INORGANIC MEMBRANES FOR CARBON CAPTURE AND POWER GENERATION

DISSertation

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ABSTRACT

Inorganic membranes are under consideration for cost-effective reductions of carbon emissions from coal-fired power plants, both in the capture of pollutants post-firing and in the direct electrochemical conversion of coal-derived fuels for improved plant efficiency. The suitability of inorganic membrane materials for these purposes stems as much from thermal and chemical stability in coal plant operating conditions as from high performance in gas separations and power generation.

Hydrophilic, micro-porous zeolite membrane structures are attractive for separating CO₂ from N₂ in gaseous waste streams due to the attraction of CO₂ to the membrane surface and micropore walls that gives the advantage to CO₂ transport. Recent studies have indicated that retention of the templating agent used in zeolite synthesis can further block N₂ from the micropore interior and significantly improve CO₂/N₂ selectivity. However, the role of the templating agent in micro-porous transport has not been well investigated.

In this work, gas sorption studies were conducted by high-pressure thermo-gravimetric analysis on Zeolite Y membrane materials to quantify the effect of the templating agent on CO₂, N₂, and H₂O adsorption/desorption, as well as to examine the effect of humidification on overall membrane performance. In equilibrium conditions, the N₂ sorption enthalpy was nearly unchanged by the presence of the templating agent, but the N₂ pore occupation was reduced ~1000×. Thus, the steric nature of the blocking of N₂ from the micropores by the templating agent was confirmed. CO₂ and H₂O sorption enthalpies were similarly unaffected by the templating agent, and the micropore occupations were only reduced as much as the void volume taken up by the templating agent. Thus, the steric blocking effect did not occur for molecules more strongly attracted to the micropore walls. Additionally, in time-transient measurements the CO₂ and H₂O mobilities were significantly enhanced by the presence of the templating agent. This meant that small re-
strictions in the micropores were beneficial to the transport of molecules with some attraction to the micropore walls. Further evidence of this effect were discovered in transport studies on Zeolite Y membranes, in which small amounts of residual water were observed to enhance the CO₂ permeance in a similar way as the templating agent in the powder. However, the effect was only observed for dry CO₂ streams and previously humidified membranes. H₂O affinity for the zeolite framework was so high and mobility in the micropores was so low that even 0.8 mol% H₂O included in the gas stream was enough to reduce CO₂ transport by 100×. This poses a serious concern for carbon capture by zeolite Y membrane in coal-fired power plants: the waste stream must be dehumidified first.

In the long-term, raising the efficiencies of fossil-fuel power plants is preferable to post-combustion capture for cost- and resource-effective carbon emissions reduction. Supplementing combustion of the fuel with electrochemical conversion by solid oxide fuel cell (SOFC) shows promise in this effort. Thin-film (<1μm thick) SOFCs have recently exhibited power densities at low temperature (LT) that rival those of thick-film, high-temperature designs, with improved stability and quick ramp times. Low operating temperatures also provide the potential for fast, high-volume production, but so far high-performing LT-SOFCs have all been made by micro-fabrication methods.

In this work, thin-film LT-SOFC modules were fabricated by colloidal processing and their performance was demonstrated. Nano-particulate colloid syntheses, dip-coating, and rapid thermal processing methods yielded fine-particle membrane microstructures, with high porosity and conductivity in the platinum/gadolinium-doped ceria (GDC) composite electrodes and density in the yttria-stabilized zirconia (YSZ) electrolytes. Power densities of >1000 W/m² at 450°C and ~5000 W/m² at 600°C were achieved, and the modules ran >100hrs at peak power after 8 thermal cycles. Thus it was demonstrated that high-performing LT-SOFCs can be produced with large-scale methods.
Dedicated to

my mother and father for their
unwavering support, and to Heidi for
inspiration.
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My family, in particular my mother Carol, has always been there for me. With love and thanks!
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**FIELDS OF STUDY**

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>v</td>
</tr>
<tr>
<td>Vita</td>
<td>vi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xii</td>
</tr>
<tr>
<td>List of figures</td>
<td>xiv</td>
</tr>
<tr>
<td>List of Symbols</td>
<td>xix</td>
</tr>
<tr>
<td>Greek variables</td>
<td>xix</td>
</tr>
<tr>
<td>Roman variables and constants</td>
<td>xx</td>
</tr>
<tr>
<td>Abbreviations and chemical formulas</td>
<td>xxiii</td>
</tr>
<tr>
<td>Chapter 1 Inorganic membrane applications</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Overview</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Scope</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Gas separation</td>
<td>3</td>
</tr>
<tr>
<td>1.3.1 Membrane characteristics</td>
<td>3</td>
</tr>
<tr>
<td>1.3.2 Gas separation membrane performance parameters</td>
<td>5</td>
</tr>
<tr>
<td>1.3.3 CO₂-capture performance goals</td>
<td>7</td>
</tr>
<tr>
<td>1.3.4 Membrane materials</td>
<td>7</td>
</tr>
<tr>
<td>1.4 Power production: SOFCs</td>
<td>10</td>
</tr>
<tr>
<td>1.4.1 Background</td>
<td>10</td>
</tr>
<tr>
<td>1.4.2 SOFC Performance</td>
<td>17</td>
</tr>
</tbody>
</table>
Chapter 2 Gas Sorption on Zeolite NaY, 1: Equilibrium ................................................................. 23
  2.1 Introduction ................................................................................................................................. 23
    2.1.1 Membrane synthesis and performance ................................................................................. 23
    2.1.2 Gas sorption thermodynamics ............................................................................................... 25
    2.1.3 The H₂O problem, part 1 ....................................................................................................... 28
    2.1.4 Sorption capacity and the templating agent .......................................................................... 29
  2.2 Experimental ................................................................................................................................. 30
    2.2.1 Powder samples ...................................................................................................................... 30
    2.2.2 High-pressure thermo-gravimetric analysis (HP-TGA) .......................................................... 30
    2.2.3 Volumetric sorption by Micromeritics ASAP2020 ................................................................. 32
  2.3 Results and discussion .................................................................................................................. 32
    2.3.1 PSD, XRD, SEM and EDX ........................................................................................................ 32
    2.3.2 Equilibrium Isotherms ............................................................................................................ 34
    2.3.3 Sorption capacity .................................................................................................................... 37
    2.3.4 Sorption thermodynamics ....................................................................................................... 38
  2.4 Conclusions .................................................................................................................................. 40

Chapter 3 Gas Sorption on Zeolite NaY, 2: Time-Transients .......................................................... 41
  3.1 Introduction ................................................................................................................................... 41
    3.1.1 Molecular mobility .................................................................................................................. 41
    3.1.2 The H₂O problem, part 2 ....................................................................................................... 43
  3.2 Experimental .................................................................................................................................. 44
    3.2.1 Powder samples ...................................................................................................................... 44
    3.2.2 High-pressure thermal gravimetric analysis (HP-TGA) .......................................................... 44
    3.2.3 Data analysis .......................................................................................................................... 45
  3.3 Results and discussion .................................................................................................................. 45
    3.3.1 Isotherms ............................................................................................................................... 46
    3.3.2 Activation energy .................................................................................................................... 50
  3.4 Conclusions .................................................................................................................................. 52
6.3 Results and discussion .............................................................................................................96
  6.3.1 Electrolyte quality ...........................................................................................................96
  6.3.2 SOFC performance .......................................................................................................105
6.4 Comparisons to literature ....................................................................................................110
6.5 Conclusions .........................................................................................................................111

Conclusions ..................................................................................................................................113
  Zeolite NaY for carbon capture ..............................................................................................113
  Future work ............................................................................................................................114
  Colloidal processing of SOFC materials ..............................................................................114
  Future work ............................................................................................................................116

Bibliography ................................................................................................................................117

Appendix A Data tables ...............................................................................................................129
  A.1 Equilibrium sorption parameters ......................................................................................129
  A.2 Time-transient sorption parameters with Ar .................................................................132
  A.3 Time-transient sorption parameters with N2 .................................................................138

