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Metallic membranes for N2 separation & post-combustion CO2 capture improvement

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METALLIC MEMBRANES FOR N_2 SEPARATION & POST-COMBUSTION CO_2 CAPTURE IMPROVEMENT

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CO_2 Summit II: Technologies and Opportunities

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Outline

I. Introduction

II. Motivations

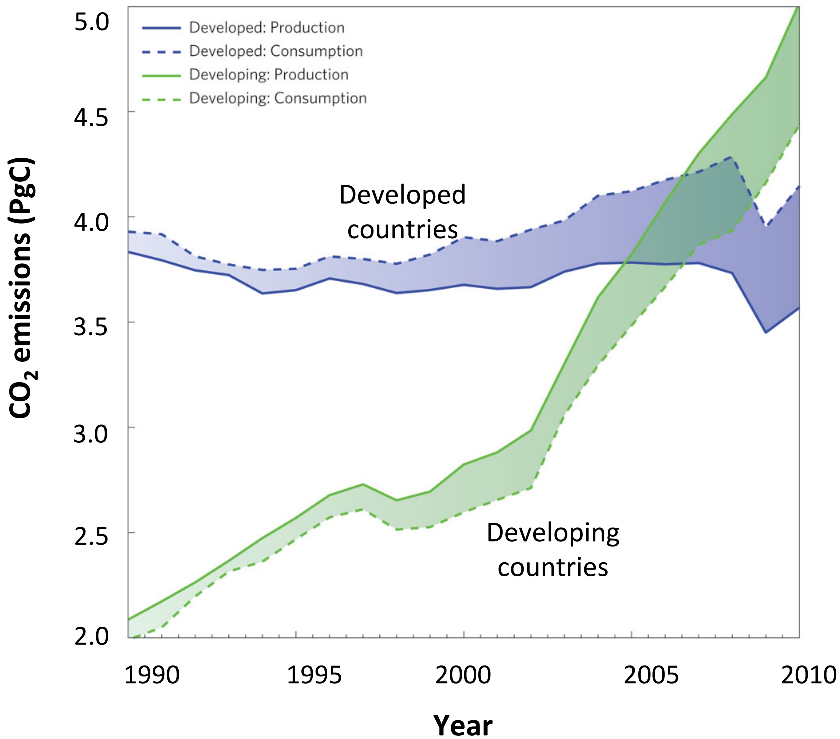
III. Gas separation by membrane

   i. N_2 – separation

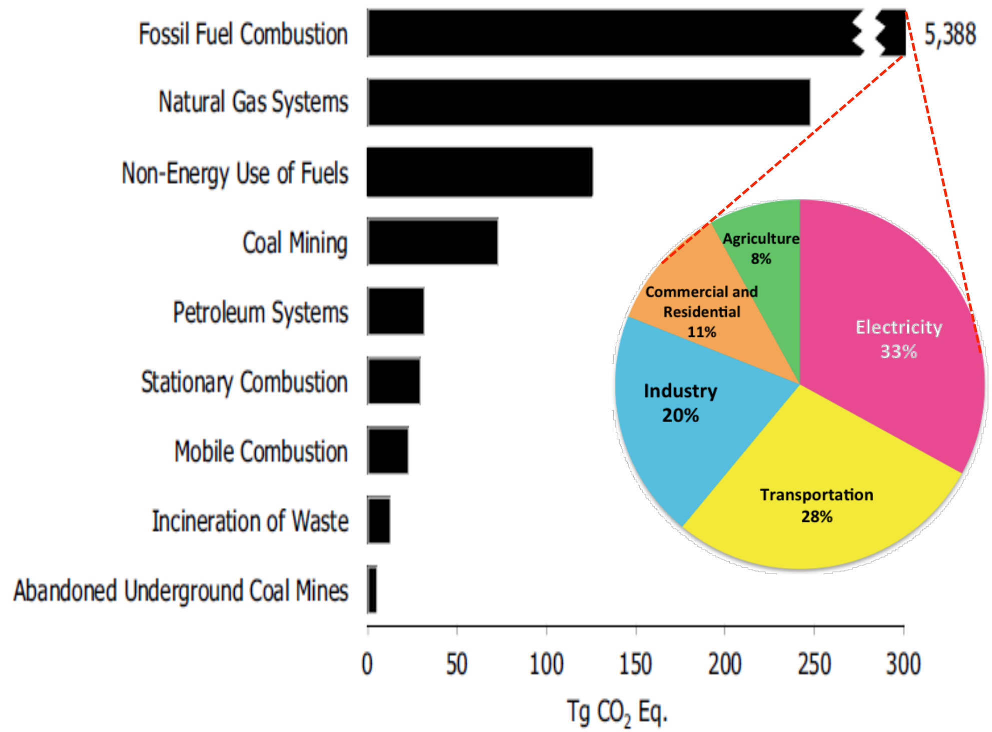
IV. Conclusion and Future Works

CO_2 Emissions

Historic Global CO_2 emissions[1]



CO_2 emissions in US[2]



CO_2 emissions are growing

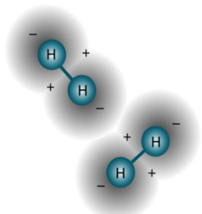
Atmospheric CO_2 concentration is correlated with global average temp.

