, except for the elements with a negative $E_{\text{seg12}}$: La, Ag, Cd, Sn, Au, Hg, Ti, Pb and Bi. Due to the similarity with binary membranes, we can safely assume that the same surface segregation will be seen relative to the bulk as relative to layer 2. We know that this can be reversed by contact with e.g. hydrogen gas [23], but this has not been studied for the present systems yet.
3.2. Adsorption of sulfur on the alloy surfaces

We now turn to the adsorption of sulfur on the alloy surfaces. In this study a sulfur coverage of 0.25 monolayers (ML) was used, which is one S atom per unit cell. This has been depicted in Fig. 4 for the Pd$_{11}$Ag$_3$Au$_2$ model from Fig. 1. The sulfur atom was placed at the threefold hollow site before relaxation, following previous knowledge about sulfur adsorption on Pd [2]. In most of the cases the relaxation procedure did not change this significantly, except in situations where the initial site was between surface atoms with very different affinity towards S. As an example, S moved towards the Pd–Pd bridge position when starting from a site with two Pd neighbors (with a strong affinity towards S) and one Ag neighbor (with weaker S affinity).

For models with more than one element at the surface, there is also more than one inequivalent threefold site within the surface unit cell. We have therefore calculated the adsorption energy of most inequivalent threefold sites, except those which obviously display significantly weaker S adsorption than that of the Pd$_3$ threefold site. We have in all cases used the site with fcc stacking, which means that the metal atom directly below is in the 3rd layer, and not the one with hcp stacking, which has a metal atom directly below in the 2nd layer. This means that we may have neglected some situations where S binds more strongly to an atom in the 2nd layer at the hcp site. However, since it is likely that this effect is significantly weaker than direct bonding to a surface atom, we expect that this has not influenced our conclusions.

We first present the calculated adsorption energies $E_{\text{ads}}$ which are computed according to the formula

$$E_{\text{ads}} = E(\text{Slab} + \text{adsorbed S}) + E(\text{H}_2(\text{gas})) - E(\text{Slab}) - E(\text{H}_2S(\text{gas}))$$

That is, the adsorption energy is defined as the relative binding strength of sulfur at the surface with hydrogen existing as H$_2$ gas, compared to sulfur released in the gas phase as H$_2$S. The slab models being compared are the same with and without adsorbed sulfur. The energies of H$_2$ and H$_2$S have been calculated by placing the molecules in a large periodic unit cell with sufficient vacuum between the molecules to avoid interaction between the periodic images. Competing adsorption of hydrogen was not considered, since tests have shown that this does not influence the results significantly [4]. Table 2 presents $E_{\text{ads}}$ for the models containing Cu as an example.

We see that the adsorption energies range from $-1.45$ to $-1.12$ eV for the 10 different adsorption models that were studied. The most stable adsorption energy ($-1.45$ eV) is selected as 'the' adsorption energy in what follows, since the most stable adsorption is most relevant for the temperature where S in the adsorbed state is released to the gas phase as H$_2$S (assuming full surface coverage of S).

We note that the most stable adsorption on Pd–Ag–Cu can be found at the 202-310 model. This should be compared to the energy of the pure models, where model 400-211 with the pure Pd surface is most stable (this can be read out of Fig. 3, since the segregation energy of Cu is positive). One could argue that only the most stable pure surface (400-211) should be considered, since solid state diffusion of Cu from subsurface to the surface layer would be necessary to obtain a surface similar to that of models 202-310 (with 50% Pd and 50% Cu) from the surface of model 400-211 (with 100% Pd). However, it is established that such diffusion can happen at temperatures relevant for membrane operation. Also, it is likely that this happens already during activation of the membrane, where the presence of oxygen and/or hydrogen can reverse the segregation of the uppermost atom layers. Previous research on supported films [24–28] has shown that membranes must be activated by exposure to air or other oxidizing atmospheres at a temperature in the range of 300–400 °C in order to obtain values for the hydrogen permeability representative for bulk diffusion.