Appendix B Distribution list .......................................................................................................139
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 5.1:</td>
<td>Success of organic additives for 120mM platinum colloid synthesis       75</td>
</tr>
<tr>
<td>Table 5.2:</td>
<td>Optimized formulations for Pt-colloid synthesis and Pt/GDC composite dipping suspension                        76</td>
</tr>
<tr>
<td>Table 5.3:</td>
<td>Optimized formulations for GDC/YSZ suspensions.                      77</td>
</tr>
<tr>
<td>Table 5.4:</td>
<td>Effect of Pt content and heat-treatment temperature on the RT conductivity of 2 layer Pt/GDC electrodes. Red highlights are samples of similar HT temp (650°C)                                   86</td>
</tr>
<tr>
<td>Table 6.1:</td>
<td>Optimized formulations for Pt-colloid synthesis and Pt/GDC composite dipping suspensions.                           103</td>
</tr>
<tr>
<td>Table 6.2:</td>
<td>Optimized formulations for Pt-colloid synthesis and Pt/GDC composite dipping suspensions.                           105</td>
</tr>
<tr>
<td>Table 6.3:</td>
<td>SOFC module performance, comparisons to literature                   111</td>
</tr>
<tr>
<td>Table A.1:</td>
<td>Equilibrium sorption parameters: $ZYN_{0TA}$.                        129</td>
</tr>
<tr>
<td>Table A.2:</td>
<td>Equilibrium sorption parameters: $ZYN_{0TA}$.                        130</td>
</tr>
<tr>
<td>Table A.3:</td>
<td>Equilibrium sorption parameters: $ZYN_{0TA}$.                        131</td>
</tr>
<tr>
<td>Table A.4:</td>
<td>Equilibrium sorption parameters: $ZYN_{TA}$.                         131</td>
</tr>
<tr>
<td>Table A.5:</td>
<td>Time-transient sorption parameters: $ZYN_{0TA}$, CO$_2$.             132</td>
</tr>
<tr>
<td>Table A.6:</td>
<td>Time-transient sorption parameters: $ZYN_{0TA}$, H$_2$O.             133</td>
</tr>
<tr>
<td>Table A.7:</td>
<td>Time-transient sorption parameters: $ZYN_{0TA}$, N$_2$.              133</td>
</tr>
<tr>
<td>Table A.8:</td>
<td>Time-transient sorption parameters: $ZYN_{TA}$, CO$_2$.              134</td>
</tr>
<tr>
<td>Table A.9:</td>
<td>Time-transient sorption parameters: $ZYN_{TA}$, H$_2$O.              135</td>
</tr>
<tr>
<td>Table A.10:</td>
<td>Time-transient sorption parameters: $ZYN_{TA}$, N$_2$.               136</td>
</tr>
<tr>
<td>Table A.11:</td>
<td>Lumped time-transient sorption parameters: all samples, gases        137</td>
</tr>
</tbody>
</table>
Table A.12: Lumped time-transient sorption parameters: exchanged with $\text{N}_2$. ....... 138
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Figure 1.1:</strong></td>
<td>Idealized pore size control by (left) layering, (right) impregnation</td>
<td>4</td>
</tr>
<tr>
<td><strong>Figure 1.2:</strong></td>
<td>Transport mechanisms: (Left) High ( T/)low ( p ), ballistic, low selectivity. (Middle) Low ( T/)high ( p ), condensation, low permeability. (Right) Mid ( T/)mid ( p ), sorption-activated diffusion, high selectivity, high permeability</td>
<td>4</td>
</tr>
<tr>
<td><strong>Figure 1.3:</strong></td>
<td>Faujasite-type (FAU) zeolite structure. From [43]</td>
<td>8</td>
</tr>
<tr>
<td><strong>Figure 1.4:</strong></td>
<td>Thermodynamic efficiencies of fuel cell and combustion plant with temperature</td>
<td>12</td>
</tr>
<tr>
<td><strong>Figure 1.5:</strong></td>
<td>SOFC and circuit schematic</td>
<td>14</td>
</tr>
<tr>
<td><strong>Figure 1.6:</strong></td>
<td>Example SOFC performance plots. (Left) Voltage loss with current density. (Right) Open-circuit voltage, voltage loss, and peak power density. ( T_1 &lt; T_2 &lt; T_3 )</td>
<td>17</td>
</tr>
<tr>
<td><strong>Figure 1.7:</strong></td>
<td>SOFC temperature regimes</td>
<td>21</td>
</tr>
<tr>
<td><strong>Figure 2.1:</strong></td>
<td>Solid surface, modeled as grid of equidistant sorption sites, some occupied by CO(_2) molecules. Here, ( \theta = C_i / C_i^{\max} = 4/18 \approx 0.22 )</td>
<td>25</td>
</tr>
<tr>
<td><strong>Figure 2.2:</strong></td>
<td>Solid surface, modeled as grid of equidistant sorption sites with heterogeneous sorption energy. Lower energy sites are more likely to be occupied by adsorbate</td>
<td>27</td>
</tr>
<tr>
<td><strong>Figure 2.3:</strong></td>
<td>CO(_2) occupancy gradient develops in response to difference in feed and permeate partial pressures</td>
<td>28</td>
</tr>
<tr>
<td><strong>Figure 2.4:</strong></td>
<td>HP-TGA setup. Bubbler was only used in time-transient measurements discussed in chapter 3</td>
<td>31</td>
</tr>
<tr>
<td><strong>Figure 2.5:</strong></td>
<td>XRD and PSD results on powder samples</td>
<td>33</td>
</tr>
<tr>
<td><strong>Figure 2.6:</strong></td>
<td>Representative SEM images of powder samples</td>
<td>33</td>
</tr>
</tbody>
</table>
Figure 2.7: Equilibrium isotherms, CO₂ and N₂ on ZY₉₀TA, ZY_TA powders. Note that N₂ sorption for ZY_TA was rescaled by 10³. ............................................................... 35

Figure 2.8: Literature comparison: Sorption capacity, isosteric heat [75,76,79]. ...... 36

Figure 2.9: Equilibrium isotherms, H₂O on ZY₉₀TA, ZY_TA powders. ......................... 36

Figure 2.10: Sorption capacity of CO₂, N₂, H₂O on ZY₉₀TA, ZY_TA powders. .... 38

Figure 2.11: LHS of (2.1), CO₂, N₂, H₂O on ZY₉₀TA, ZY_TA powders. .............. 39

Figure 3.1: Example of time-transient isotherms, ads/desorption. Heat treatment conducted prior to start of experiment. ................................................................. 45

Figure 3.2: CO₂ time-transient isotherms on ZY₉₀TA and ZY_TA. (Top) adsorption, (bottom) desorption). Pressure was 1 atm. ................................................................. 46

Figure 3.3: H₂O time-transient isotherms on ZY₉₀TA and ZY_TA. (Top) adsorption, (bottom) desorption. Partial pressure of H₂O was 2970kPa. ...................... 48

Figure 3.4: Isosteric sorption heats vs. loading. Calculated from sorption fits. .......... 49

Figure 3.5: Normalized time-transient isotherms. Adsorption isotherms normalized to the saturation amount (wt% adsorbed at t = ∞). Desorption isotherms normalized to the adsorption saturation and residual amount (wt% remain at t = ∞). .......... 50

Figure 3.6: Mobility activation plots in Ar: a) CO₂ and b) H₂O. Slope of the lines are activation energy, u_m. Intercepts are ln(b). .......................................................... 50

Figure 3.7: Time-transient experiments using N₂ as carrier gas in place of Ar. Relevant parameters can be found in Appendix A.3. ................................................. 51

Figure 3.8: Multiple-gas trade-off experiment on ZY₉₀TA at 1 atm to determine the effect of CO₂ on H₂O desorption. (Buoyancy corrected.) ...................... 52

Figure 4.1: Zeolite NaY membrane performance measurements taken by Dr. Krenar Shqau, membranes provided by Jeremy White. ............................................... 56

Figure 4.2: Zeolite NaY membrane performance measurement setup. Feed and sweep were in crossflow, but are shown in parallel here for simplicity. .................. 57

Figure 4.3: Calculated Zeolite NaY occupancy and mobility for gas composition 70mol% N₂, 14mol% CO₂ and 16mol% H₂O. (Left) ZY₉₀TA, (right) ZY_TA. ........ 58

Figure 4.4: CO₂ permeance: membrane measurements vs. calculated values. $P_{CO₂} = 20kPa$. ................................................................................................. 60
Figure 4.5: (Left) NoTA membrane CO₂ permeance. (Right) NoTA membrane CO₂/N₂ selectivity. Gas composition: \( p_{CO_2} = 20 \text{kPa}, \ p_{N_2} = 80 \text{kPa}, \ p_{H_2O} = 800...1600\text{Pa} \) ................................................................................................................. 61

Figure 5.1: 4-point conductivity measurement setup, adapted from [135]. .................. 70

Figure 5.2: TGA, DSC, and XRD on GDC and YSZ powders dried from aqueous suspension. ................................................................................................................... 78

