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Permeation of “Hydromer” Film: An Elastomeric Hydrogen-Capturing Biopolymer

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Permeation of "Hydromer" Film: An Elastomeric Hydrogen-Capturing Biopolymer

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Abstract

This report analyzes the permeation resistance of a novel and proprietary polymer coating for hydrogen isotope resistance that was developed by New Mexico State University. Thermal gravimetric analysis and thermal desoprtion spectroscopy show the polymer is stable thermally to approximately 250 °C. Deuterium gas-driven permeation experiments were conducted at Sandia to explore early evidence (obtained using Brunauer–Emmett–Teller) of the polymer's strong resistance to hydrogen. With a relatively small amount of the polymer in solution (0.15%), a decrease in diffusion by a factor of 2 is observed at 100 and 150 °C. While there was very little reduction in permeability, the preliminary findings reported here are meant to demonstrate the sensitivity of Sandia's permeation measurements and are intended to motivate the future exploration of thicker barriers with greater polymer coverage.

ACKNOWLEDGMENTS

CONTENTS

FIGURES

NOMENCLATURE

AFM	Atomic Force Microscopy
BET	Brunauer–Emmett–Teller
DOE	Department of Energy
FTIR	Fourrier-Transformed Infrared
H	Hydrogen
MS	Mass Spectrometer
NMSU	New Mexico State University
SNL	Sandia National Laboratories
TGA	Thermo-gravimetric Analysis

1. INTRODUCTION

New Mexico State University researchers have discovered a polymer that may act as a barrier to hydrogen permeation, so is a candidate material to reduce profit-draining H_2 losses in oil refining. While NMSU graduate student David Johnson was developing the biological means to produce hydrogen gas [1,2], he discovered a very unusual yeast species that captured and stored H_2. The yeast cells produced a biopolymer outside of the cell that retained hydrogen gas. Intriguingly, as more gas was produced, the elastic polymer stretched to capture and store more gas. Johnson and NMSU professor Geoffrey Smith measured the contents of these bubbles and found the internal gas concentration to range from 50 – 60% H_2 gas. Further work funded by the NMSU business incubator Arrowhead Center revealed that the biopolymer was indeed extruded from the cell, and the polymer has since been purified (Smith et al. Patent Pending.).

The novel biopolymer has been characterized by Brunauer–Emmett–Teller (BET) analysis to show that permeability of H is impeded to below the detection limit of NMSU's equipment. Further characterization by Fourrier-Transformed Infrared (FTIR) spectroscopy has shown that the biopolymer does not match when screened against thousands of known compounds in FTIR libraries from Aldrich Chemical and the Georgia Crime Lab. This novel material can be readily manufactured by vat fermentation and is now being developed for the oil refinery industry as a way to prevent H gas loss due to leakage and pipeline corrosion during processing.

This short report summarizes the first hydrogen permeation tests conducted at Sandia of this novel biopolymer's ability to block hydrogen.

2. EXPERIMENTAL

2.1. ThermoGravimetric Analysis (TGA) and Mass Spectrometry

Initial tests were performed to characterize the outgassing and general volatility of the polymer deposited on a Ni foil. The TGA was used to measure the change in mass of the sample as it is heated. The evolved gas is routed to the MS for identification in units of atomic mass.

Sample prep: 100 uL of approximately 5% hydromer were added to each of four Aluminum TGA crucibles. The filled crucibles were placed in an oven at 50 C for 30 minutes to accelerate water evaporation. The resulting sample formed a white film at the bottom of the crucible.

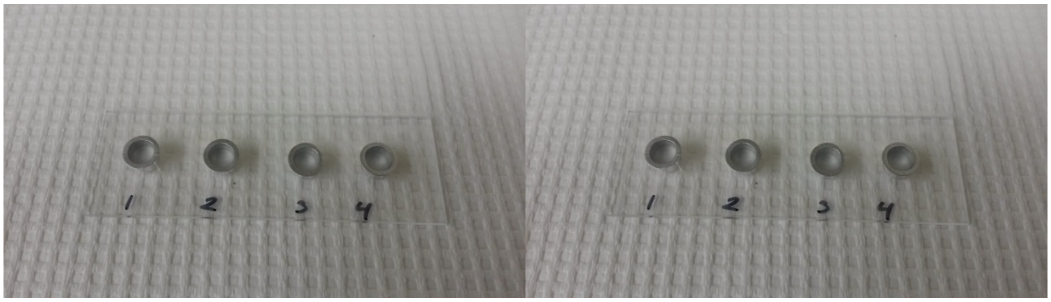

Figure 1. Left, crucibles of hydromer sample before TGA, and right, after TGA. Samples 1 and 2 were analyzed in Ar, while 3 and 4 were analyzed in "air" (N2/O2: 80/20).