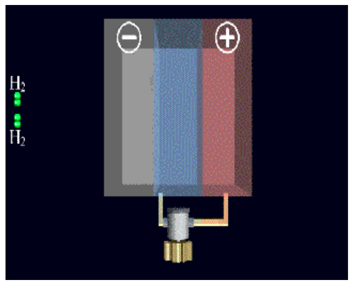
Fossil fuel combustion for electricity generation and transportation is the major contribution to the current CO_2 emissions

[1] Peters, Glen P, et. al.. "Rapid Growth in Co2 Emissions after the 2008-2009 Global Financial Crisis." *Nature Climate Change* 2, no. 1 (2012): 2-4.
[2] Ref. 2012 U.S. Greenhouse Gas Inventory Report, Chapter 2

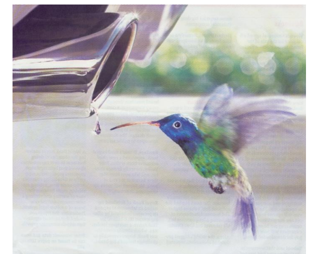
Membrane use

1 - Pd-based Membrane Reactor → for Producing/Separating H_2 → for onboard application



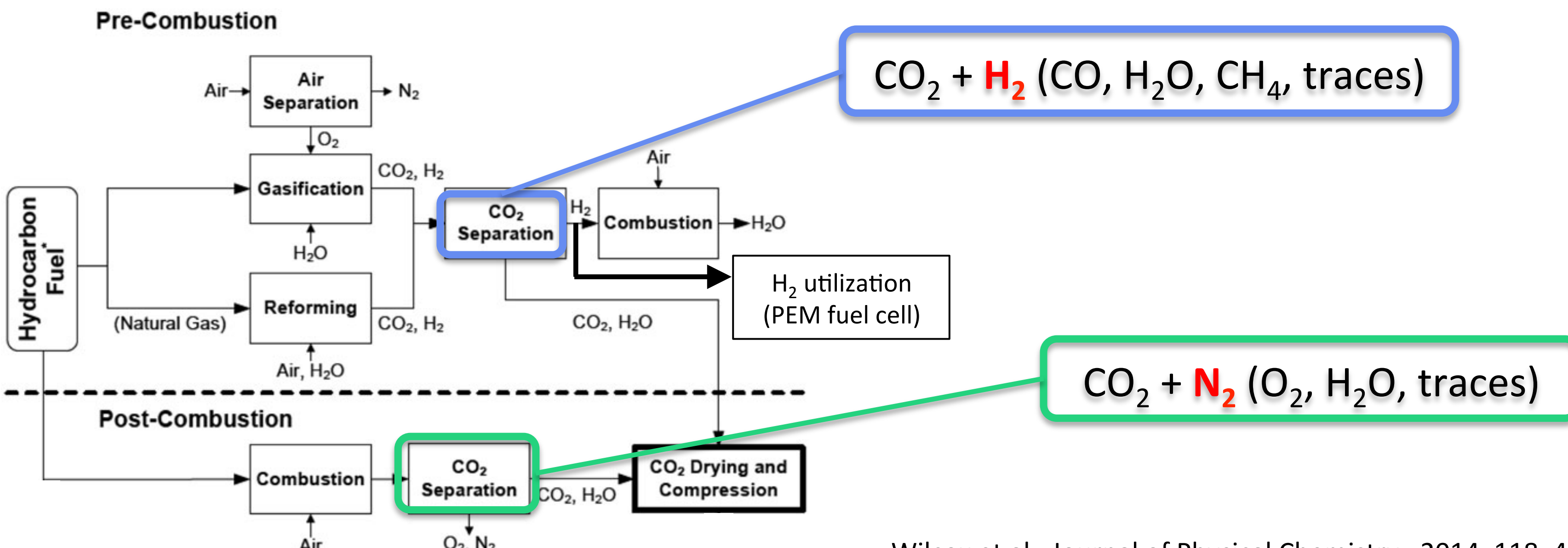


PEM Fuel Cell



Hydrogen powered Fuel Cell vehicles only emit ***water***.

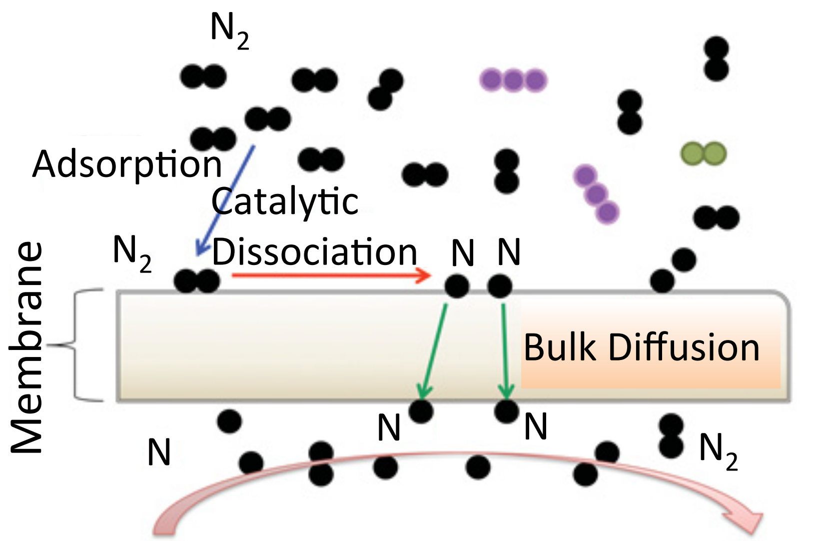
2 – Metallic Membrane → for Gas Separation