Figure 5.3: (Left) Dialysate conductivity data during dialysis. (Right) Raman spectra on GDC colloid, pre- and post-dialysis................................................................. 79

Figure 5.4: DLS spectra. (Left) Aged GDC colloid. (Right) GDC vs. YSZ colloids, each aged ~1 week. ......................................................................................................... 80

Figure 5.5: GDC membrane thickness vs. heat-treatment temperature and method. N₂ NSSGP permeance at 30°C included for RTP 500°C .................................................. 82

Figure 5.6: GDC cross-section prepared by FIB, (Left) SEM and (Right) TEM. \( AKP30 = \alpha\text{-alumina, Sumitomo, 300nm particle size.} \) ...................................................... 83

Figure 5.7: Pt/GDC electrode membrane fabrication steps. (Left) Alumina support. (Middle) Dried, dip-coated support. (Right) RTP heat-treated membrane..................... 84

Figure 5.8: Pt/GDC electrode (Ode1) on macroporous alumina support: (Left) 1, (Middle) 2, (Right) 3 dipped layers. ...................................................................................... 84

Figure 5.9: Pt/GDC electrode (Ode1) and Pt paint: (Left) Conductivity vs. temperature, (right) thermal resistivity coefficient (slope). Literature values from [152]. 87

Figure 5.10: GDC, YSZ conductivity from 4-pt. vdP measurements. .................... 88

Figure 6.1: (Top) Spiral-wound SOFC stack. (Bottom) Proposed SOFC module..... 91

Figure 6.2: PTFE tape mask geometries for retaining bare portion of electrode for current collection. ........................................................................................................ 93

Figure 6.3: Gas cell assembly drawing. Faces, screws, and fittings are SS 316. Gaskets are Thermiculite 815. Additional sealing with Ceramabond where needed, typically between o-ring and SOFC.............................................................. 95
Figure 6.4: SOFC and gas cell assembly: (Left) SOFC with Ode1 current collector. (Middle) Thermiculite gasket with Ode2 current collector in center. (Right) Gas cell assembled, positioned in furnace. ................................................................. 95

Figure 6.5: Examples of electrolyte defects before defect elimination steps. (Left) Optical microscopy. (Right) SEM. (Top) Pop-out defect type, (bottom) crack defect type. 97

Figure 6.6: Selected results from microwave output consistency evaluation. (Left) 100ml, 40% power. (Right) 50ml, 20% power. ........................................................ 98

Figure 6.7: Effect of microwave treatments on GDC colloidal particle size. .......... 99

Figure 6.8: Effect of microwave treatments on GDC. XRD, Raman spectra. XRD was measured on powder dried at 50°C. ................................................................. 99

Figure 6.9: Heat treatment of dried colloid powders to show effect of microwave treatments on solid yields. ............................................................................... 100

Figure 6.10: SEM images of FIB-prepared cross sections. (Upper left): Example of trench dug by FIB for analyzing crack. (Upper right): Crack originating between layers of electrode. (Lower left): Cross-section in proximity of pop-out type defect shows delamination between electrode layers. (Lower right): Crack originating from support-electrode interface. ............................................................................. 101

Figure 6.11: SEM images of FIB-prepared cross sections: (Top) Before and (Bottom) after optimization of electrode dipping suspensions. .............................. 102

Figure 6.12: Full SOFC module: (A) Top-view of module, photograph. (B) SEM image of cross-section. (C) and (D) TEM images of cross-section. The vertical channels were likely damage from FIB. ......................................................... 104

Figure 6.13: SOFC module, GDC electrolyte, I-V and power density. ........... 106

Figure 6.14: SOFC modules, YSZ electrolyte, I-V and power density. ........... 107

Figure 6.15: SOFC modules, YSZ electrolyte with GDC interlayer, I-V and power density. Ode1: Air, 100sccm. Ode2: H₂ + 3% H₂O 150sccm. ..................... 108

Figure 6.16: SOFC module, GDC/YSZ bi-layer electrolyte, area-specific resistance and associated activation energy. Ode1: Air, 100sccm. Ode2: H₂ + 3% H₂O 150sccm. 109
Figure 6.17: SOFC module, GDC/YSZ bi-layer electrolyte, area-specific resistance and associated activation energy. Ode1: $\text{H}_2 + 3\% \text{H}_2\text{O} 150\text{scm}$. Ode2: Air, 100scm. 110
LIST OF SYMBOLS

Greek variables

\( \alpha_{1/2} \) : Single-gas selectivity for species 1 over species 2, no units.

\( \alpha_{1/2} \) : True selectivity of membrane for species 1 over species 2, no units.

\( \Gamma_l \) : Maximum volumetric concentration of species \( l \) by geometric argument, units: \( \text{mol/cm}^3 \).

\( \varepsilon_r \) : Dielectric constant, units: \( \text{F/m} \).

\( \eta_{\text{Carnot}} \) : Thermodynamic efficiency of a heat engine, or “Carnot” engine.

\( \eta_{\text{Cell}} \) : Thermodynamic efficiency of galvanic cell, no units.

\( \eta_f \) : Dynamic viscosity of fluid \( f \), units: \( \text{Pa}\cdot\text{s} \).

\( \theta \) : Fraction of total sites occupied.

\( \theta_l \) : Fraction of total sites occupied by species \( l \).

\( \theta^f_l \) : Fraction of total sites occupied by species \( l \) on the feed|permeate sides of membrane.

\( \kappa^{-1} \) : Debye length, units: \( \text{m} \).

\( \mu_l \) : Chemical potential of species \( l \), units: \( \text{J/mol} \).

\( \mu_l \) : Electrochemical potential of species \( l \), \( \text{J/mol} \).

\( \mu^0_l \) : Standard chemical potential, \( \text{J/mol} \).

\( \nu_l \) : Number of species \( l \).

\( \Phi_l \) : Electrical potential of species \( l \), units: \( \text{V} \).

\( \Phi^{\text{ thermo}} \) : Thermodynamic factor, no units.
\( \Delta \Phi^{\text{activation}} \): Voltage loss due to reaction activation energy, units: V.

\( \Delta \Phi^{\text{diffusion}} \): Voltage loss due to mass transfer resistance, units: V.

\( \Delta \Phi^{\text{el}} \): Voltage loss due to slow reaction kinetics, units: V.

\( \Delta \Phi^{\text{OC}} \): Voltage drop across fuel cell in open circuit conditions, units: V.

\( \Delta \Phi^{\text{Ohm}} \): Voltage loss due to Ohmic resistance, units: V.

\( \Delta \Phi^{\text{OC, Nernst}} \): Total voltage drop, or “Nernst potential” across fuel cell, units: V.

\( \Delta \Phi^{\text{true}} \): Voltage drop across cell that is available for the circuit, units: V.

\( \Delta \Phi^0 \): Standard reaction potential, units: V.

\( \rho \): Electrical resistivity, units: \( \Omega \cdot \text{m} \).

\( \rho_f \): Mass density of fluid \( f \), units: \( \text{kg/m}^3 \).

\( \rho_s \): Mass density of sphere, units: \( \text{kg/m}^3 \).

\( \sigma_l \): Electrical conductivity of species \( l \), units: \( \Omega^{-1} \cdot \text{m}^{-1} \).

\( \tau_l^T \): Characteristic time for diffusion of species \( l \) at temperature \( T \), units: s.

**Roman variables and constants**

\( A \): Area, units: \( \text{m}^2 \).

\( b_l \): Molecular mechanical mobility of species \( l \), units: \( \text{mol} \cdot \text{s/kg} \).

\( b_l^0 \): Unconditional molecular mechanical mobility, (“unconditional” meaning all neighboring sites are available for hopping transport), units: \( \text{mol} \cdot \text{s/kg} \).

\( b_l^T \): Temperature-independent, unconditional mechanical mobility, units: \( \text{mol} \cdot \text{s/kg} \).

\( c_l^p \): Concentration of gas \( l \) in permeate, units: mol.

\( c_l^f \): Concentration of gas \( l \) in feed, units: mol.

\( C_l \): Volumetric concentration of gas \( l \), units: \( \text{mol/m}^3 \).

\( C_l^{\text{Ads,Des,r=\infty}} \): Volumetric concentration of gas \( l \) in the limit that time goes to infinity; calculated by fitting exponential curve to adsorption|desorption time-transient isotherm, unit: \( \text{mol/m}^3 \).
\( C_{i}^{\text{max}} \)  “Sorption capacity”; “saturation amount”; temperature-dependent maximum volumetric concentration of gas \( l \), units: mol/m\(^3\).

d: Distance, units: m.