The TGA experiment ramps the temperature from RT to 550 ^{o}C at approximately 10 ^{o}C /min. Post-TGA the samples visually had a carbonaceous black appearance. Analysis of TGA-MS data confirmed that indeed gases composed of CO_2 and C were the primary constituents of the mass lost during heating. In both inert (Argon) and simulated air (N_2/O_2: 80/20) atmospheres the significant loss of mass occurs from 250 to 400^{o}C, with a much lower rate of loss occurring before and after this window (See Figs 2 and 3). The loss of mass in Ar shows a stepped progression whereas in N_2/O_2 the loss is much more continuous. In each case the loss of mass is essentially identical.

Based on this data we estimate hydrogen gas permeation studies can be carried out up to 250 ^{o}C, before the film begins to degrade.

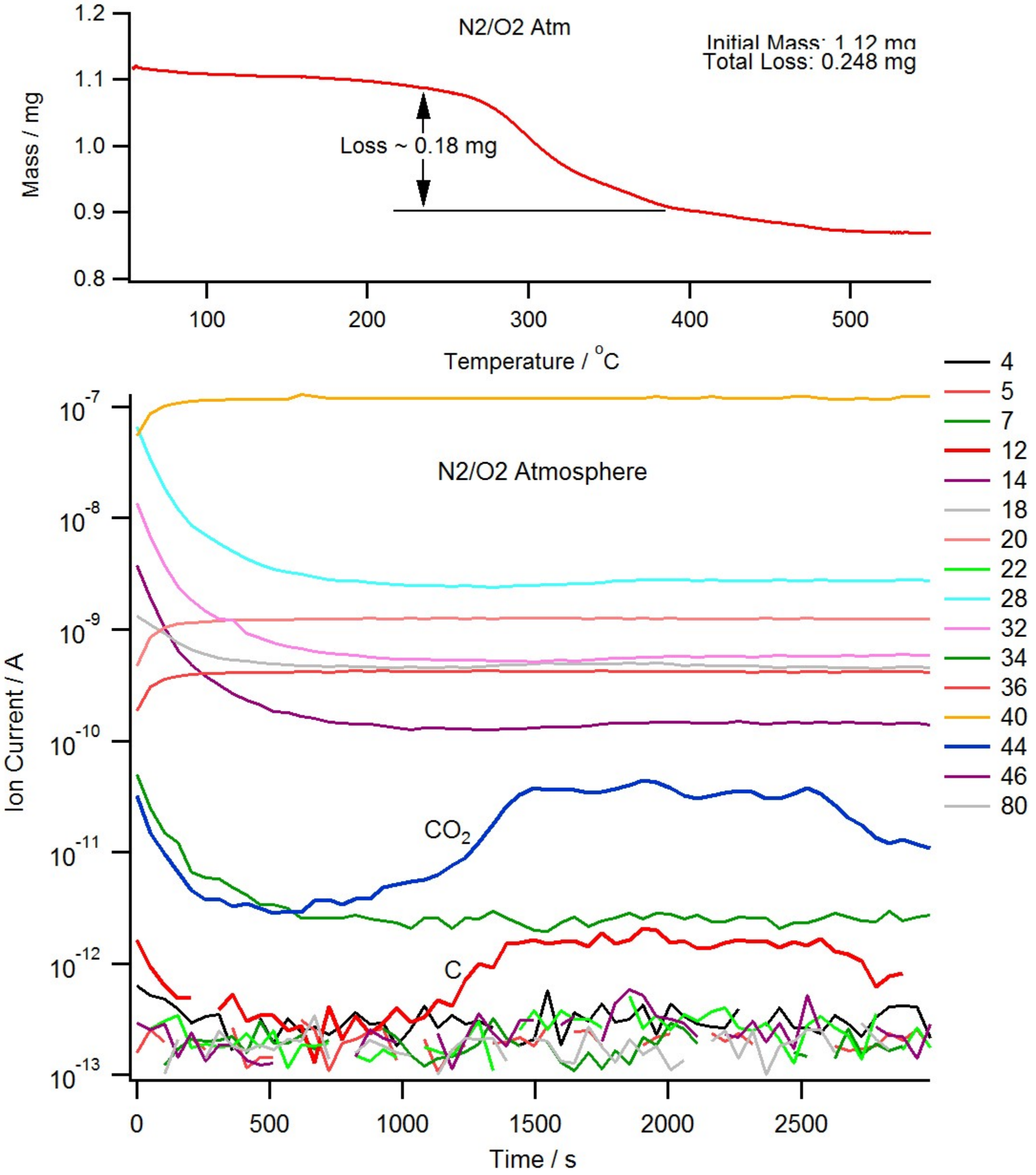

Figure 2. TGA (top) and mass spectra (bottom) of dried hydromer in an air-like oxygen containing atmosphere. The primary atomic masses detected during the significant loss of mass correspond to carbon dioxide and carbon.