The adsorption energies calculated along the lines above have been presented in Fig. 5 for the ternary models, compared with binary Pd$_3$Ag and pure Pd. We first note that there is a trend across

**Table 2**

<table>
<thead>
<tr>
<th>Model</th>
<th>Surface neighbors</th>
<th>$E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-211</td>
<td>Pd$_1$</td>
<td>$-1.24$</td>
</tr>
<tr>
<td>301-211</td>
<td>Pd$_{10}$TM</td>
<td>$-1.33$</td>
</tr>
<tr>
<td></td>
<td>Pd$_2$</td>
<td>$-1.45$</td>
</tr>
<tr>
<td>202-310</td>
<td>Pd$_{10}$TM</td>
<td>$-1.45$</td>
</tr>
<tr>
<td></td>
<td>Pd$_{12}$TM</td>
<td>$-1.43$</td>
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<tr>
<td>310-211</td>
<td>Pd$_1$</td>
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</tr>
<tr>
<td>211-211</td>
<td>Pd$_{12}$TM</td>
<td>$-1.37$</td>
</tr>
<tr>
<td>112-310</td>
<td>Pd$_{10}$TM</td>
<td>$-1.38$</td>
</tr>
<tr>
<td>121-301</td>
<td>Pd$_{12}$TM</td>
<td>$-1.12$</td>
</tr>
<tr>
<td>022-400</td>
<td>Ag$_{12}$TM</td>
<td>$-1.24$</td>
</tr>
</tbody>
</table>
the periodic table, albeit not as clear as for the segregation behavior; the adsorption energy is first decreasing, and then increasing when the atom number increases within a row. The trend is consistent with the trend for transition metal–sulfur binding energies (defined as the cohesive energy per metal–sulfur bond) across the periodic table [29]. We also see that, compared to the adsorption energy on pure Pd, most of the ternary models exhibit a significantly stronger adsorption (more negative adsorption energy) of S. This indicates a very strong binding of sulfur on these compounds, and may be used to exclude many of the metals as good additives for sulfur resistance – if strong sulfur adsorption automatically designates blocking of surface sites for hydrogen adsorption. The most favorable additives in this respect can be found in almost the same regions where surface segregation is favorable; to the right of Ni, Rh, and Pt in the periodic table.

Even if the information in Fig. 5 can already be used to indicate tendencies of sulfur adsorption on ternary membrane materials, it is more useful to quantify the effect of stronger adsorption energies in terms of the lowest release temperature \( T_{\text{rel}} \) at which adsorbed sulfur on the 111 surface will react with \( \text{H}_2 \) to form gaseous \( \text{H}_2\text{S} \) and \( \text{S} \) thus is released from the surface. We have done this by using literature data for the Gibbs free energy of the gas species \( \text{H}_2 \) and \( \text{H}_2\text{S} \) (\( \Delta G_{\text{H}_2\text{S}} \) and \( \Delta G_{\text{H}_2} \)) for comparison, and neglecting the entropy and temperature dependence of the adsorption strength (which should be very small compared to that of the gases). This has been included in a comparison of the surface free energy of the surface with adsorbed sulfur \( G_{\text{surf(Ads)}} \) with the surface free energy of the pure slab \( G_{\text{surf(Slab)}} \):

\[
G_{\text{surf(Ads)}} - G_{\text{surf(Slab)}} = [E_{\text{ads}} + \Delta G_{\text{H}_2\text{S}} - \Delta G_{\text{H}_2}] - RT \ln(p_{\text{H}_2\text{S}}/p_{\text{H}_2})/A
\]

The surface unit cell area is \( A \), and the partial pressures \( p_{\text{H}_2} \) and \( p_{\text{H}_2\text{S}} \) of \( \text{H}_2 \) and \( \text{H}_2\text{S} \) are the only remaining parameters; we assume that \( p_{\text{H}_2\text{S}}/p_{\text{H}_2} = 20 \times 10^{-6} \) in the following. The release temperature \( T_{\text{rel}} \) for the adsorbed S species can now be found by solving the equation

\[
G_{\text{surf(Ads)}} - G_{\text{surf(Slab)}} = 0
\]

That is, when the surface free energy of the surface with adsorbate is higher (less stable) than that of the pure surface (or more relevant, vacant surface adsorption sites corresponding to a locally pure surface), \( S \) will combine with \( \text{H}_2 \) in the gas phase to form \( \text{H}_2\text{S} \). A second order polynomial parameterization of the experimental free energies was used in order to solve Eq. (5) analytically. Alternatively, Eq. (5) can be used to quantify the \( \text{H}_2\text{S} \) pressure at which the surface will be covered with \( S \) at a given temperature. We have used \( T=450 \, ^\circ\text{C} \) for such calculations. The results are displayed in Fig. 6.