Wilcox et al., Journal of Physical Chemistry , 2014, 118, 4238–4249

Inorganic Metallic Membranes

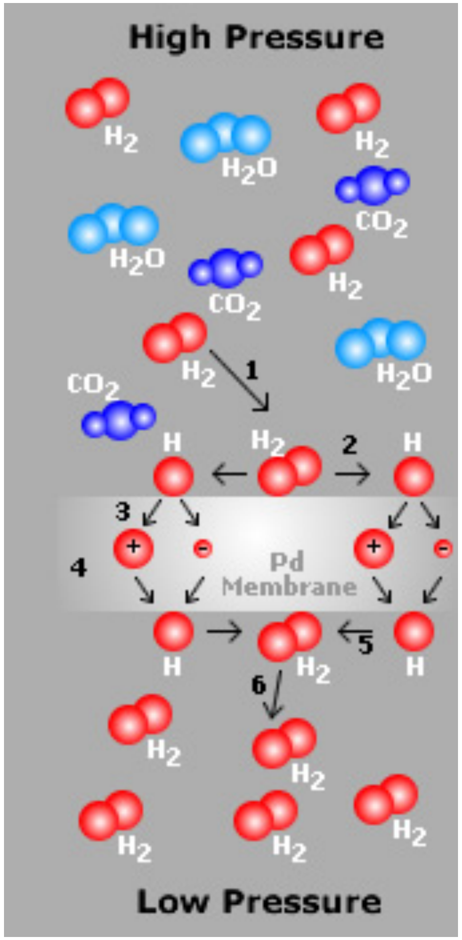
Niobium, Vanadium, Tantalum



Solution/diffusion mechanism

1. adsorption
2. dissociation
3. the chemisorbed molecule dissociates into atomic form H· or N·
4. diffusion
5. recombination
6. desorption

Palladium and its alloy



Permeation Mechanism

Permeating Flux through dense membranes is governed by:

Permeability of the membrane, *Pe*

Thickness of the membrane, δ

Difference in partial pressure across the membranes, $(p^n_{i,retentate} - p^n_{i,permeate})$

$$J_i = \frac{Pe}{\delta} \cdot (p^n_{i-retentate} - p^n_{i-permeate})$$

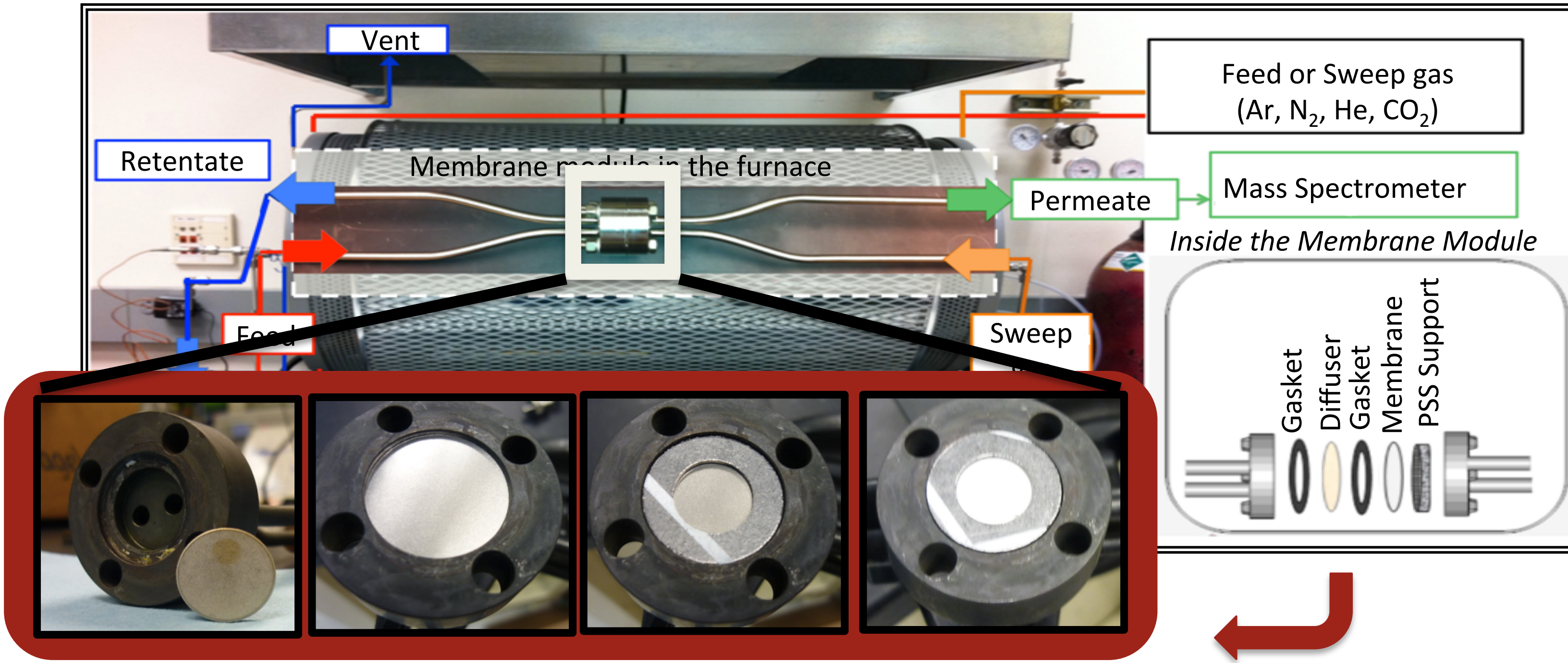
Where i = N_2 or H_2

Limiting step determined by exponent:

- n = 0.5, bulk permeation limited diffusion
- n = 1.0, surface reaction limited diffusion

$$(\text{Ideal selectivity})\ \alpha_{i/\text{He},\,CO_2} = \frac{\text{Permeance}_i}{\text{Permeance}_{\text{He},\,CO_2}}$$

Set-up for N_2 Permeation Tests



Metallic Foil Membranes:

- Niobium
- Vanadium
- Tantalum

Permeation Test Operating Conditions:

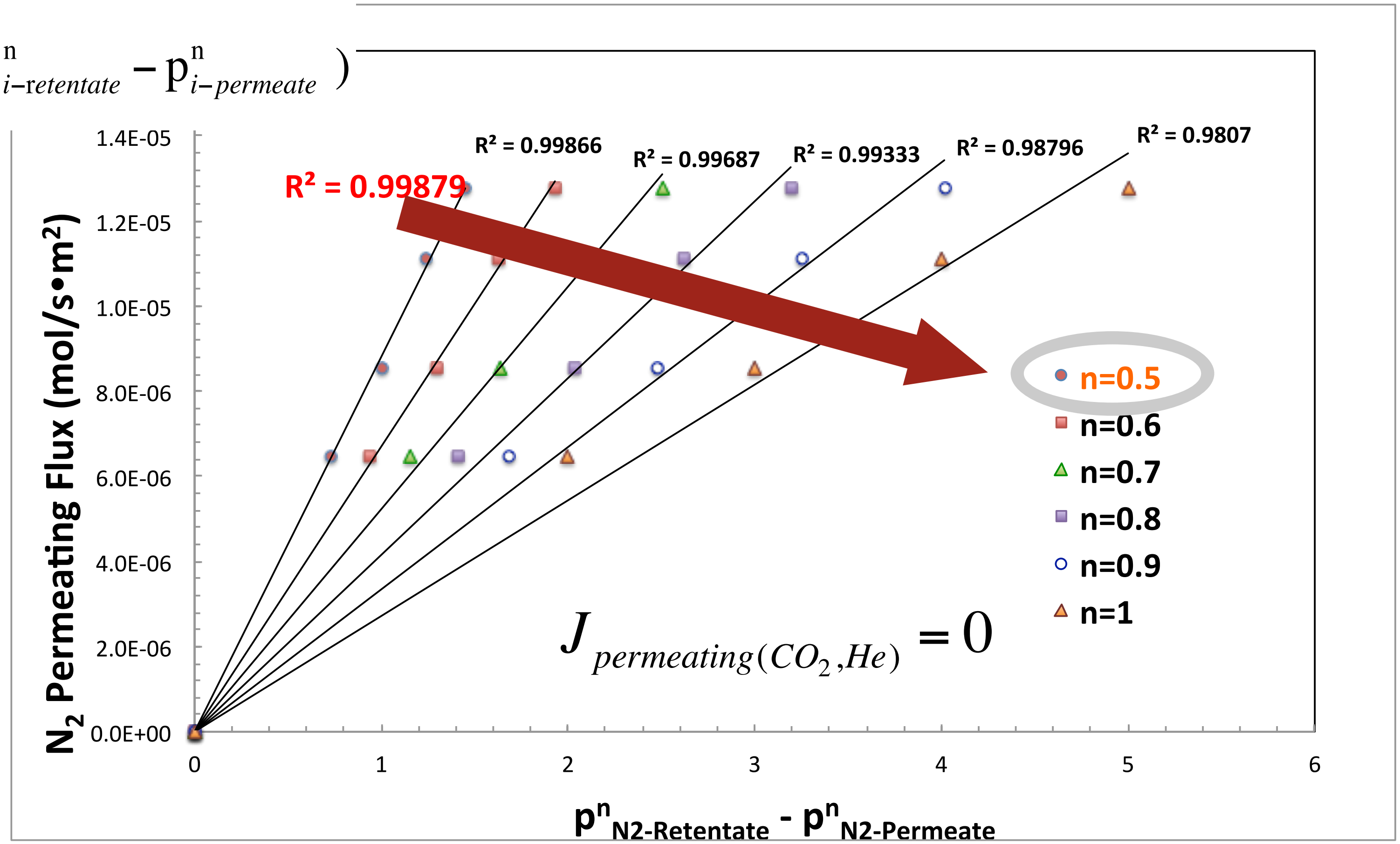
- Temperature: 400 °C
- Permeate pressure: 1 bar
- Sweep gas: Ar (50 mL/min)
- Retentate pressure: 3 – 6 bar

Gases Used:

- N_2
- CO_2
- He

Nb Foil (40 μm) - N_2 permeation tests

$$J_i = \frac{Pe}{\delta} \cdot (p^n_{i-retentate} - p^n_{i-permeate})$$



Similar to a Pd-based membrane for H_2 separation, N_2 molecules preferentially permeate through metallic membrane by the solution-diffusion mechanism

V Foil (40 μm) - N_2 permeation tests

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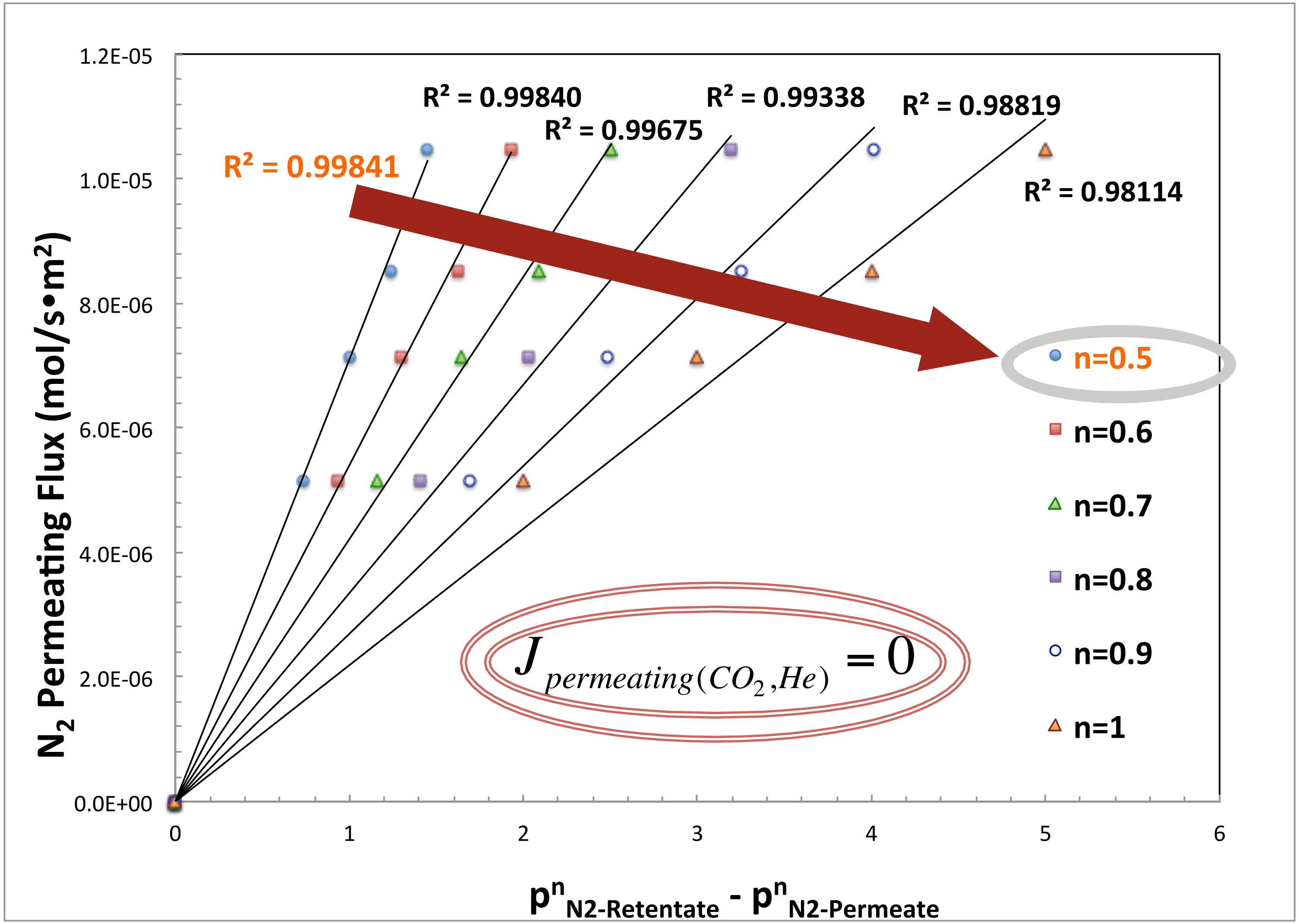
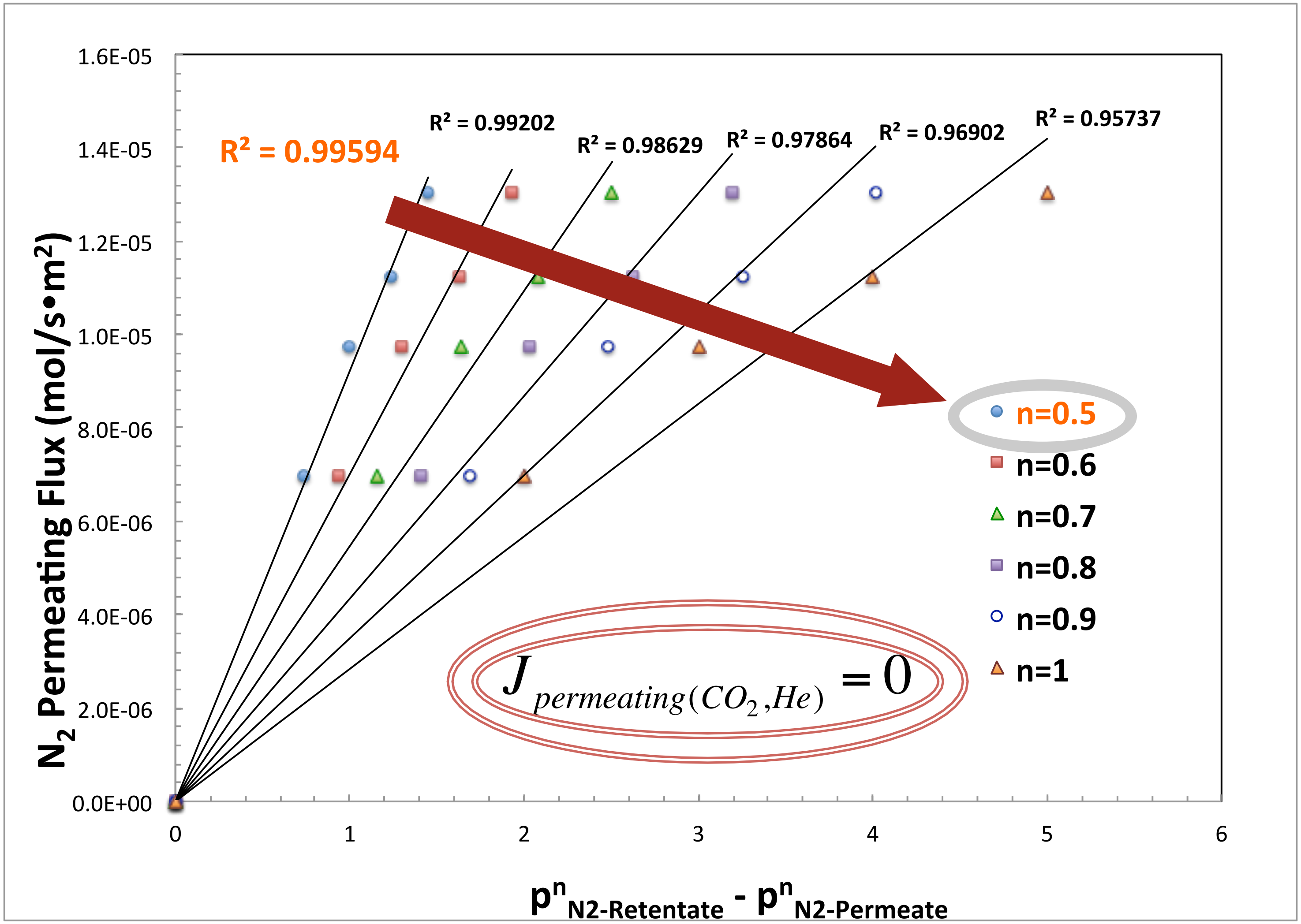
N_2 - Separation