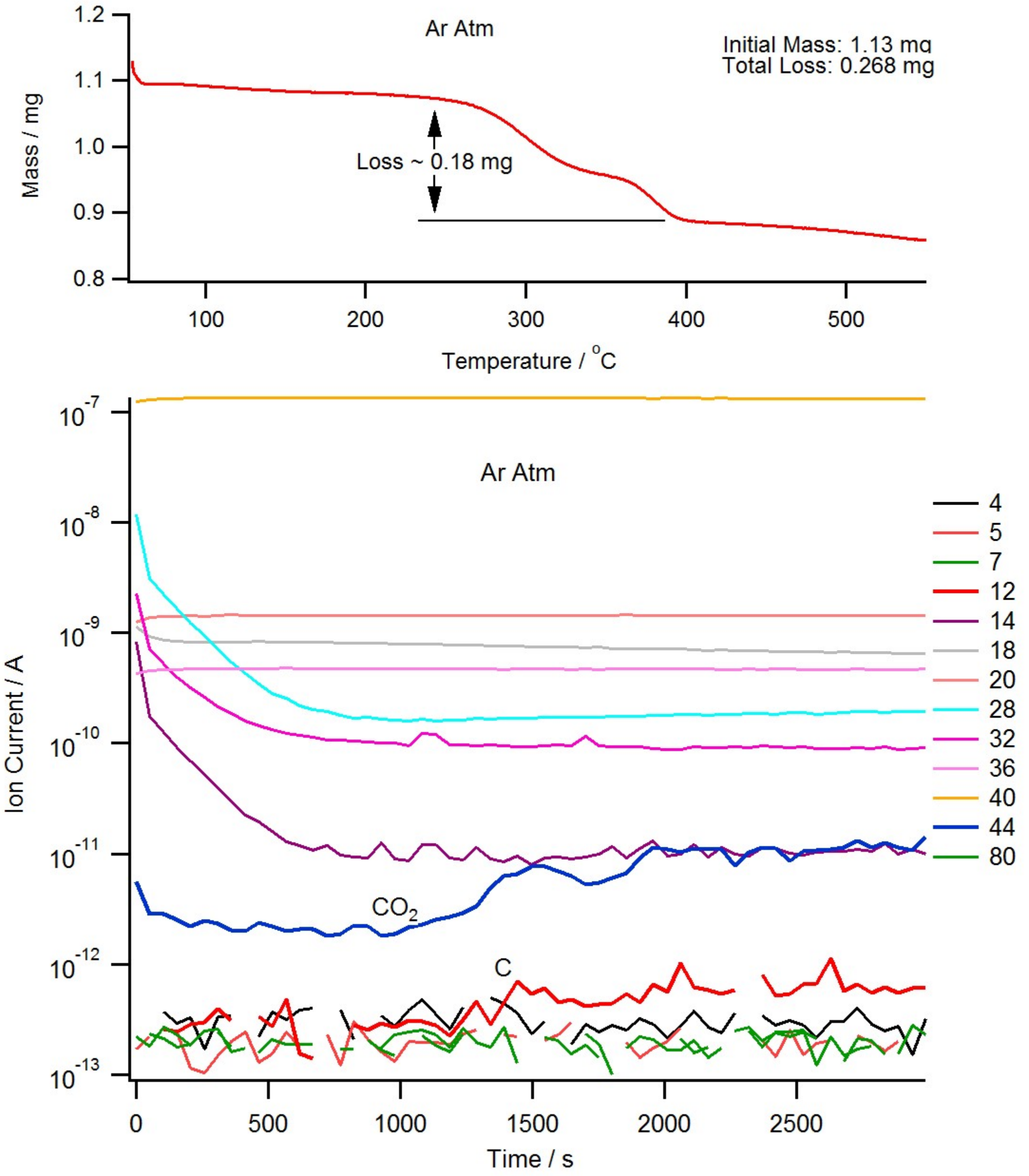

Figure 3. TGA (top) and mass spectra (bottom) of dried hydromer in an inert Ar containing atmosphere. The primary atomic masses detected during the significant loss of mass correspond to carbon dioxide and carbon. Note the pronounced step in mass loss occurring around 350 C. This appears to coincide with the slight dip, and then resurgence of CO2 evolved from the sample (dark blue trace).

2.2 Deuterium Permeation

We tested the ability of the current preparation to block hydrogen permeation. About 600 uL of 0.15% hydromer in water was deposited and allowed to dry on a 25mm diameter Ni foil (250 um thick). The Ni was pre-cleaned by ethanol and UV-Ozone treatment for 15 minutes. The coated foil is then used as a membrane between a deuterium pressurized chamber and a vacuum chamber fitted with a residual gas analyzer (RGA) to measure the flux of deuterium through the membrane.