\( D_{l} \): Diffusion constant of component \( l \), units: m\(^2\)/s.

\( D_{l}^{0} \): Temperature-independent diffusion constant, units: m\(^2\)/s.

\( f \): Correlation factor of the mechanical mobility to the total site vacancy concentration, no units.

\( \tilde{f} \): Conditional parameter of the mechanical mobility, between zero and one, no units.

\( f_{l}^{e} \): Permeance of species \( l \) in single-gas conditions, units: mol/(m\(^2\)·s·Pa).

\( f_{l} \): Permeance of species \( l \) in mixed-gas conditions, units: mol/(m\(^2\)·s·Pa).


\( F \): Force, units: N.

\( g \): Acceleration due to gravity, 9.8m/s\(^2\).

\( \Delta G \): Gibbs free energy, units: J/mol.

\( h \): Height, units: m.

\( \mathbf{h}^{a} \): “Sorption affinity”; molar enthalpy of adsorption, units J/mol.

\( \Delta h^{0} \): Standard molar enthalpy change, units: J/mol.

\( i_{l} \): Current of species \( l \), units: A.

\( j_{l} \): Molar flux of species \( l \), units: mol/(m\(^2\)·s)

\( j_{e} \): Electron current density, units: A/m\(^2\).

\( k_{\text{B}} \): Boltzmann constant, \( 1.3806488 \times 10^{-23} \) m\(^2\) kg/(s\(^2\) K)

\( K_{l} \): Temperature-dependent Langmuir constant for species \( l \), no units.

\( K_{l}^{0} \): Temperature-independent Langmuir constant for species \( l \), no units.

\( K_{l}^{0,LF} \): Temperature-independent Langmuir-Freundlich constant for species \( l \), no units

\( K_{l}^{0,T} \): Temperature-independent Toth constant for species \( l \), no units

\( K_{l}^{\text{LF}} \): Temperature-dependent Langmuir-Freundlich constant for species \( l \), no units
\( K_{T}^{l} \): Temperature-dependent Toth constant for species \( l \), no units

\( KE_{\text{Brown}} \): Kinetic energy of a particle due to Brownian motion, units: J or J/mol.

\( \ell \): Characteristic length of diffusion, also length between electrodes in voltage measurement, units: m.

\( l \): Transporting or sorbing species.

\( m \): Generalized Langmuir exponent, no units.

\( n \): Generalized Langmuir exponent, no units.

\( n_e \): Number of electrons involved in reaction, no units.

\( N_i \): Number of dissolved ions in solution, no units.

\( p^0 \): Reference pressure, here 101,325 Pa.

\( p^f_p \): Total pressure on feed|permeate side of membrane, units: Pa.

\( P_{\text{cell}} \): Power density, units: W/m^2.

\( P_{\text{cell}}^{\text{max}} \): Max or “peak” power density.

\( q_e \): Charge of an electron, \( 1.60217657 \times 10^{-19} \) C.

\( Q \): Reaction quotient, no units.

\( r_s \): Radius of sphere, units: m.

\( R \): Ideal gas constant, \( 8.3144621 \) J/(mol·K)

\( R \): Resistance, units: Ω.

\( R_{\text{sh}} \): Sheet resistance, units: Ω.

\( t \): Time, units: s.

\( t_h \): Time for free-falling spherical particle to drop from height \( h \) assuming laminar fluid flow around sphere. Units: s.

\( t_t \): Transmittance of species \( l \), no units.

\( T \): Temperature, units: K.

\( T_{\text{HT}} \): Heat-treatment or “soak” temperature, units: °C.

\( T_{\text{in}} \): “Input” temperature; temperature of hot reservoir of a heat engine, units: K.

\( T_{\text{out}} \): “Output” temperature; temperature of cold reservoir of a heat engine, units: K.

\( u^D \): Activation energy for diffusion, units: J/mol.

\( u^m \): Activation energy for mobility, or “hopping” energy, units: J/mol.
$U_{\text{max}}$: Saturation energy, units J/mol.

$U_{\text{in}}$: Total chemical energy in the heat engine system, units: J.

$U_{\text{out}}$: Chemical energy in the heat engine system available to do work, units: J.

$v_j$: Drift velocity of component $i$, units: m/s.

vdP: van der Pauw, in reference to a method of 4-point sheet resistance measurement.

$X$: Membrane thickness, units: m.

$Z_i$: Ionization strength, or absolute valence state, of ion $i$ in solution.

**Abbreviations and chemical formulas**

Al$_2$O$_3$: Aluminum oxide; alumina.

ASR: Area-specific resistance, units: $\Omega$/m$^2$.

CeO$_2$: Cerium oxide; ceria.

CO$_2$: Carbon dioxide.

CTP: Conventional thermal processing.

DLS: Dynamic laser scattering.

DSC: Differential scanning calorimetry.

EDX: Energy-dispersive x-ray spectroscopy.

EtOH: Ethanol.

GDC: Gadolinia-doped ceria.

FAU: Faujasite-type structure

FIB: Focused ion beam.

FR: Frequency response.

FTIR: Fourier-transform infrared spectroscopy.

Gd(NO$_3$)$_3$·6H$_2$O: Gadolinium nitrate hexahydrate. Gadolinium precursor in GDC-colloid synthesis.

H$_2$O: Water.

H$_2$PtCl$_6$·6H$_2$O: Chloroplatinic acid hexahydrate. Platinum precursor in Pt-colloid synthesis.

HP-TGA: High-pressure thermal gravimetric analysis/analyzer.

HT: High temperature.
ID: Inner diameter.
IEP: Isoelectric point.
IT: Intermediate temperature.
LHS: Left-hand side.
LT: Low temperature.
MD: Molecular dynamics.
N₂: Nitrogen.
NaOH: Sodium hydroxide.
NaY: Designation of zeolite meaning Faujasite-type structure with Si/Al >1.5, sodium cations present.
NH₄⁺: Ammonium ion.
(NH₄)₂Ce(NO₃)₆: Ammonium cerium nitrate. Precursor in ceria/GDC colloid synthesis.
NO₃⁻: Nitrate ion.
NOₓ: NO or NO₂ gas.
NMR: Nuclear magnetic resonance.
OCV: Open circuit voltage.
OD: Outer diameter.
Ode1: Electrode deposited on support.
Ode2: Electrode deposited on electrolyte.
PSD: Particle/pore size distribution.
PTFE: Polytetrafluoroethylene.
PVA: Polyvinyl alcohol.
PVAc: Polyvinyl acetate.
PVP: Polyvinylpyrrolidone.
PZT: Point of zero charge.
QENS: Quasi-elastic neutron scattering.
RH: Relative humidity.
RHS: Right-hand side.
RT: Room temperature (20-25°C).
RTP: Rapid thermal processing.
SA: Surface area.
SCCM: Standard cubic centimeters per minute.
SECA: Solid-state Energy Conversion Alliance.
SEM: Scanning electron microscope/microscopy.
SiO₂: Silicon oxide; silica.
SOFC: Solid oxide fuel cell.
STP: Standard temperature (298K) and pressure (101,325 Pa).
TEOS: Tetraethylorthosilicate.
TEM: Transmission electron microscope/microscopy.
TGA: Thermal gravimetric analysis.
TMA: Tetramethylammonium ion.
TMAOH: Tetramethylammonium hydroxide.
TA: Templating agent.
X: Designation of zeolite meaning Faujasite-type structure with Si/Al < 1.5.
XRD: X-ray diffraction.
YSZ: Yttria-stabilized zirconia.
Yte: Electrolyte.
ZA: Zeolite A.
ZYNoTA: Zeolite Y powder or membrane with no templating agent present.
ZYTA: Zeolite Y powder or membrane for which no steps have been taken to remove the templating agent.
CHAPTER 1

INORGANIC MEMBRANE APPLICATIONS

In this chapter, historical and scientific background is provided and the motivation for the work is established. Membrane applications are first discussed broadly, and then the discussion is split into the two fields most relevant to the work: membranes for gas separation and membranes for power generation. In each case, membrane performance concepts are outlined which will be used in the later chapters of the thesis.

