Self-Assembling Monolayers to Reduce Hydrogen Permeation in Canadian Pipelines

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1 Abstract

2 Introduction

The government of Canada is working on powering a sustainable and clean energy economy with hydrogen. In accordance with the goals set in the Canada 2030 Emissions program [1], there is a need for high volume transportation of hydrogen gas to various parts of the nation. Many different institutions are working on the production, testing and utilization of hydrogen and hydrogen-based systems. An important factor in the realization of the hydrogen economy is the transportation goals, which need to be met, for the equipment to be functioning. Government of Canada plans to send hydrogen blended with natural gas through the Canadian pipelines spreading out 840,000 km [2].

Fundamental problem with transporting hydrogen through the current aged pipelines is hydrogen embrittlement. Hydrogen embrittlement occurs when metals become brittle as a result of the introduction and diffusion of hydrogen into the metal. In aged pipelines, there are numerous "stress sites", which are fractures, cracks, wears and tears due to environmental impact on the pipeline steel, which are highly susceptible to hydrogen diffusion and thus embrittlement. A plan to change all existing networks, along with shorter life span of an average pipeline makes it economically responsible to transport hydrogen through the current infrastructure. There is a need for a coating which can re-purpose current pipelines for transport of hydrogen.

3 Research Approach

We worked with the hypothesis: "Self-assembled monolayer coatings that are just a few molecules in thickness will reduce the diffusion of hydrogen gas through steels used in Canadian pipelines, thereby mitigating the risk of catastrophic failure arising from hydrogen embrittlement." There has been previous research on the topic based around thick coatings, which increased the risk of hydrogen embrittlement. This was because hydrogen would diffuse through the coating and form a layer of concentration in the fractures, causing a higher amount of hydrogen flux through the steel. We hypothesize that fundamental research of a monolayer, single molecular layer thick, would negate the problem of increased concentration while reducing the hydrogen flux, and as a result reduce the risk of hydrogen embrittlement.

In our experiment we use Fluoroalkyl (C10) phosphonic acid [Fig. 1]. FPA has already been researched for its monolayer deposit methods as well as hydrophobicity on metallic surfaces. Another reason for choice of FPA is due to the self-assembling nature of the molecule. The deposit method is as follows: first we clean the sample coupon using, sonication methods, with acetone, methanol and DI water. After which the coupon is heated at 100°C for 30 minutes. After which it is placed in a solution of Methanol and FPA for 24 hours to allow for assembling of the monolayer. 24 hours later it is removed from the solution, rinsed in methanol, dried, and again heated for 30 minutes at 100°C. The phosphonic acid group ionically bonds[Fig. 1] with the first layer of iron atoms, creating a strong bond, unlikely to deteriorate over time . The fluoroalkyl groups create steric hindrance, demotivating the molecular hydrogen molecule to dissociate and pass through the steel.

Contact angles[Fig. 2] were measured to test the existence of the monolayer as well as the hydrophobicity of the coating. Results showcased a 116° angle with the monolayer on compared to 31.5° on dry steel, proving to us that the monolayer is indeed deposited and hydrophobic. X-ray photo-electron spectroscopy (XPS) further confirms presence of monolayer[Fig.3]. Since the coating is largely a long fluorine chain, we can see the fluorine spike in the XPS results. The XPS machine used in this use case measures the first 10nm of the material given (i.e. steel coupon). Since the first 10nm of the monolayer applied steel shows Iron as well as Fluorine, we can infer that we have a thin coating that is few molecules thick at most.

4 Experimental Design

To simulate pipeline hydrogen conditions inside the lab, we used a Devanathan-Stachurski H-cell [4]. Figure 5 shows the use of 2 permeation cells with the metal sample in the middle. A power supply was used to provide current to the platinum control electrodes, causing hydrolysis, in the entry cell, near the sample. This simulated the effect of hydrogen gas being present near the membrane of the steel pipelines. The entry cell is filled with 0.1M $NaSO_4$, and the exit cell is filled with 0.1M $NaOH$ solution. As the hydrogen passes through the steel sample, it is oxidized in the exit cell, releasing an electron. We then used an electrode to measure the electron current in the exit cell. Using this current, we can use techniques (as described in textbook [3] to determine the hydrogen flux, and hydrogen diffusion coefficient [3] (measure of hydrogen permeability of a material). In our experiments, we tested stainless steel 430 (430SS) and API 5L X70 steel (X70) under identical controlled environments. Our key indicators for minimized hydrogen embrittlement are the hydrogen

diffusion coefficient and flux. Flux quantifies the mols of hydrogen passing through a m2 of area of steel per second (mol/m2s) and hydrogen diffusion coefficient, which is a direct measure of hydrogen permeation quality of the material tested. The goal is to minimize both indicators through use of FPA monolayer, thus reducing the risk of hydrogen embrittlement in Canadian pipelines.