While higher temperatures are favorable for decreasing the time needed to reach steady state permeation, our previous TGA measurements show the polymer degrades (burns) around 250°C. We therefore chose to keep our permeation temperatures at or below 150°C.

Our tests found that the hydromer coated Ni showed only a modest decrease in the apparent diffusivity over pure Ni (see Figures 3 and 4). We concluded that this is likely due to the very low concentration of polymer in the solution (0.15%) and also the non-uniform coverage of the surface, as shown in the AFM images above, which would lead to polymer build-up around the center of the member with very little around the edges. The latter leaving a very small barrier to the gas.

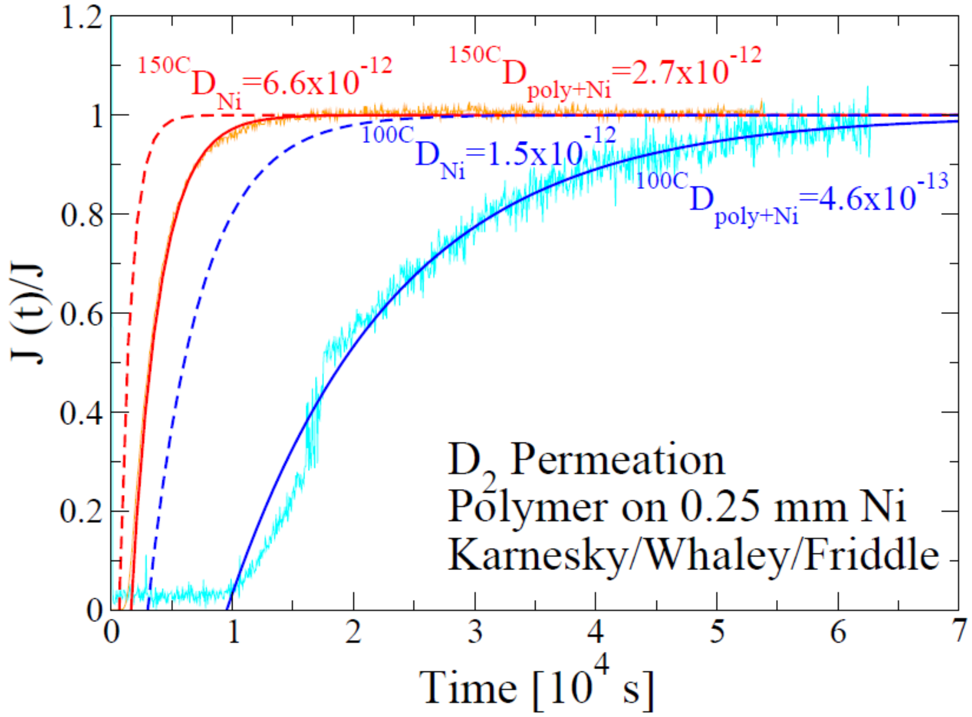

Figure 4. Permeation of deuterium with time for the coated Ni sample at 100 C and 150 C, and the bare Ni cases taken from the literature (dashed lines). Solid lines are single-factor Fourier fit to the data.

