Supplementary Information for "Hydrogen weakens interlayer bonding in layered transition metal sulfide $Fe_{1+x}S$"

Aravind Krishnamoorthy[1,2], Minh A. Dinh[1,3], and Bilge Yildiz[1,2,3,*]

[1]Laboratory for Electrochemical Interfaces, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

[2]Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

[3]Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

*Email - aravindk@mit.edu

Keywords: Hydrogen, embrittlement, passive film, corrosion, van der Waals, transition metal chalcogenide, exfoliation

1. Comparison of results from the DFT-D2 and optB86b functionals

In Figure S1, we compare the tensile stress-strain diagrams computed for mackinawite crystals containing both types of hydrogen interstitials (at 50% concentration) as well as hydrogen-free mackinawite crystals using both the DFT-D2 functional as well as the optB86b functional. The primary difference between these two non-local correlation functionals is that the semi-empirical DFT-D2 functional contains fitting parameters (named C6 and R0) that can be freely varied. The optB86b does not contain any analogous empirically variable parameters. The figure demonstrates that while the DFT-D2 functional systematically underestimates van der Waals binding energies, the trends between the different interstitial types are remarkably similar between the two different functionals.

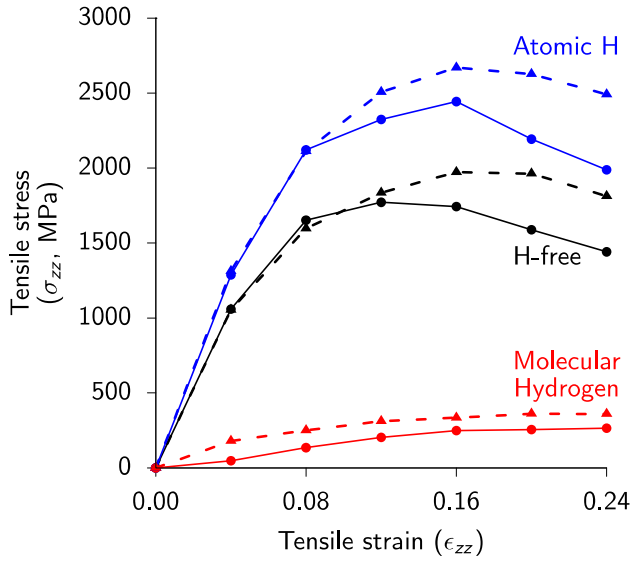

Figure S1: The tensile stress-strain curve for mackinawite crystals containing different configurations of hydrogen interstitials computed using the DFT-D2 (solid/circles) and optB86b (dashed/triangles) correlation functionals shows that the qualitative behavior of the interstitial configurations is consistent between the two different functional types.

2. Influence of hydrogen concentration on the mechanical properties of hydrogenated mackinawite

In order to understand the dependence of the weakening of interlaminar binding on the hydrogen concentration, we calculated the stress-response of mackinawite crystals to uniaxial tensile strain ε_{zz} along the [001] direction for three different hydrogen defect concentrations, H:Fe = 0, 0.125 and 0.50 respectively. Figure S2 shows that even at the relatively lower hydrogen defect concentration of 0.125, which corresponds to a single H_2 molecule in the interlaminar region and is therefore the lowest possible defect concentration in this simulation setup, there is a significant weakening of interlayer binding resulting in a 80% reduction in tensile strength.

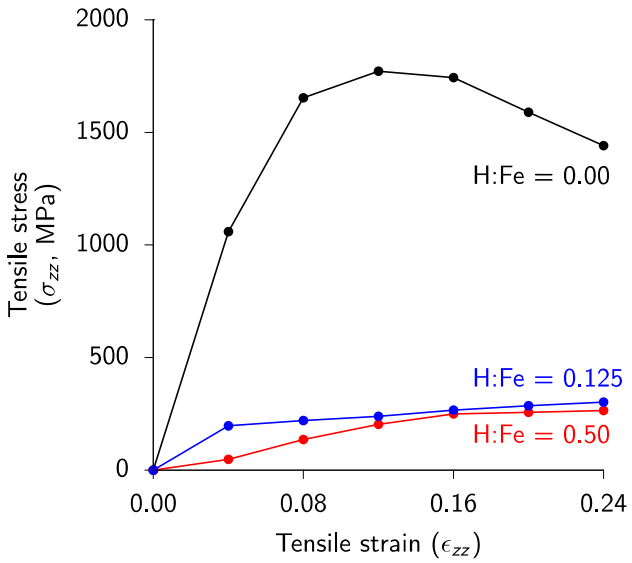

Figure S2: The tensile stress-strain curve for mackinawite crystals containing different concentrations of molecular hydrogen interstitials show that even lower concentrations of hydrogen result in significant decrease in interlayer van der Waals binding.