1.1 Overview

There is a broad consensus among researchers that anthropogenic carbon emissions are contributing to long-term increases in global temperature and drastic changes to the environment, including sea level rise which will likely devastate coastal regions around the world [1]. The potential damage due to sea level rise was the impetus for the case Massachusetts v. Environmental Protection Agency before the Supreme Court of the United States, the majority opinion of which in 2007 was that the Environmental Protection Agency was required under the Clean Air Act to regulate CO\textsubscript{2} as an air pollutant [2]. Even before that decision but particularly afterward, industries, government agencies and research institutions scaled up efforts to increase the efficiencies of major emitters of CO\textsubscript{2} such as motor vehicles [3,4] and power plants [5,6]. The coal industry has become a major target for pollution control. In 2011, 31\% of CO\textsubscript{2} emissions in the United States came from burning coal [7], 91\% of which was generated for electric power. U.S. coal production is not projected to change much over the next 30 years, while in Asia coal production already dwarfed than in the U.S. and is projected to rise another 70\% by 2040. What sets coal apart from motor vehicles is the centralization of its emissions. Nearly all of the CO\textsubscript{2}
emitted by the U.S. coal industry comes from approximately 7000 power plants and 19,000 large-scale independent generators across the country. Over 10% of those power plants are already >35 years old, which is well beyond their intended lifetimes (<30) [8]. Thus, the next few decades will present the U.S. with excellent opportunities to raise efficiencies of power production and significantly reduce CO₂ emissions.

The above discussion is not to imply that the drive for plant efficiency is entirely conservationist in nature. The World Coal Association estimated that every 1% increase in power plant efficiency translates to 2-3% reduction in coal consumption [9]. Thus, such upgrades are desirable for cost savings as well as resource conservation.

In a coal-fired power plant, the heat that is released from burning the coal is used to boil water. The steam turns a turbine, which provides mechanical energy that is translated into electric power. One strategy to reduce air pollution in this process is to capture CO₂ from the gaseous waste stream for sequestration [4] or for use in the chemical industry [5]. This is an important short-term strategy for carbon emission reduction because existing plants can be retrofitted for post-combustion CO₂ capture. A second, more long-term, strategy is to increase plant efficiency by replacing or combining the combustion/steam/turbine system with an electrochemical conversion process such as a solid-oxide fuel cell (SOFC). The latter strategy in particular may also be applied to natural gas and methane combustion, as well as residential and mobile applications [10].

1.2 Scope

Inorganic membranes are considered for both post-combustion CO₂ capture and electrochemical conversion processes. This thesis discusses both. First the characterization of zeolite NaY membrane materials for carbon capture from coal flue-gas streams is discussed. Equilibrium and time-transient sorption data are presented, the performance of zeolite NaY membranes is predicted, and the results are compared to experimental observations in order to better understand membrane performance in a range of conditions. Then the colloidal syntheses of SOFC electrode and electrolyte materials are described, followed by presentations of the fabrication and characterization of ultra-thin low-temperature SOFCs for cost-effective power generation from coal syngas.
1.3  **Gas separation**

A membrane is a barrier between two environments that is generally permeable for one or more transporting species of particle, ion, or molecule, while being impermeable to others. The property of such discrimination between species is known as *selectivity*. For gaseous selection the membrane is placed between a feed stream and a sweep stream or vacuum and transport occurs spontaneously. This is one of the distinct advantages of membrane separation: aside from feed pressurization and vacuum if needed, the process requires no external work, no chilling or regeneration of sorptive media, and hence can be made energy and cost-efficient.

Large-scale industrial gas membrane processes include: H$_2$ separation from ammonia purge streams [11], CO$_2$/CH$_4$ separation [12], and nitrogen purification [13], most of which involve polymer-based membrane systems in large part because high-performing polymers can be made cheaply in large quantities and with a wide range of selective properties [13]. Inorganic membranes tend to be more expensive to manufacture [14], and processing for high-performance can be more challenging to scale up [15]. Hence inorganics are reserved for those processes that involve high temperatures [16], certain catalysis [17], harsh chemical environments such as biosyngas [18] or coal flue-gas waste streams containing sulfurous compounds [5], and fuel cell electrolytes for power production from impure or carbonaceous fuels [10].

1.3.1  **Membrane characteristics**

Inorganic membranes tend to be distinct from their organic counterparts by the rigidity of their structures and are often categorized by function, synthesis/processing, or pore size. According to the IUPAC classification [19], a macroporous membrane has pore diameter Ø > 50nm, a mesoporous membrane has 2 < Ø < 50nm, and a microporous membrane has Ø < 2nm. A dense membrane has no pores extrinsic to its crystal structure, though structures with intracrystalline voids large enough to house unmodified molecules, such as zeolites, are often described as both “dense” (in the intercrystalline sense) and “porous” (in the intracrystalline sense). Permeation and selection properties are tailored by the layering of membranes or the impregnating of membrane pores as shown in figure
1. Mechanical strength for very thin membranes is provided by larger-pore supporting layers which can be made thicker with less sacrifice to transport efficiency.

Figure 1.1: Idealized pore size control by (left) layering, (right) impregnation.

Figure 1.2: Transport mechanisms: (Left) High $T$/low $p$, ballistic, low selectivity. (Middle) Low $T$/high $p$, condensation, low permeability. (Right) Mid $T$/mid $p$, sorption-activated diffusion, high selectivity, high permeability.

Molecular sieving is the process by which gas separation occurs simply because the retained species do not fit in the pores, but categorization by pore size is somewhat superficial for circumstances in which physical or chemical bonding is involved in the transport mechanism. CO$_2$ and N$_2$ molecules, for example, are close enough in size and mass to render molecular sieving ineffective, even for microporous membranes. To separate CO$_2$
from a gaseous mixture while retaining N\textsubscript{2}, a membrane material can be chosen with a particular adsorptive affinity for CO\textsubscript{2}, given certain operating conditions, to increase the likelihood that CO\textsubscript{2} will occupy the membrane pores over that of the less adsorptive N\textsubscript{2} [20]. This sorption-activated separation mechanism is illustrated in figure 1.2, and it is this phenomenon that is exploited in the technique for CO\textsubscript{2} capture from coal flue-gas streams discussed in this thesis. Hence, CO\textsubscript{2}/N\textsubscript{2} separations $>1000$ can be achieved using mechanisms such as that shown in figure 1.2 [21], but the transport tends to be far slower for inorganics than for their organic counterparts of the same thickness [22]. The way to alleviate this has been to reduce inorganic membrane thicknesses down to submicron scale. Unfortunately, mechanical instability inhibits the use of ceramics, particularly below thicknesses of $\sim0.5\text{mm}$, unless they are supported [14]. Ceramic supporting structures offer excellent mechanical stability but are thick and thus can be bulky and resistive to mass transfer. Organic supporting structures can be mechanically stable and highly permeable, not to mention cost-effective, but their use as supports for ceramic membranes has so far been hindered by the high temperatures required for conventional ceramics processing. However, with the use of advanced syntheses [20], and sintering techniques such as rapid thermal processing (RTP), fabricating submicron-thick ceramic membranes on organic supports may become feasible in the future.

### 1.3.2 Gas separation membrane performance parameters

Membrane performance is described in the literature by two key measured quantities: permeance and selectivity. The permeance of a membrane, $f_i$, in SI units of mol/$(m^2\cdot s\cdot Pa)$, is the molar flux, $j_i$, of species $l$ transporting across the active area of the membrane, over the pressure drop, $\Delta p$, from feed (f) to permeate (p) side of the membrane [23]:

$$f_i = \frac{j_i}{\Delta p}$$  \hspace{1cm} (1.1)

If $l$ is the only species present in the feed, a modifier “s” is assigned to the parameter to signify that the measurement was taken in single-gas conditions. This is a critical distinction because in mixed conditions, gas-to-gas interference and interactions can have profound effects on membrane performance, effects on which membrane technologies often
rely. Thus, the distinction must also be made for the selectivity parameter, which is the ratio of the permeance of one gas over that of a competitor. In single gas conditions the selectivity of species $l_1$ over species $l_2$, $\alpha_{l_1/l_2}^s$, is calculated by [23]

$$\alpha_{l_1/l_2}^s = \frac{f_{l_1}^s}{f_{l_2}^s}$$

(1.2)

Single-gas permeance can be measured by a dead-end, or “non-stationary” setup [24]. In mixed-gas conditions, the observed permeance ratio is called the “true” selectivity, measured by gas chromatograph on a so-called “Wicke-Kallenbach” [25] configured setup as described in section 4.2, and calculated by

$$\alpha_{l_1/l_2} = \frac{f_{l_1}}{f_{l_2}} = \frac{c_{l_1}^p}{c_{l_2}^p}$$

(1.3)

