Theoretical and experimental investigations of N₂-selective membranes

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Abstract

Coupled theoretical and experimental investigations on the feasibility of N₂ permeation through dense metallic membranes comprised of vanadium have been carried out. Due to the strong-binding nature of vanadium, electronic structure calculations have shown that the material is soluble to atomic N following catalytic dissociation. Bench-scale flux experiments followed by material characterization validate a solution-diffusion transport mechanism. Applications of a N₂-selective membrane include CO₂ capture from coal or natural gas-fired power plants, natural gas purification, and ammonia synthesis.

Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

Existing coal-fired power plants in the U.S. provide over 320 GW of power capacity [1] which represents approximately 50% of all power generated in the US and is responsible for more than 35% of annual carbon dioxide (CO₂) emissions [2, 3]. In China, the installed capacity of coal-fired power plant is approximately 640 GW [4] and it is roughly 110 GW in India [5]. Nearly all of the CO₂ emissions from power generation in China, which accounts for more than 40% of annual CO₂ emissions, derived from coal [6]. Meanwhile, approximately 50% of the annual CO₂ emission in India comes from the electricity and heat generation which 69% of the electricity in India generated from coal [6]. Currently, amine scrubbing is the most common option for post-combustion capture technologies for CO₂ as it has proven to be feasible for smaller-scale applications including natural gas purification and the food and beverage industry. It is unclear whether this technology will be the optimal choice to tackle the scale of CO₂ emitted on an annual basis (~ 30 Gt worldwide).

The main objective of this study is to develop N₂-selective catalytic membrane technology with potential applications to indirect CO₂ capture. The N₂-selective membrane technology benefits from the driving force of N₂ in flue gas (~73 wt.%) streams for indirect CO₂ capture while nitrogen diffuses
through the metallic membrane to the permeate side of the membrane during separation. Using H$_2$ as a sweep gas, the N$_2$-selective membrane may also have the co-benefit of producing ammonia, which will be the focus of future work.

In this study, metallic membranes made from alloys of Ru and earth-abundant Group V metals, such as V and Nb, are considered for catalytic selective N$_2$ separation. Group V metals, located at the far left of the transition metals in the periodic table are known to bind adsorbates too strongly to serve as effective catalysts. However, due to this property, these metals may act to successfully dissociate and transport atomic nitrogen through their crystal lattice. Figure 1 illustrates the schematic of a nitrogen-selective membrane reactor for a post-combustion capture application. Similar to a traditional palladium-based H$_2$-selective membrane, nitrogen molecules preferentially adsorb on the catalytic membrane and dissociate to two nitrogen atoms. The atomic nitrogen diffuses through the crystal lattice by hopping through the interstitial crystal sites of the bulk metal, ultimately leading to atomic nitrogen on the permeate (or sweep) side of the membrane.

Fundamental investigations of molecular nitrogen and atomic nitrogen adsorption, dissociation, and potential subsequent atomic diffusion of N$_2$ within the Group V metals, specifically, vanadium (V) are performed using density functional theory (DFT) electronic structure theory. These studies are coupled with experimental N$_2$ permeability measurements on micron-thick foils of V and Nb in a high-temperature membrane reactor. The permeability of H$_2$ in palladium (Pd) is selected as a target reference case since these membranes are well-studied and have been used in small-scale on-site hydrogen generation units for laboratory, military and industrial applications since 1960’s [7].

\[ \text{Figure 1 Schematic of catalytic N}_2\text{-selective metallic membrane with ammonia synthesis.} \]

### 2. Computational Methodology

All calculations are based on plane-wave density functional theory (DFT) and performed using the Vienna \textit{ab-initio} simulation package (VASP)\cite{8, 9}. The electron-ion interactions are represented by the projector-augmented wave (PAW) approach \cite{10, 11} and the electron exchange correlation effects are described by a generalized-gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional \cite{12} with a plane-wave expansion with a cutoff of 600 eV. The surface Brillouin zone
integration is calculated using Monkhorst-Pack mesh [13] of $7 \times 7 \times 1$ and $7 \times 7 \times 7$ for surface and bulk study, respectively. During geometry optimization, the conjugate-gradient (CG) algorithm is applied to relax the ions into their instantaneous ground state, and electron smearing with a width of 0.05 eV (surface) or 0.1 eV (bulk) is employed via the first-order Methfessel-Paxton technique [14] for improved convergence. Geometry convergence is achieved when the forces on all unconstrained atoms are less than 0.02 eV/Å.