5 Results

The results [Fig. 8] are shown in graphs for 430SS [Fig. 6] and X70 [Fig. 7]. The following tables display the hydrogen diffusion coefficient and flux of each steel sample tested and their monolayer versions.

Value	430SS	430SS with Monolayer
Hydrogen Diffusion	3.98×10^{-12}	1.77×10^{-12}
Hydrogen Flux	18.72×10^{-8}	7.24×10^{-8}

Value	X70	X70 with Monolayer
Hydrogen Diffusion	4.68×10^{-12}	0.51×10^{-12}
Hydrogen Flux	8.02×10^{-8}	1.45×10^{-8}

We see a 2 times reduction in the hydrogen diffusion coefficient (H. deff) in 430 stainless steels. In the case of X70 steel we see a 10 times reduction in the hydrogen diffusion coefficient. Both the flux and the H. deff are calculated using standard literature methods [3].

6 Discussion

Canadian pipeline is made typically using X70 and X80 steels. A 10 times reduction in the diffusion of hydrogen through these steels outlines possible steps we can take to bring the pipelines up to standard for safely transporting hydrogen gas through. Hydrogen embrittlement is caused by the flux of hydrogen atoms through steel, and thus a reduction in the flux of the steel using our monolayer, we can reduce the risk caused by hydrogen embrittlement. These results showcase that the FPA molecule works at a fundamental level of

small molecules thick, however there are many variables which need to be tested further. We will be testing the durability of the monolayer and its resistance to extreme temperatures, physical trauma and changes in pressurization. For the monolayer to function in a field environment, it must withstand changes in the environment, be resistant to impurity and maintain integrity with minimal loss in volume. Further test planning is currently under progress. Most notably, in coordination with the NRC we are conducting burst disk tests to explore high pressure hydrogen embrittlement burst fracture threads, to understand how the monolayer affects the integrity of the steel. Additionally, acknowledging the symptoms of fluorinated molecules causing environmental deterioration, we will be conducting tests with non-fluorinated phosphonic acid.

7 Conclusion

A hydrogen-based energy economy serves the need for the energy sector to be powered by a clean and renewable resource. Work is progressing on energy production systems utilizing hydrogen as fuel, and as the demand of the gas increases, so must the supply. Government of Canada plans to utilize current pipelines to transport blended hydrogen with natural gas. The key problem being hydrogen embrittlement caused by diffusion of hydrogen atoms through pipeline steel membrane. Our FPA monolayer reduces the ability for hydrogen to dissociate and permeate the steel. We prove a 10 times reduction in the hydrogen diffusion coefficient in pipeline steels (X70). Further work to test integrity over time and trauma is being conducted.

8 Figures

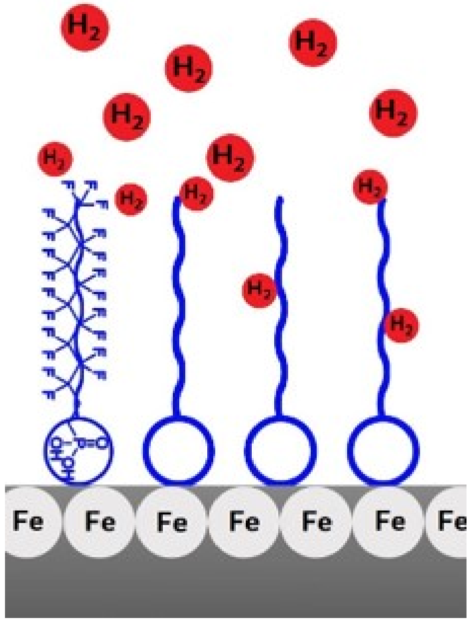

Figure 1: A visual representation of the monolayer at a molecular level. The phosphate-oxide group bonds with the iron on the surface of the steel.

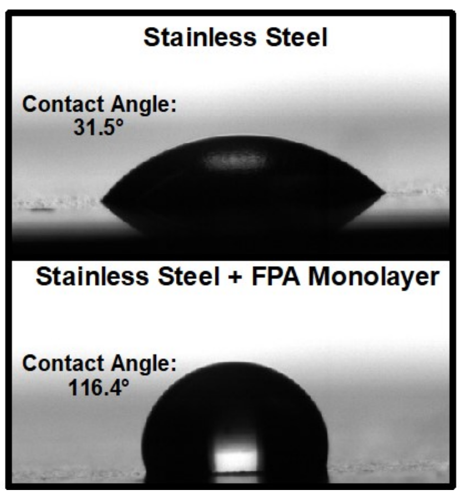

Figure 2: This is the contact angle measurements. The top image shows the steel under normal conditions with a drop of water and the bottom image shows the same steel with a monolayer coating, now displaying hydrophobic qualities.