We can now draw some conclusions from our results. First of all, we need to define a threshold for \( T_{\text{rel}} \) reflecting typical operating conditions, which can be used as a criterion for potential additives. We have chosen to use the requirement \( T_{\text{rel}} < 600 \, ^\circ\text{C} \) when \( p_{\text{H}_2\text{S}}/p_{\text{H}_2} = 20 \times 10^{-6} \), based on experience with such systems and the available literature. This is equivalent with requiring that the maximal hydrogen adsorption \( p_{\text{H}_2\text{S}}/p_{\text{H}_2} > 0.3 \times 10^{-9} \) when \( T=450 \, ^\circ\text{C} \). With this requirement, we can conclude that Mn, Cu, Zn, Ga, Cd, In, Sn, Pt, Au, Hg, Ti, Pb, and Bi are potential additives. Following our starting hypothesis, this means we cannot exclude them from further study, since their sulfur adsorption strength is rather low. Another way of stating this is that the above-mentioned additives will not lead to significant blocking of hydrogen adsorption sites by sulfur, which means that the hydrogen permeability will not be drastically reduced compared to pure Pd,Ag when \( \text{H}_2\text{S} \) is present. This evaluation does not take into account the possible blocking of hydrogen adsorption sites by sulfur, which means that the hydrogen permeability will not be drastically reduced compared to pure Pd,Ag when \( \text{H}_2\text{S} \) is present. This evaluation does not take into account the possible blocking of hydrogen adsorption sites by sulfur, which means that the hydrogen permeability will not be drastically reduced compared to pure Pd,Ag when \( \text{H}_2\text{S} \) is present. 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This evaluation does not take into account the possible blocking of hydrogen adsorption sites by sulfur, which means that the hydrogen permeability will not be drastically reduced compared to pure Pd,Ag when \( \text{H}_2\text{S} \) is present. This evaluation does not take into account the possible blocking of hydrogen adsorption sites by sulfur, which means that the hydrogen permeability will not be drastically reduced compared to pure Pd,Ag when \( \text{H}_2\text{S} \) is present. This evaluation does not take into account the possible blocking of hydrogen ad...
account other important issues like toxicity and volatility, which obviously will reduce the above list of potential additives. Among the remaining promising additives in this respect are Cu and Au, which are already known to be beneficial additives in binary Pd alloys.

It is important to be aware of the relatively large uncertainty connected with DFT calculations, primarily because the exchange-correlation term is not represented exactly (we used the PBE-GGA). The calculated energies can usually be trusted within a range of 0.1 eV; this corresponds to a change of around 60 °C in the release temperature and a factor of around 5 in the maximal \( H_2 \)S pressure. This should not be confused with the numerical accuracy of our calculations, which is in the order of 1 meV. Furthermore, only one surface termination has been studied (the close-packed (111) surface), and other surfaces could exhibit higher sulfur tolerance for some of the excluded ternary compounds. Even if these are less abundant surfaces than the (111) surface (which is most stable for most fcc metals), they may exist in large enough quantities to allow for efficient transport through the surface despite the (111) surface being blocked by strongly adsorbed S. Also, we have only used one value of \( p_{H_2S}/p_{H_2} \) in Fig. 6(a), 20 × 10⁻¹⁰. If this is reduced (increased) by an order of magnitude, the release temperature decreases (increases) by around 100 °C from a level of around 500 °C. Accordingly, if the temperature in Fig. 6(b) is increased by 100 °C, the maximal \( H_2 \)S concentration increases by around an order of magnitude. Finally, it may be reasonable to open for alloys with slightly higher release temperatures than the intuitive threshold, since a certain exchange of adsorbates can also be expected below the release temperature. If we assume that all this adds up to choosing 800 °C as our threshold temperature (corresponding to a maximal \( H_2 \)S concentration of \( 1.4 \times 10^{-10} \)), we should also include Fe, Co, and Y among the potential additives.