The Climbing Image Nudged Elastic Band (CI-NEB) method developed by Jónsson and co-workers [15] is used to determine the minimum energy paths (MEPs) and corresponding transition states for N$_2$ dissociation on the vanadium surface, the subsurface diffusion of atomic N into the vanadium surface, and the diffusion of atomic N in the bulk vanadium. Once the initial and final configurations of a process are known, an interpolated chain of configurations (images) between the initial and the final states is created. The intermediate configurations (images) are connected by springs and relaxed simultaneously to the MEP, through which the highest-energy configuration climbs uphill to the saddle point [15]. The nature of the transition state found by the CI-NEB method is determined by diagonalizing a finite difference construction of the Hessian matrix with displacements of 0.015 Å. Only N atoms are allowed to move, while V atoms are kept fixed at their relaxed geometries.

2.1 Nitrogen interactions on the V(110) surface and in the subsurface layers

The V(110) surface is modeled by cleaving the bulk V crystal along the (110) plane with an optimized lattice constant of 2.98 Å, which compares well against the experimentally measured distance of 3.024 Å [16]. The surface slab of V is simulated as three-dimensional infinite periodic structures by defining a supercell and periodic boundary conditions in all three principal axes. The surface slab consists of seven layers with four V atoms per layer in a $2 \times 2$ arrangement. A 15 Å vacuum region is placed above the surface to avoid dipole interactions from periodic images. During the simulation, the bottom four layers of the V(110) surface are frozen at the estimated bulk parameters and the remaining top three layers and the adsorbate, i.e., N$_2$ molecule or N atoms are allowed to relax to their optimized geometries. The adsorption is assumed to occur on only one side of the slab. In Figure 2(a), the top view of the V(110) surface with labels for the available adsorption sites for molecular N$_2$ and atomic N adsorption are shown. There are four possible sites on the surface: the top site, the short-bridge site (SB), the long-bridge site (LB) and the three-fold hollow site (TF). Figure 2(b) shows the schematic side view of the V(110)-N$_2$ surface for N$_2$ molecule sit at the top site, in which the tilting angle ($\theta$) is indicated.

![Figure 2 Schematic of (a) the top view with possible adsorption sites on the V(110) surface: 1-top, 2-short-bridge (SB), 3-long-bridge (LB), 4-three-fold hollow (TF) and supercell with yellow dash line for $2 \times 2$ used in this study; (b) the side view of V(110)-N2, in which $\theta$ is the tilting angle.](image-url)
In case of N absorption in the subsurface layers, the N atom may reside at two possible interstitial sites, i.e., the octahedral site (O-site) and the tetrahedral site (T-site) as presented in Figure 3(a) and 3(b). The adsorption energy of molecular N\textsubscript{2} on the V(110) surface is calculated with respect to the isolated N\textsubscript{2} molecule (eV/N\textsubscript{2}), whereas the adsorption/absorption energy of atomic N on/in the V(110) surface is determined per one N atom (eV/N). The calculated N\textsubscript{2} bond length is 1.113Å and a vibrational frequency is 2421 cm\textsuperscript{-1}. These values are in fairly good agreement with the experimental data of 1.098Å and 2359 cm\textsuperscript{-1} \[16\]. From these two equations, a more negative value indicates a more preferable adsorption site on the V(110) surface.

2.2 Nitrogen interactions in the bulk vanadium

The bulk metal crystal lattices of V and its alloys with Ru are modeled using a periodic 2\times2\times2 bcc cell, which corresponds to a supercell of 16 atoms. Based on the phase diagram of VRu alloys, the total concentration of the ruthenium atoms must be kept below 40\% to ensure that the bcc structure of V is not compromised \[17\]. The model of the VRu alloy is constructed by replacing V atoms with Ru atoms at specific nearest-neighbor locations surrounding the tetrahedral (T-) and octahedral (O-)sites of adsorbate atom (i.e., N or O atom). The binding energy of atomic N in the bulk vanadium is calculated by Equation (2). Simulations are conducted at different adsorbate concentrations corresponding to c = 0.0625 at.\%, 0.125 at.\%, and 0.25 at.\%. The adsorbate is placed at the specific interstitial locations and all atoms are allowed to relax to their equilibrium positions. Aside from the binding energy of the adsorbate residing in the crystal lattice, the atomic charge of the adsorbate is calculated using a Bader charge analysis \[18-20\] to understand the charge distribution within the crystal lattice. Cell expansion as a function of N concentration within the bulk phase, is also taken into account in the solubility and diffusivity predictions. For absorption at the T-sites, the correction due to the change in zero-point energy (ZPE) between the free nitrogen gas and the interstitial nitrogen is also included. The ZPE for interstitial nitrogen is determined by fixing the metal atoms and then using the forces generated from displacing the nitrogen atoms to calculate the Hessian matrix.
3. Experimental Procedure