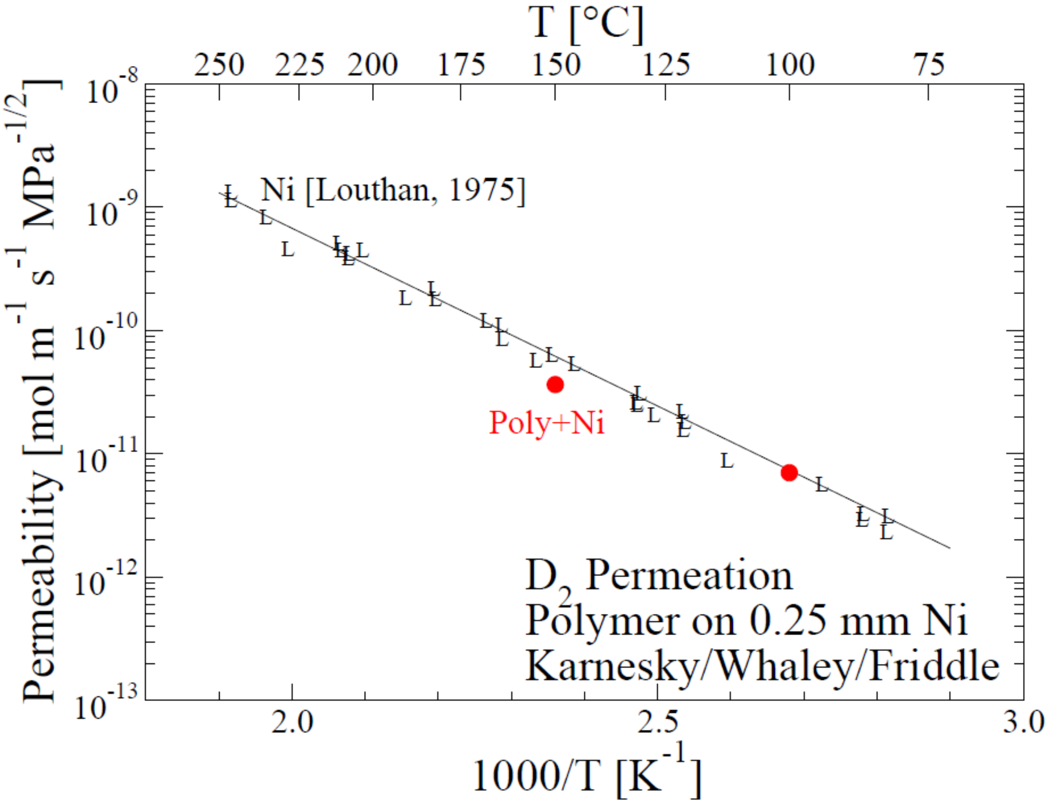

Figure 5. Permeability versus temperature of the hydromer-coated Ni at 100 C and 150 C along with literature data of bare Ni.

We find there is only a reduction factor of approximately 2 at 150 C and it seems to be diffusion controlled (the apparent diffusivity is 2.4x lower; the permeability is 2.3x lower). The permeability at 100 C shows virtually no reduction.

Based on the reduced kinetics demonstrated in Figure 4, we are seeking funding to explore a greater coverage of the polymer to see if the permeation resistance demonstrated in the pilot BET tests extend to larger samples and more sensitive instruments.

3. REFERENCES

1. V. Gadhamshetty, D.C. Johnson, N. Nirmalakhandan, G.B. Smith, and S. Deng, Feasibility of biohydrogen production at low temperatures in unbuffered reactors, in: *Int. J. Hydrog. Energy*, Vol.34, pp. 1233–1243, 2009.
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