

# Hydrogen Dissociation on Palladium-Sulfide Surfaces

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## Introduction

Dense, Pd-based membranes have received significant attention for separation of H<sub>2</sub> from mixed gas streams, such as syngas produced from coal. Pd readily adsorbs and dissociates molecular hydrogen and subsequently allows rapid transport of the hydrogen-atoms through its bulk. Recombination of hydrogen-atoms on the opposite surface of the membrane and desorption of molecular hydrogen completes a sequence that effectively separates hydrogen from all other components of the mixed gas stream [1].

Exposure of the metallic membrane to sulfur gases, such as H<sub>2</sub>S, can reduce transport rates by poisoning the ability of the surface to dissociate hydrogen and/or by reacting with the membrane to form a metal-sulfide layer that impedes H-atom diffusion through the bulk. Our previous reports of non-zero hydrogen transport through a palladium membrane with a Pd<sub>4</sub>S scale layer suggest that the Pd<sub>4</sub>S surface itself is active for hydrogen dissociation [2, 3]. The goal of this work is to acquire a fundamental understanding of hydrogen dissociation on the Pd<sub>4</sub>S surface by experimentally characterizing its composition and applying the first-principles Density Functional Theory (DFT) method to examine dissociation pathways and energetics. We demonstrate that Pd<sub>4</sub>S surfaces can possess significant dissociation activity, suggesting that low rates of H-atom diffusion through the Pd<sub>4</sub>S bulk may limit overall transport rates in the separation application.

## Materials and Methods

A 100 micron thick Pd foil was converted to Pd<sub>4</sub>S by exposure to H<sub>2</sub>S at 650 C. The product Pd<sub>4</sub>S foil was mounted in a stainless steel ultrahigh-vacuum (UHV) chamber (10<sup>-10</sup> torr base pressure) for analysis by Angle Resolved X-ray Photoemission Spectroscopy (AR-XPS) and Low Energy Ion (He<sup>+</sup>) Scattering Spectroscopy (LEISS). AR-XPS provides information on the composition depth profile within the near-surface region, ~5-10 atom layers. LEISS probes composition of the top-surface.

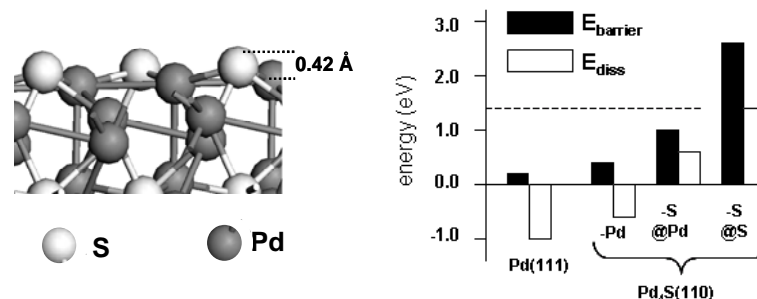
We employed DFT coupled with concepts from thermodynamics to investigate the relative stability of the low-index Pd<sub>4</sub>S surfaces [4,5]. The Nudged Elastic Band (NEB) technique was used to examine the pathways for H<sub>2</sub> dissociation on the surfaces [6].

## Results and Discussion

AR-XPS results confirm Pd:S = 4:1 stoichiometry in the near-surface region of the sulfided palladium—about 5-10 atom layers. LEISS analysis suggests that the top-layer may be slightly enriched in S relative to the rest of the near-surface. DFT calculations show that, for each of the Pd<sub>4</sub>S low-index planes (111, 100, 110, 001), an “S-terminated” variant—in which S

atoms reside slightly above surface Pd atoms (for example, Figure 1 illustrates the sulfur-terminated Pd<sub>4</sub>S(110) surface)—is most stable.

Dissociation energies and barrier heights to dissociation were calculated for the low-index Pd<sub>4</sub>S terminations. Results for Pd<sub>4</sub>S(110), which are typical for all Pd<sub>4</sub>S terminations, are compared to clean Pd(111) in Figure 2. Relative to Pd(111), dissociation barriers and energies are less favorable for both the S-terminated (“-S”) and Pd-terminated (“-Pd”) surfaces of Pd<sub>4</sub>S(110). Dissociation energetics on the S-terminated faces depend significantly on reaction pathway: a mechanism in which H<sub>2</sub> interacts primarily with surface Pd atoms (“@Pd”) is more favorable than one in which H<sub>2</sub> interacts with surface S atoms (“@S”).



**Figure 1.** Side view of the S-terminated Pd<sub>4</sub>S(110) surface. Topmost S atoms reside above the plane of topmost Pd atoms

**Figure 2.** Energy diagrams for H<sub>2</sub> dissociation on Pd(111) and Pd<sub>4</sub>S(110) surfaces. Dotted line shows TST-estimation of the “critical” barrier height for the separation application

For reference, the dissociation barrier height at which dissociation becomes the rate-limiting step in the dissociation-H-diffusion separation sequence, estimated by Transition-State Theory (TST), is shown as the dotted line in Figure 2. Reaction paths having E<sub>barrier</sub> lower than the “rate-limiting” value exist on both the Pd- and S-terminated Pd<sub>4</sub>S surfaces, demonstrating the possibility that low rates of H-atom diffusion through the Pd<sub>4</sub>S bulk, and not dissociation rates, limit overall transport rates in the separation application.

## Significance

These results contribute to the basis for rational design of poison-tolerant dense metal H<sub>2</sub> purification membrane systems and to understanding of Pd-catalysis in general.

## References

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