In (1.2), $c$ is the molar concentration. The difference between single-gas and true selectivities can offer insights to the dominant transport mechanisms in a given set of conditions. In microporous membranes two types of competitive transport are defined. In type I, the concentrations of $l_1$ and $l_2$ in the micropores are low and are effectively independent of one another, and so $\alpha_{l_1/l_2}^s \approx \alpha_{l_1/l_2}$. Thermal fluctuations in this case affect both species almost equally, so type I selectivity has weak $T$-dependence [26]. In type II, the micropore concentration of $l_1$ is high while that of $l_2$ is low. This result can arise from the sorptive affinity of the membrane surface for $l_1$, and the lack of such affinity for $l_2$ as illustrated in figure 1.2, and the interference of species $l_1$ on the transport of $l_2$ results in a very large, if not effectively infinite, $\alpha_{l_1/l_2}$. This behavior will not be reflected in the single-gas data, and so in certain conditions $\alpha_{l_1,l_2}^s \ll \alpha_{l_1/l_2}$. The permeance of $l_1$, and the true selectivity, is heavily dependent on temperature in this case, and due to reduced adsorption at some high temperature the true and single gas selectivities will converge [26].
1.3.3 CO₂-capture performance goals

Carbon capture from coal-fired flue-gas waste stearnas is to occur immediately following desulfurization, when the gas stream is at 57°C, ~1atm, and fully humidified. The simplified molar composition is 16% H₂O, 14% CO₂ and 70% N₂, with small residual amounts of H₂S and other compounds. The US Department of Energy (DOE) requires that at least 90% of the CO₂ is removed with 95% purity in the captured stream [22,27,28]. However this is accomplished, the cost of electricity is not to rise more than 35%. Given such a cost constraint, feed pressurization is not likely to be practical beyond what is possible with a blower, and dehumidification processes are undesirable. For a membrane process, the project goals translate to minimum CO₂ permeance of 10⁻⁶ mol/(m²·s·Pa) and a CO₂/N₂ selectivity of ~200 [29,30,31]. The problem of H₂O for CO₂ separation will be discussed in 2.1.3, 3.1.2, and 4.3.2.

1.3.4 Membrane materials

Inducing fast, type II CO₂/N₂ selectivity at pressure and temperature ranges practical for use in a coal plant requires exploiting the sorptive activity of CO₂, which in turn requires a microporous membrane structure. But a microporous structure does not have to be intrinsic to the material and can be achieved in many ways. As illustrated in figure 1.1, a macro- or mesoporous structure of α-alumina, γ-alumina, titania, or zirconia particles, or carbon structures can be impregnated with a pore-filling substance to reduce the pore size [21,32]; filled with a liquid condensate through which the CO₂ is permeable [33]; or with surface modification the affinity of the pore walls for CO₂ may be strong enough that the pore size is restricted by layers of adsorbed CO₂ [34]. However success for CO₂/N₂ selectivity has so far been limited in these techniques, rarely >30 at p ≤ 200kPa [35], and when they do exhibit high selectivity it comes at the expense of permeance, rarely above 1-5 x 10⁻⁸ mol/(m²·s·Pa) while maintaining high selectivity [32,36]. This trade-off between selectivity and permeance is not limited to these technologies, but has been well documented for nearly all membrane designs, typically presented as a “Robeson plot”, in which the two parameters are set on the x and y-axes and it is clear that the upper-right region, representing both high permeance and high selectivity, is typically void of data.
Microporous silica membranes prepared by sol-gel method with CO$_2$ permeance $10^{-6}$ mol/(m$^2$·s·Pa) and CO$_2$/N$_2$ < 5 were reported by de Vos and Verweij [38], while Ku-roaka et al. [39] achieved CO$_2$/N$_2$ > 60 but the CO$_2$ permeance was $7 \times 10^{-8}$ mol/(m$^2$·s·Pa). CO$_2$/N$_2$ selectivities of ~80 were achieved using carbon membranes on γ-alumina/α-alumina supporting structures, but with CO$_2$ permeance ~6 $\times$ 10$^{-9}$ mol/(m$^2$·s·Pa) [32]. Investigations into highly selective graphene-derived structures [40, 41] appear promising, with tight microstructural control for tailoring the selective properties, though it is too early in development to give definitive permeance/selective performance values. Currently, the most success for scalable inorganic membranes for CO$_2$ capture has been reported for zeolite materials.

Zeolites are 3-dimensional crystalline frameworks formed by connected SiO$_2$ tetrahedra that outline uniformly shaped and distributed pores big enough to fit alkali/alkaline earth ions and other molecules such as water [42]. There are over 40 categories of zeolite structures that occur in nature and over 150 that are made synthetically in laboratories and industry [42], and each of those categories is further subdivided by broad ranges of cation substitutions.

**Figure 1.3:** Faujasite-type (FAU) zeolite structure. From [43].
Recently, fast CO₂/N₂ separations have been reported for faujasite-structured zeolites (FAU). The FAU structure is a maze of so-called α-cages, β-cages, and double 6-rings, as shown in figure 1.3. The interiors of the β-cages and double-6 rings are able to house alkali/alkaline earth ions but have been shown by molecular simulation [44] as well as implied by experiment [45] to be inaccessible to extraframework molecules, even as small as H₂O. However, small gases such as H₂O, CO₂, N₂, with hard-sphere diameters of 0.28, 0.39, and 0.37 nm respectively, can occupy the α-cages, ~1.2nm in diameter. Each α-cage is accessible through 4 windows ~0.74nm in diameter [46].

The interactions of gas molecules with the FAU structure is in large part determined by the extent to which the Si⁴⁺ framework cations have been replaced by Al³⁺, which results in a localized negative charge that makes the framework more hydrophilic. FAU with Si/Al ratio < 1.5 is referred to as Zeolite X, Si/Al > 1.5 is known as Zeolite Y. The resident Na⁺ cations can also be substituted by K⁺, Li⁺, and many others. Thus, FAU is subdivided by the Si/Al ratio and the resident alkali/alkaline earth cation. [47]

Hasegawa et al. [48] grew NaY membranes from NaX seeds on α-alumina support tubes and measured CO₂ permeances and CO₂/N₂ selectivities of 1.3 x 10⁻⁶ mol/(m²·s·Pa) and 10⁻30. They saw a significant rise in selectivity and only a slight decline in permeance when Na⁺ was substituted for K⁺. A membrane that exhibits high CO₂/H₂ separation is very likely to also perform well for CO₂/N₂. Sandstrom et al. [18] reported CO₂ permeances >10⁻⁶ mol/(m²·s·Pa) for high Si/Al FAU membranes which maintained CO₂/H₂ selectivity ~5 in the presence of small amounts of H₂S. Giannakopoulos et al. achieved CO₂/H₂ of 19 with CO₂ permeance of 1.3 x 10⁻⁷ mol/(m²·s·Pa) [49].

In this work, detailed equilibrium and time-transient sorption studies were conducted on zeolite NaY seed crystals similar to those used in the fabrication of membranes reported by White et al [20]. CO₂ permeances >10⁻⁷ mol/(m²·s·Pa) were observed for membranes with >550 CO₂/N₂ selectivity. One of the key findings in that work was the effect of residual tetramethylammonium (TMA) templating agent (TA) in the micropores which reduced N₂ permeance by >100× but caused only a 2-3× reduction in CO₂ permeability. Similar effects were found for CO₂/H₂, as well. This work seeks to explain this phenome-
non in terms of the thermodynamic driving force for transport and diffusion of gas molecules in the micropores.

## 1.4 Power production: SOFCs

### 1.4.1 Background

In some respects, the fundamentals of fuel cell operation were byproducts of experiments and research carried out in the 19th century. In the early 1800s, Davy [50] and later Grove [51] split water by applying a voltage between two platinum electrodes. When the applied voltage was removed, they noted a reverse current generated by the spontaneous recombination of hydrogen and oxygen gases. When a fuel such as hydrogen and an oxidant are separated by a barrier, the system can be said to store the chemical energy that is released upon the reaction of the two substances. Advances in thermodynamics in the mid-19th century revealed the contrasts between two basic methods of harnessing this stored energy: combustion processes and direct electrochemical conversion [50].