3.1 Pure gas permeation experiments

A bench-scale high-temperature membrane reactor has been designed and used to investigate N$_2$ permeability through the membrane foils comprised of Group V metals. An image of the experimental set-up is shown in Figure 4 with the feed, retentate, permeate, and sweep streams labeled accordingly. Permeation tests are performed for pure N$_2$, Argon and Helium gases to quantify the N$_2$ permeation via solution-diffusion mechanism. The membrane module assembly has been selected similar to the one at TDA Research and is custom manufactured from Hastelloy X alloy because of its durability at elevated temperatures, showing high performance up to temperatures of 1177 °C [21]. Due to the high temperatures required for N diffusion through metals, the membrane has been tested over a range of temperatures from 200 to 1000 °C. The sample membrane foil and intermetallic diffusion barrier (e.g., alumina paper type APA-3, Zircar Ceramics) is housed onto the Hastelloy X porous support (custom-made with 0.75-inch outer diameter and 0.125-inch thickness, media grade 100, Mott Corporation) within the module, and graphite gaskets are used to seal the membrane.

Permeation tests are carried out using two different analysis instruments, i.e., a soap bubble flow meter and an electron ionization quadrupole mass spectrometer (EI-QMS) with a sensitivity in the low ppm range. In gas permeation experiments, the initial step is to measure the flux of an inert gas (Argon or Helium) through the membrane at the desired temperature and the pressure gradient to identify the leak flux resulting from the surface defects of the metallic membrane foil. N$_2$ flux through the surface defects is calculated from this inert gas permeation measurements using Knudsen diffusion correction. The difference between the overall N$_2$ flux data obtained from N$_2$ permeation experiments and the Knudsen normalized N$_2$ flux data obtained from the inert gas permeation experiments demonstrates the actual N$_2$ flux obtained from the solution-diffusion mechanism. Establishing calibration curves that relate the intensity (from the EI-QMS detector) to the concentration enables the direct measurement of the permeate N$_2$ concentration [22].

Figure 4 Set-up for the membrane permeation test
3.2 Materials and sample characterization

The membrane samples tested in this work are provided from Goodfellow and consist of dense pure (99.8+ wt%) Vanadium (V) and Niobium (Nb) foils with 0.04 mm thickness and 25.4 mm diameter. The foil samples are supplied as light tight foils which are free from any visible pinholes. Membrane foils are placed onto a custom made Hastelloy X porous support with dimensions of 3.175 mm thickness and 19.05 mm diameter obtained from Mott Corporation. Upon completion of the flux testing, the membrane samples are removed from the test apparatus and the surfaces of the samples were analyzed by X-Ray Diffraction (XRD). The data reduction was carried out with PHI MultiPak Software. XRD diffractograms for the tested and clean V foils were obtained on a PANalytical X'Pert PRO x-ray diffraction system with Cu Kα radiation (45kV, 40mA). Analyses were performed in the Stanford Nanocharacterization Laboratory at Stanford University.

4. Theoretical Results

4.1 Adsorption energy of molecular nitrogen and atomic nitrogen on V(110)

The adsorption energies of N₂ and the atomic N have been studied at 0.25ML coverage by placing one N₂ molecule or one atomic N on the supercell. As shown in Figure 6, three local minima for N₂ adsorption on V(110) and two local minima for N adsorption on V(110) have been discovered. The adsorption energies as well as the optimized structural parameters for these stable geometries are presented in Table 1. It is useful to compare the adsorption energies from this work to the previous theoretical study of N₂/Fe(111) [23]. The N₂ adsorbed states at the top, SB and LB site on V(110) are considered to be similar to the well-known γ, α’ and α state of N₂/Fe(111), respectively. The calculated adsorption energies of N₂/Fe(111) at 1/3 ML coverage are -0.35 eV for the γ state, -0.17 eV for the α’ state, and -0.41 eV for the α state. In case of atomic N adsorption, the calculated adsorption energy is -1.4 eV on the unreconstructed Fe(111) surface. However, it is suggested that the reconstruction of the top layer of the Fe(111) surface takes place to form islands of the c(2×2)-N/Fe(110)-type [24], with an adsorption energy on this reconstructed surface of ~ -2.4 eV. In case of atomic N adsorption on the V(110) surface, the reconstruction of the V(110) surface after N adsorption is also noticed.