Ta Foil (40 μm) - N_2 permeation tests



High N_2 Selectivity, Very Low Flux

400 °C

N_2 Permeating Flow rate [L/m²/day]

Δp [bar]	Nb	Ta	V
2	34	28	40
3	45	40	57
4	62	45	62
5	68	57	73

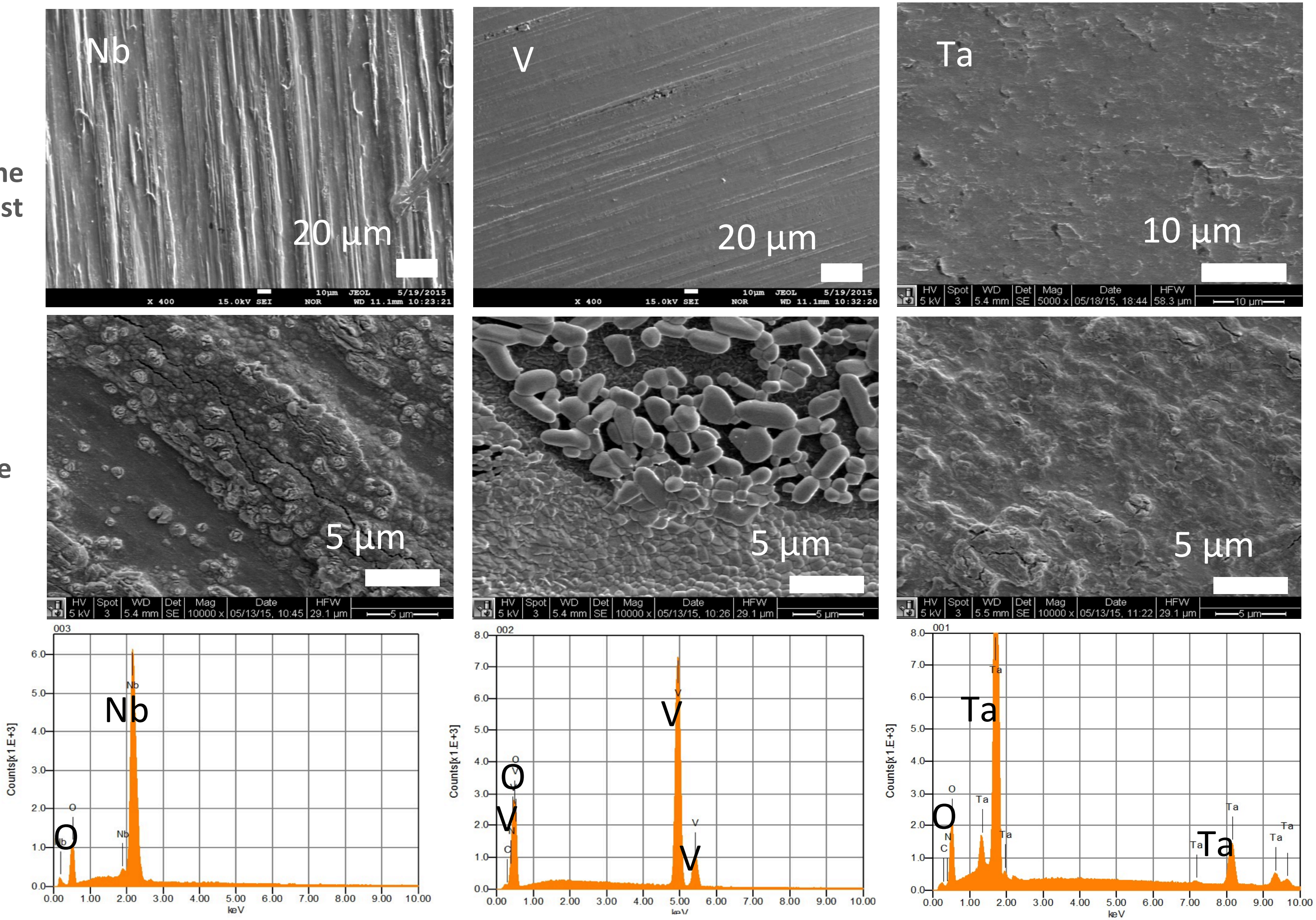
- Metallic membranes (V, Nb, Ta) are entirely selective for N_2 over He and CO_2 ($\alpha = \infty$)
- Fluxes are low
- Metallic thin films, an order of magnitude thinner than foils, may lead to significantly higher fluxes