How does that compare to experiments? A recent study of ternary Pd–Ag–TM membranes compared how rapidly the hydrogen flux dropped and recovered for membranes with TM = Au, Cu, Mo, and Y [30]. According to our hypothesis, Au and Cu should perform well in this respect, Y should be intermediate, while the Pd–Ag–Mo membrane should be completely blocked by sulfur due to the strong binding energy between Mo and S. This is true for Au and Cu, which both lead to enhanced \( H_2 \) flux recovery rates from \( H_2 \)S contamination compared to pure Pd–Ag membranes. However, it turns out that the Pd–Ag–Mo membrane did not perform any worse than the others; contrary, it exhibited faster \( H_2 \) flux recovery from \( H_2 \)S contamination in relative terms than all the other membranes in the study (Fig. 3 in Ref. [30]). This means that the sulfur adsorption energy cannot be the only descriptor for sulfur inhibition. We believe that a rationalization may be found in a description of a potential TM additive to Pd–Ag: it should be present in the surface region (i.e. not too strong segregation towards the bulk) and it should not bind sulfur too strongly (i.e. not too high release temperature of \( S \)).

In effect we return to almost the same conclusions as our original hypothesis, due to the already mentioned correspondence between S adsorption strength and segregation tendency. The remaining question is where to place the threshold for ‘allowed’ segregation energies: How large segregation energy \( E_{seg12} \) designates ‘too strong’ segregation? To require \( E_{seg12} < 0 \) (segregation towards surface) is clearly too strict, since temperature and entropy would lead to finite population of TM at the surface even with \( E_{seg12} > 0 \). Also, as mentioned before, we can only expect our DFT calculations to be reliable within ~0.1 eV. A reasonable requirement could thus be \( E_{seg12} < 0.2 \) eV. This combined with the requirement \( T_{rel} < 600 °C \) leads to the following potential additives: Cu, Zn, Ga, Cd, In, Sn, Pt, Au, Hg, Ti, Pb, and Bi. If the requirement is lifted to \( E_{seg12} < 0.4 \) eV and \( T_{rel} < 800 °C \), Co and Y can also be included among the potential ones.

The present study did not investigate sulfide formation. As discussed above, the irreparable formation of Pd₄S₈ at the surface region may be most detrimental for the performance of Pd-based hydrogen membranes, leading to failure of the membrane. This study should thus be complemented by a screening of the most promising materials with respect to sulfide formation in order to reach a more conclusive recommendation. This may also include the formation of Ag sulfides, Cu sulfides and mixed metal sulfides. Such a study is under way [34]. Furthermore, the added transition metals may change the diffusivity and solubility of hydrogen in the bulk alloy, even at rather low concentration – this effect is presently under investigation in our laboratory [10,30]. Another possible effect of adding a third element to PdAg based membranes is to change the kinetics of dissociative hydrogen adsorption at the alloy surface, as well as the reverse desorption reaction on the permeate side. Finally, the interplay with other adsorbents like \( H_2 \), \( H_2O \), or CO₂ could shed further light on how to design optimized materials for particular membrane applications.

The only exception is La, which exhibits both a very high calculated release temperature and clear tendency to segregate towards the surface.

We may nevertheless learn important lessons from the present results. It is instructive to note that pure Pd and Pd–Ag are among the systems with lowest release temperature in this study, even if it is well-known that they exhibit poor sulfur resistance. The main reason for this is the detrimental formation of sulfides like Pd₄S₈, which leads to loss of membrane material and eventual rupture and breakdown. This was exemplified by a recent experimental study, which showed that Au is among the most promising additives for improving sulfur tolerance compared to pure Pd and the Pd–Cu alloy system [31,32]. The most important role of Au is then to hinder irreparable formation of Pd₄S₈ in the surface layer, since this is much less pronounced for Pd–Cu and Pd–Au alloys than for pure Pd and Pd–Ag alloys. This is consistent with previous atomistic calculations which concluded that formation of Pd₄S₈ was thermodynamically feasible for most pure Pd and binary Pd–Ag surfaces, while Pd–Cu and Pd–Au did not display such behavior [33].
4. Conclusions

This modeling study was performed to identify potential transition metal (TM) additives that can be used to improve sulfur tolerance of ternary Pd–Ag–TM membrane alloys. It was found that the atomic segregation of TMs played an important role in the stability of adsorbed sulfur on the alloy surface. Without the presence of sulfur, only a few elements were found to segregate to the surface layer of Pd or Pd–Ag. This was reversed for many of the additives when sulfur was adsorbed on the surface of ternary Pd–Ag–TM compounds. The reason for this effect was due to formation of very stable sulfur adsorbates, which correlate with bulk sulfides with large formation energies. The tendency to sulfur adsorption was quantified by the free energy of adsorption, which was used to calculate a ‘release’ temperature; this was defined as the temperature at which sulfur adsorption is not energetically favored in a gas mixture of H₂ containing a fraction of 20%.

References