Table 1. Adsorption energies, geometry information and vibration frequency of adsorbed states

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>E_{ads} (eV/N₂)</th>
<th>r(N-N) (Å)</th>
<th>h(N-surf) (Å)</th>
<th>θ (°)</th>
<th>Vibrational Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecular Adsorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>-0.54</td>
<td>1.134</td>
<td>2.025</td>
<td>0</td>
<td>2155.32</td>
</tr>
<tr>
<td>SB</td>
<td>-2.27</td>
<td>1.334</td>
<td>1.298</td>
<td>90</td>
<td>1086.84</td>
</tr>
<tr>
<td>LB</td>
<td>-2.82</td>
<td>1.304</td>
<td>1.268</td>
<td>90</td>
<td>1233.00</td>
</tr>
<tr>
<td><strong>Atomic Adsorption</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LB</td>
<td>-4.75 (-2.37 eV/N)</td>
<td>-</td>
<td>0.311</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TF</td>
<td>-4.33 (2.16 eV/N)</td>
<td>-</td>
<td>0.980</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
From Table 1, based on a comparison of the adsorption energies, \( \text{N}_2 \) and atomic N binds significantly stronger on the V(110) surface. The stronger adsorption energy can be explained by the concept of the d-band center model [25]. As we move left along the periodic table within the transition metal series, we can expect the stronger bonding between the adsorbate and the transition metal because the d-band center shifts up in energy and the number of anti-bonding states above the Fermi level increases, leading to a stronger bond. Since V and Fe are both transition metals in the 3d series and since V is nearest to the left in the series, the adsorption energy on V surfaces is expected to be stronger than on Fe surfaces, which is the case here.

4.2 Nitrogen dissociation pathway on V(110)

The dissociation process of \( \text{N}_2/\text{V}(110) \) is determined by employing the CI-NEB approach as discussed in the Section 2. The initial state for dissociation is indicated by a large \( r(\text{N-N}) \) distance and a small vibration frequency implying a significantly weakened N-N bond. Therefore, according to Table 1, \( \text{N}_2 \) at the SB site is expected to be the initial state for dissociation. This is equivalent to the dissociation process of \( \text{N}_2/\text{Fe}(111) \) where the \( \alpha^* \) state is the initial state. The final state of the dissociation process is obviously the atomic N at the LB site. During the CI-NEB calculation, four intermediate images are inserted between the initial and final states. The zero of energy corresponds to the total energy of the initial image. The dissociation barrier on the V(110) surface is ~0.4 eV, which is comparable to the dissociation barrier of \( \text{N}_2 \) on Fe(111) and Ru(0001)-step at ~0.3 eV and ~0.4 eV, respectively [26]. Therefore, the dissociation barrier on V(110) is in fact in the same range as the dissociation barrier of \( \text{N}_2 \) on Fe(111) and Ru(0001)-step surfaces, which are the common catalysts for the ammonia synthesis process.

4.3 Atomic nitrogen in the subsurface layers of V(110) and diffusion from surface to subsurface

In the case of atomic nitrogen in the subsurface layers, we also discover that nitrogen atom prefers the O-site, as similar in the bulk. Once we initially place the nitrogen atom at the subsurface T-site and allow the system to relax, the nitrogen atom will eventually move either to the surface or to the subsurface O-site. The binding energy of nitrogen in the subsurface O-site is -2.29 eV/N, which is relatively close to the binding energy of nitrogen in the bulk vanadium. The distortion to the host bcc lattice is observed when nitrogen atom is present in the subsurface. From Figure 5, we can see that one surface V atom that is coordinated to nitrogen atom at the subsurface O-site is pushed toward vacuum by ~0.47Å. This distortion of the bcc lattice occurs to reduce strain in the subsurface.