Combustion processes such as conventional vehicle engines and coal power plants use the energy released in fuel oxidation to move pistons and turn turbines, through which mechanical and electrical energy is generated. The limitation of such an indirect use of chemical energy is simply derived from the Carnot cycle; the maximum theoretical efficiency of which (\( \eta_{\text{Carnot}} \)) is given by [52]

\[
\eta_{\text{Carnot}} = \frac{U_{\text{out}}}{U_{\text{in}}} = \frac{T_{\text{in}} - T_{\text{out}}}{T_{\text{in}}} \tag{1.4}
\]

where \( U_{\text{in}} \) is the amount of available chemical energy, \( U_{\text{out}} \) is the usable, non-heat, energy generated by the engine. \( T_{\text{in}} \) and \( T_{\text{out}} \) are the engine input and output temperatures, respectively. 100% efficiency requires that \( U_{\text{in}} = U_{\text{out}} \), which is only possible if \( T_{\text{out}} = 0K \) and/or \( T_{\text{in}} = \infty \). Unfortunately these conditions are impossible to meet and impractical to even approach. Thus with a practical \( T_{\text{out}} \) of 300K, \( \eta_{\text{Carnot}} \) is 63…77% for input temperatures of 800…1300°C. Actual engines achieve much lower efficiencies, ~40%, due to entropic and premature heat losses [52]. Treatments of irreversible thermodynamics yield better approximations for power plant efficiency by taking the square root of the RHS of (1.4).
The most important consequence of (1.4) is that efficiency increases with $T_{in}$ and thus efforts to increase combustion engine efficiencies often involve developing ways to burn hotter without producing excessive NOx compounds.

In *direct electrochemical conversion*, also known as *galvanic cell conversion*, ions move across an otherwise impermeable barrier, or electrolyte, and electric power is generated from the required counter-flow of electrons across a circuit. The efficiency of this process, $\eta_{cell}$ is given by [53,54]

$$\eta_{cell} = \frac{\Delta G(T)}{\Delta h^0} = \frac{nF\Delta \Phi^{OC}}{\Delta h^0}$$

In (1.5), $\Delta G(T)$ is the free energy change of the overall conversion reaction at temperature $T$, $F$ is Faraday’s constant, $n$ is the number of electrons involved in the reaction, $\Delta h^0$ is a reference molar enthalpy change for the reaction and $\Delta \Phi^{OC}$ is the open circuit voltage, derived in section 1.4.2. In contrast to (1.4), the only limitation in (1.5) is the internal energy of the fuel [51]. Just as important is the fact that because $\Delta \Phi^{OC}$ decreases with $T$, the galvanic efficiency increases with decreasing $T$. This observation is sketched in figure 1.4 from which it is clear that, from a thermodynamic perspective, efforts to improve electrochemical conversion efficiency drive to lower operating temperatures.

Thermodynamics is only part of the story, however. Fast kinetics and diffusion drive fuel cell operation to higher temperatures—above 800°C in the case of many solid-oxide fuel cell designs—and this is a problem that has plagued SOFC research from the outset.
Toward the end of the 19th century, the realization of efficiency limitations inherent to combustion processes led Ostwald to suggest that a galvanic system be used to generate power from coal as opposed to a steam turbine [50]. The first solid-state gas cell, however, was not designed for this purpose but was constructed in the 1890s by Nernst as a lamp [50]. One of the principle problems with the Nernst lamp was the external heat source required for operation and its warm-up time, on the order of hours, and this among other reasons led to metal filament lamps surpassing the Nernst lamp in light production applications [10]. But Nernst’s legacy in fuel cell research was his hypothesis, later confirmed by Baur and Pries and detailed by Wagner [10], that oxygen carried charge through many solid oxide mixtures at elevated temperature—particularly stabilized zirconia [50]. A solid-oxide electrolyte is similar to the ceramic rod in Nernst’s lamp. The ion-conducting electrolyte forms a barrier between two gas phases and a difference in the partial pressure of oxygen across the electrolyte results in a driving force for oxygen ion transport. However ionic transport requires first the cathodic reduction of O₂ gas to O²⁻ ions, and then the anodic oxidation of the ions post-transport. The simplified reactions can be written as

\[ \text{Cathode: } \text{O}_2 + 4e^- \rightarrow 2\text{O}^{2-} \]
\[ \text{Anode: } 2\text{O}^{2-} \rightarrow 2\text{O}_2 + 4e^- \]
Cathode: \( \frac{1}{2} \text{O}_2 + 2e^- \rightarrow \text{O}^{2-} \) 

Anode: \( \text{O}^{2-} \rightarrow \frac{1}{2} \text{O}_2 + 2e^- \)  

These electrode reactions in turn require the counter-flow of electrons through an electrode-to-electrode circuit. In the simplest case, the result of these requirements is the symmetric system illustrated in figure 1.5. The electrolyte (Yte) is a fully dense, gastight material with high oxygen ion transference. The electrodes (Ode1, Ode2) conduct both ions and electrons, either within a single matrix or as a composite, and exhibit catalytic properties favorable to the reduction of oxygen gas at the cathode and the oxidation of oxygen ions at the anode. The electrode-to-electrode circuit consists of a resistive load and a voltmeter.
Figure 1.5: SOFC and circuit schematic.

The movements of charge carriers in the solid phase of SOFC components are modeled as charged species “hopping” from site to site on a Langmuir lattice. The concentration of lattice sites occupied by charge carrier species \( l \) is \( \theta_l \), and the concentration of vacant sites is thus \( (1-\theta_l) \). The carrier chemical potential is then related to the occupied and vacant site concentrations by

\[
\mu_l = \mu_l^0 + RT \ln \left( \frac{\theta_l}{1-\theta_l} \right) \quad (1.7)
\]
In (1.7), $\mu_i^0$ is the concentration-independent standard potential and $R$ is the ideal gas constant. The driving force for carrier transport on the lattice is fully described by the change in electrochemical potential, $\tilde{\mu}_i$ defined for each carrier species as \[54\]

$$\tilde{\mu}_i = \mu_i + z(q_e)\Phi_i = \mu_i^0 + RT \ln \left( \frac{\theta_i}{1 - \theta_i} \right) + z(q_e)\Phi_i$$ \tag{1.8}$$

In (1.8), $z$ is the number of electrons associated with the carrier, $q_e$ is the magnitude of electron charge, and $\Phi_i$ is the electrical potential. In equilibrium conditions, as shown in figure 1.5, the electrochemical potential must be the same everywhere, but this is not necessarily true for the species occupations across the gas/electrode, circuit/electrode, and electrode/electrolyte interfaces. Abrupt changes in species concentrations across interfaces are compensated by differences in material constants ($\mu_i^0$) and electrical potential ($\Phi_i$).

There is no driving force in figure 1.5, and thus the current across the load will be zero, but when oxygen partial pressures move away from equilibrium conditions, the cathode and anode reactions proceed toward equilibrium and ionic diffusion occurs in the electrolyte. Electrochemical potential gradients develop and a measureable voltage drop is observed to increase until the open-circuit voltage is reached, at which point the electrochemical potential gradients will become static. The voltmeter needs a small amount of current to register a voltage, so there will be some small leak of electrons and the system will not be entirely static during measurement. In addition, due to the electron-chemical potential gradient of the (unbuffered) electrons in the electrolyte a small but non-zero electron current flows in the (nearly ideal) electrolyte.

Increasing the current through the load has the effect of draining excess electrons and supplying electrons to depleted regions. Thus, the electrode reactions and ionic transport proceed toward electrochemical equilibrium, though not ideally. It is the non-ideal nature of fuel cell components that leads to the four textbook categories of SOFC voltage loss as follows: The electrode reactions require some amount of energy to activate, which manifests in an abrupt drop in voltage at very small currents ($\Delta\Phi_{\text{activation}}$) as sketched in figure 1.6 [56]. Electron leak through the electrolyte ($\Delta\Phi_{\text{el}}$) is observed as a drop in open circuit potential similar to the effect of the activation energy. The electrode reaction kinetics also
contribute to voltage loss, which is often seen as a non-linear drop at low current density ($\Delta \Phi^{\text{reaction}}$). All of the components, but particularly the electrolyte, exhibit Ohmic-type resistance, which is seen in figure 1.6 as a linear voltage drop at mid-range currents ($\Delta \Phi^{\text{Ohm}}$). Finally, the interfaces in figure 1.5 are rarely ideal, and slow mass-diffusion, particularly with the use of porous electrodes, causes considerable voltage loss ($\Delta \Phi^{\text{diffusion}}$) at high currents [56]. All of the loss factors sum with increasing current until the voltage, and thus the generated power, is eliminated entirely. Taking losses into account, (1.5) becomes

$$\eta_{cell} = \frac{n_F \Delta \Phi^{true}}{\Delta h^0}$$

where

$$\Delta \Phi^{true} = \Delta \Phi^{OC, \text{Nernst}} - \Delta \Phi^{\text{activation}} - \Delta \Phi^{el} - \Delta \Phi^{\text{reaction}} - \Delta \Phi^{\text{Ohm}} - \Delta \Phi^{\text{diffusion}}$$

$\Delta \phi^{true}$ is a function of the current density, $j_e$, and so the area-specific power generated by the cell, $P_{cell} = \Delta \Phi^{true} \times j_e$, initially increases with $j_e$, reaches a peak, then declines to zero, as sketched in figure 1.6. Discussions of SOFC performance in the literature often include plots of $\Delta \Phi^{true}$ and $P_{cell}$, as well as tabulated values of $\Delta \Phi^{OC}$, the peak power density, $P_{\text{cell}}^{\text{max}}$, and the area-specific resistance or $ASR$, at a range of operating temperatures.