Surface Characterization by SEM and EDX

Membrane before test

Membrane after test

EDX of Metal Oxidation



Thin V membrane – Work in Progress

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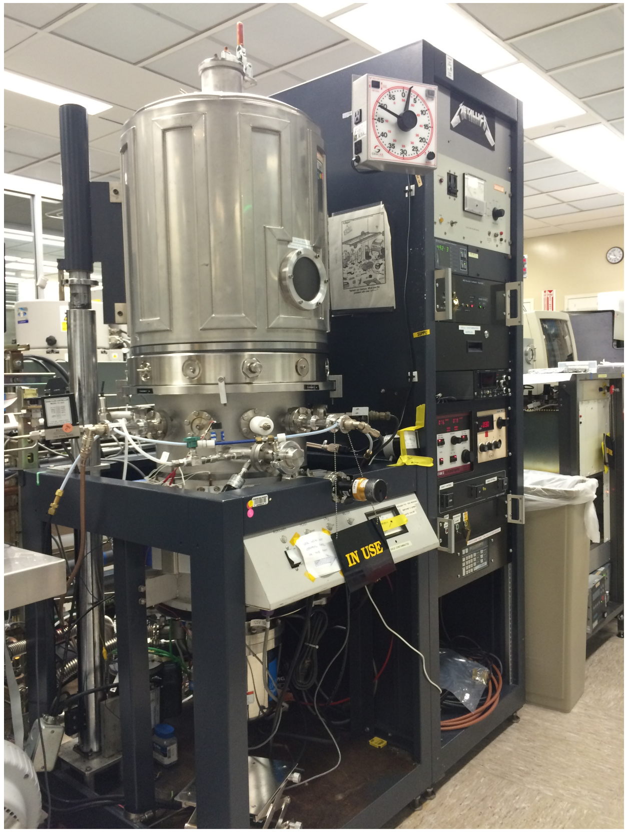
- Vanadium target: 99.95% purity
- Sputtering conditions
  - Base pressure: 1E-6 Torr
  - Ar pressure and mass flow: 5E-3 Torr, 30 mlpm
  - DC power: 75W
- Ceramic support furnished by OSU
  - 600 nm of V on the ceramic support (2 membranes)

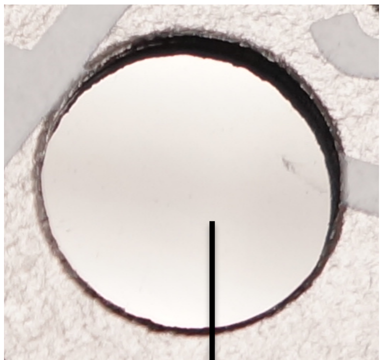


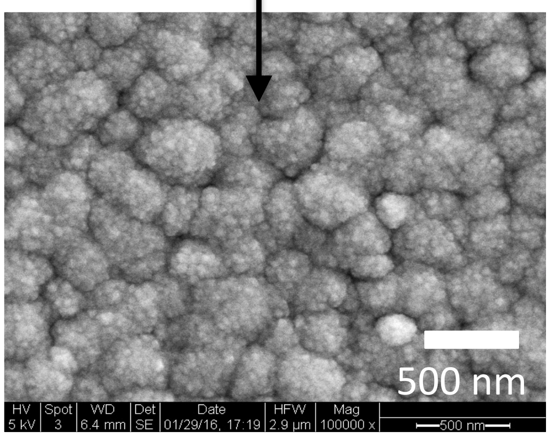
Permeation measurement

	V#1 (600 nm)	V#2 (600 nm)
Temperature [˚C]	RT, 400	RT, 100, 200, 300, 400
Δp [bar]	3, 4, 5	3, 4, 5