![Figure 5 Most stable structure of N atom in V(110) subsurface](image)

Since we have known the stable sties of the nitrogen atom on the V(110) surface and subsurface, the CI-NEB method is used to determine the minimum energy path for nitrogen diffusion into the V(110) surface as shown in Figure 6. Energy change from the reactant to the product is 0.085 eV endothermic, which
means the nitrogen atom slightly prefers to stay on the surface at the LB site. A diffusion barrier of 1.39 eV for going into the surface is obtained. At the transition state, the nitrogen atom stays in an approximate T-site. Recall that the dissociation barrier of nitrogen on the V(110) is approximately 0.4 eV, we may conclude that the subsurface diffusion can be the rate-limiting step for the entire nitrogen transportation process. This could be because nitrogen atom binds too strong on the V(110) surface. Alloying V with Ru is expected to lower the adsorption energy of atomic N on the surface as in the bulk and leads to lower diffusion barrier to the subsurface.

5. Experimental Results

5.1 Permeation results

Initial tests are performed to investigate the N₂ fluxes and underlying transport mechanism across pure V and Nb membrane foils as a function of temperature and partial pressure driving force. The flux data for tested membrane samples are reported for temperatures between 600 and 800 °C with varying feed pressures of 60 psig to 198.6 psig. At all of the temperatures considered, V membranes exhibit a linear continuous increase in the N₂ fluxes with an increase in pressure gradient indicating Knudsen flow dominant transport.

Comparison between the theoretical Knudsen ratios and the experimental flux ratios calculated from permeation tests is used to determine the underlying N₂ transport mechanism at each temperature and pressure gradient. The summary of the results are given in Table 2. As seen in Table 2, the dominant N₂ permeation mechanism is found to be Knudsen diffusion through the surface defects at 600°C for V and Nb membranes. Experimental findings also indicated N₂ transport via solution-diffusion mechanism at 800°C between 90 psig and 198.2 psi pressure gradient. By using the flux values obtained at solution-diffusion regime, N₂ permeability values were calculated and shown to range from 2.24×10⁻¹³
mol/m·s·Pa$^{1/2}$ to 3.37×10$^{-13}$ mol/m·s·Pa$^{1/2}$ for V membranes. N$_2$ permeability in V is found to be five orders of magnitude smaller compared to that of the target case of H$_2$ in Pd (around 4×10$^{-8}$ mole/m·s·Pa$^{1/2}$). The low flux observed for V and Nb membranes can be explained readily based upon the results of the electronic structure calculations previously discussed. Nitrogen binding within the crystal structure of V and Nb is too strong but may be weakened by alloying these metals with Ru, thereby enhancing the permeability by adjusting the solubility and diffusivity of atomic nitrogen within the crystal lattice.

Table 2. Variation of N$_2$, Argon and He fluxed with pressure gradient across the membrane for V and Nb at different temperatures

<table>
<thead>
<tr>
<th>$\Delta P$ (psi)</th>
<th>N$_2$/He</th>
<th>N$_2$/Ar</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Vanadium</td>
</tr>
<tr>
<td>600°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>198.2</td>
<td>0.356</td>
<td>N/A</td>
<td>Knudsen</td>
</tr>
<tr>
<td>90</td>
<td>N/A</td>
<td>1.136</td>
<td>Knudsen</td>
</tr>
<tr>
<td>800°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>198.2</td>
<td>0.449</td>
<td>N/A</td>
<td>Solution-Diffusion</td>
</tr>
<tr>
<td>102.2</td>
<td>0.437</td>
<td>N/A</td>
<td>Solution-Diffusion</td>
</tr>
<tr>
<td>90</td>
<td>N/A</td>
<td>1.635</td>
<td>Solution-Diffusion</td>
</tr>
<tr>
<td>80</td>
<td>N/A</td>
<td>0.979</td>
<td>Knudsen</td>
</tr>
<tr>
<td>70</td>
<td>N/A</td>
<td>0.784</td>
<td>Knudsen</td>
</tr>
<tr>
<td>60</td>
<td>N/A</td>
<td>0.952</td>
<td>Knudsen</td>
</tr>
</tbody>
</table>

*Theoretical Knudsen (Equation 4) N$_2$/He = 0.378, N$_2$/Ar = 1.195

5.2 Material characterization results

Various characterization experiments have been performed on the feed side of the pure V and Nb metallic membranes that were used for N$_2$ permeation experiments, with the results for the V membrane shown. Characterization using XRD in Figure 7 indicates that after the N$_2$ permeation at high temperature, the pure V develops surface nitride and to some extent oxide species. Although not necessarily favorable since this formation if penetrated deep enough into the bulk may influence N$_2$ dissociation and subsequent transport, these results validate the solution-diffusion mechanism of nitrogen permeation in these dense catalytic metallic membranes.
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References