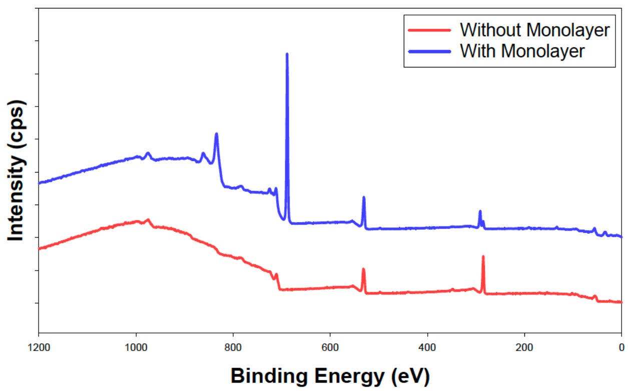

Figure 3: This is the XPS measurements of a monolayer on X70 (blue) and measurement of X70 (red). The peaks showcase the binding energy of each substance on the surface (top 10 nm of the material)

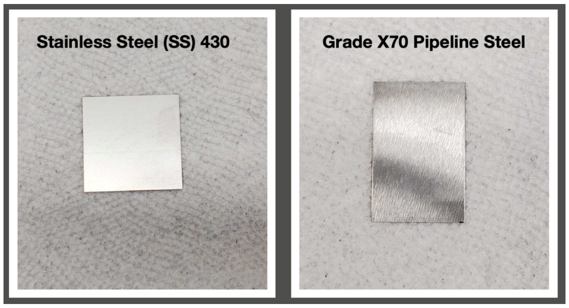

Figure 4: This is a visual aid of the samples used for measurements in the experiment. A 1 inch x 1 inch sample of 430SS and X70.

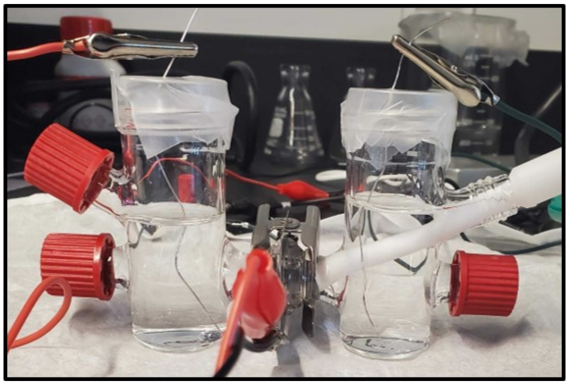

Figure 5: An image of the permeation cell used in the experiment. The samples shown above are sandwiched between these two cells. The left is the entry cell and the right is the exit cell.

Figure 6: Graph showing the current density over time for 430 stainless steel. The red curve shows the steel without the monolayer, while the blue shows the curve after a monolayer is applied to 430 stainless steel.

Figure 7: Graph showing the current density over time for X70. The red curve shows the steel without the monolayer, while the blue shows the curve after a monolayer is applied to X70.

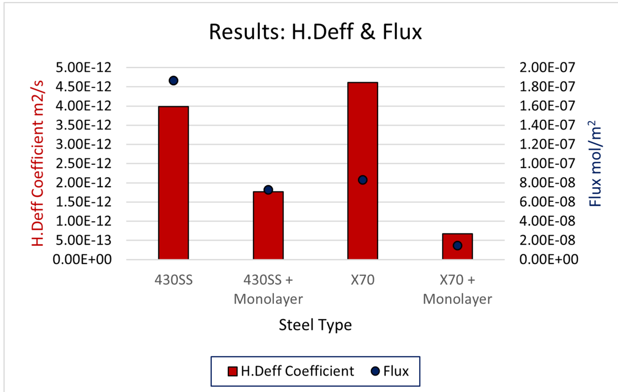

Figure 8: This bar graph shows the hydrogen diffusion coefficient (bar) and the hydrogen flux (dot) of both the steels tested in the experiments.

References

[1] The Hydrogen Strategy for Canada. Clean50 https://clean50.com/projects/lofty-ambitions-for-hydrogen-development-and-implementationof-the-hydrogen-strategy-for-canada

[2] CER - Canada's Pipeline System 2021. https://www.cer-rec.gc.ca/en/data-analysis/facilities-we-regulate/canadas-pipelinesystem/2021/crude-oil-pipeline-transportation-system.html.

[3] Nagumo, M *Fundamentals of Hydrogen Embrittlement* . (Springer Singapore, 2016). doi:10.1007/978-981-10-0161-1.

[4] Danielson, M. J. Use of the Devanathan–Stachurski cell to measure hydrogen permeation in aluminum alloys. Corrosion Science 44, 829–840 (2002).