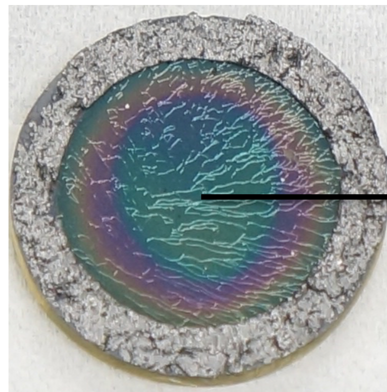
Thin V#1 membrane – Main Results

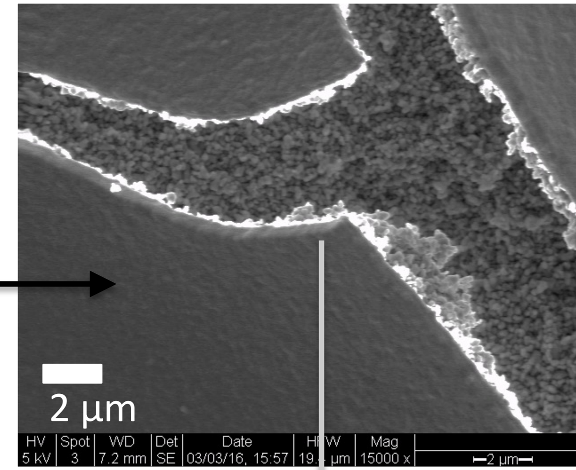
As deposited
Mirror-like finish

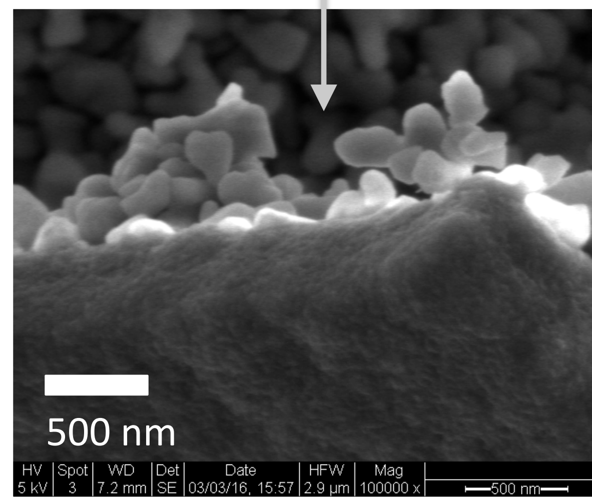




Membrane cracked
after 400 ˚C, Ar exposure



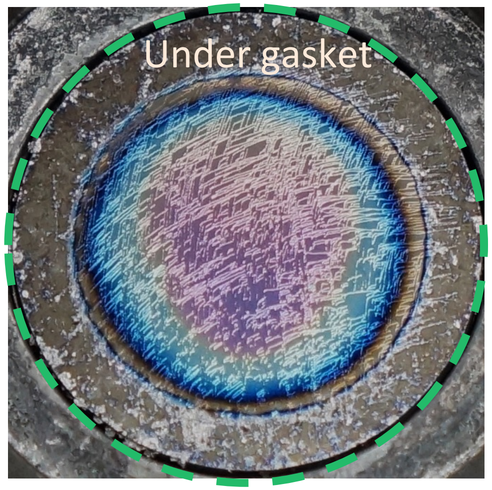




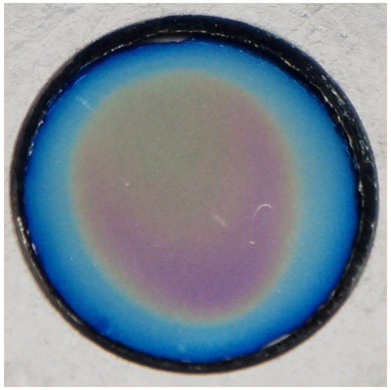
Thin V#2 membrane – Main Results

As deposited
Mirror-like finish

V#1 - After 400 ˚C



V#2 - After slow heat up to 400 ˚C



Same color changes regardless of exposure time (surface oxide)

Heating profile

- Ramp rate of 2 ˚C/min for all temperature changes
- Direct heat up: RT to 400 ˚C (6h dwell, broken) → RT
- Slow heat up: RT → 100 ˚C (12h dwell) → 200 ˚C (18h dwell) → 300 ˚C (19h dwell) → 400 ˚C (10h dwell) → RT (Not broken)

Permeation measurement → No significant selectivity observed for N_2/Ar (Knudsen ratio)
No selectivity found probably due to the dominant Knudsen flux

Conclusion

- Metallic Membrane for N_2 separation has been investigated
  - V, Nb, Ta, Fe show infinite ideal selectivity → only N_2 can permeate through the membranes
  - N_2 permeation flux through the membrane is extremely low and affected by oxidation of the surface
  - Membrane performance are improved by increasing pressure, temperature

Future work

- Prepare defect-free inorganic membrane able to work for long periods
- Fabricate composite alloy membranes for enhancing N_2 permeation flux and reducing oxidation effect.

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Thank you

for your attention!