The following sections describe these performance parameters in more detail.
1.4.2 SOFC Performance

Open circuit voltage

In this section, $\Delta \Phi^{OC}$ is derived as a function of oxygen partial pressure, $p_{O_2}$, and anion transference number, $t_{O_2^-}$, to establish its relation to the theoretical, or “Nernst” voltage, $\Delta \Phi^{OC, Nernst}$. The limitations of $\Delta \Phi^{OC}$ as a performance parameter are also discussed.

The electrolyte in most SOFC designs is a dense, oxygen anion ($O^{2-}$) conductor which separates an oxygen-rich environment such as air from a fuel such as $H_2$ or a light hydrocarbon. There were two charge carriers in the simplified redox half-reactions given in (1.6): electrons and $O^{2-}$ ions. Generally, considering non-negligible electronic conduction in the electrolyte, the one-dimensional current of charge carrier $i_i$ in a uniform matrix, $i_i$, is a function of the carrier conductivity, $\sigma_i$, and the electrochemical potential, $\tilde{\mu}_i$, according to the following relation: [57]

$$i_i = -\frac{\sigma_i}{z_iF} \frac{d\tilde{\mu}_i}{dx} \tag{1.10}$$
where \( F \) is Faraday’s constant, \( x \) is the perpendicular distance coordinate from the cathode side to the anode side of the electrolyte and \( z \) is the charge of the carriers; \((z = -2 \text{ for oxygen anions, } z = -1 \text{ for electrons})\). In open circuit conditions the total current is zero, and this allows (1.10) for the two carriers to be combined as [57]

\[
d\tilde{\mu}_{\text{O}^2^-} = \frac{2\sigma_{\text{e}}}{\sigma_{\text{O}^2^-}} d\tilde{\mu}_{\text{e}}
\]  

(1.11)

Local equilibrium between charged \( \text{O}^2^- \) ions and neutral \( \text{O}_2 \) molecules has the consequence that the reaction \( \text{O}^2^- \leftrightarrow \frac{1}{2} \text{O}_2 + 2\text{e}' \) can be written as a sum of electrochemical potentials \( \Sigma_i d\tilde{\mu}_i = 0 \), where \( v_i \) is the quantity of each species per \( \text{O}^2^- \) ion. The sum of electrochemical potentials, combined with (1.10), gives [57]

\[
d\tilde{\mu}_{\text{e}} = -\frac{1}{4} \left( \frac{\sigma_{\text{O}^2^-}}{\sigma_{\text{O}^2^-} + \sigma_{\text{e}}} \right) d\tilde{\mu}_{\text{O}_2} = -\frac{1}{4} t_{\text{O}^2^-} d\tilde{\mu}_{\text{O}_2}
\]  

(1.12)

where \( t_{\text{O}^2^-} \) is the contribution of the anionic conductivity to the total conductivity, known as the anionic transference. Combining (1.7) and (1.11) and integrating over the thickness of the electrolyte gives the open circuit voltage across the electrolyte, \( \Delta \Phi_{\text{OC}} \), in terms of the oxygen partial pressure and anion transference [57]:

\[
\Delta \Phi_{\text{OC}} = \Phi_{\text{e}}^{\text{cath}} - \Phi_{\text{e}}^{\text{an}} = \frac{RT}{4F} \int_{p_{\text{pH}}^{\text{cath}}}^{p_{\text{pH}}^{\text{an}}} t_{\text{O}^2^-} d\ln p_{\text{O}_2}
\]  

(1.13)

(1.13) is the general case for a mixed ionic-electronic conducting electrolyte. In the case of a purely ionic conductor, \( t_{\text{O}^2^-} = 1 \), and integration yields the simplified Nernst voltage [53]: \( \Delta \Phi_{\text{OC, Nernst}}^{\text{cath}} = \frac{RT}{4F} \ln \left( \frac{p_{\text{O}_2}^{\text{cath}}}{p_{\text{O}_2}^{\text{an}}} \right) \). The partial pressure ratio is the quotient of the reaction, \( Q \), and as such, considering a fuel such as hydrogen or methane only involves substituting the reaction quotient and adding the standard reaction potential, \( \Delta \Phi^0 \), to get

\[
\Delta \Phi_{\text{OC, Nernst}} = \Delta \Phi^0 + \frac{RT}{4F} \ln (Q)
\]  

(1.14)
The most important thing to note in (1.14) is that $\Delta \Phi_{\text{OC}, \text{Nernst}}$ is intrinsic to the reaction and has no dependency on material type, structure, processing or performance. To compare a measured open circuit voltage to the Nernst voltage is to assume that $t_{o^{\text{e}}} = 1$, in which case any observed deviation from the Nernst voltage is due to electrolyte defects, incomplete densification of the electrolyte or inadequate gas sealing. Such comparisons are not always valid in investigations of electrolyte materials outside the range at which $t_{o^{\text{e}}} \approx 1$ [58], and this can particularly be the case for ceria.

**Peak power and area-specific resistance (ASR)**

The peak power density of a SOFC, given in units of W/m$^2$, is the most convenient and most discussed performance parameter given in the literature. Comparisons are often drawn between SOFC materials, processes, cell designs and generators based on the peak power density alone. However this may not be wise given that the peak power density value depends on many factors in the system, including temperature, fuel type, materials structure and properties, Ohmic resistances, thermodynamics, polarization, reaction kinetics and component and interfacial microstructures. The discussion is better served by resolving sources of power loss in the individual SOFC modules, which is accomplished by a range of characterization techniques including impedance spectroscopy under ranges of fuel and oxidant compositions. The area-specific resistance at a given current density, $ASR(j_e)$, is [10]

$$ASR(j_e) = \frac{\Delta \Phi_{\text{OC}} - \Delta \Phi_{\text{true}}(j_e)}{j_e}$$  \hspace{1cm} (1.15)

A constant $\Delta \Phi_{\text{OC}}$ over all of $j_e$ in (1.14) assumes 100% fuel utilization, uniformly isothermal conditions, and ignores mass transfer in the electrodes. Correcting the ASR for deviations from these assumptions requires molecular simulations to model the mass and heat flow, particularly in the anode.

**1.4.3 Thin-film SOFCs**

The meaning of the term “thin” in SOFC research has changed over the years as new fabrication processes have made ever thinner components possible. The thinnest components
found in generators built by manufacturers supported by the Solid-state Energy Conversion Alliance (SECA) program utilize an electrochemical vapor-deposited electrolyte that is ~30 µm thick [53]. So any component thinner than that may be called “thin”. But thick-film processes such as slurry-coating already in use by manufacturers can be modified to produce films of ~10 µm [53,59]. Thus, in this thesis “thin” refers to film thicknesses <10 µm, and “ultra-thin” refers to thicknesses <1 µm.

Oxygen anion transport in bulk YSZ becomes significant above 700-800°C. These high operating temperatures are advantageous for oxidation reaction kinetics in the cathode as well as internal fuel reforming in the anode and for use in combined cycles with steam turbines. However, materials choices for the electrodes, current collectors and interconnects are severely limited to specialty ceramics that require complex and expensive processing, and do not perform as well as lower-temperature materials such as metals. Further, the high temperatures require long ramp-up and ramp-down times (see the discussion of the Nernst lamp in section 1.4.1), and due to thermal expansion and anode sintering, high-temperature (HT) SOFCs suffer from performance loss in thermal cycling and over time during operation. If the electrolyte is thin, the Ohmic anion resistance is reduced to the extent that operating temperatures under 750°C become feasible, and so cheaper and better performing materials such as metals for the interconnects and current collectors become available. Ramp times, thermal expansion and instability are significantly reduced. 500-750°C is the so-called “intermediate temperature” (IT) regime, as shown in figure 1.7. If the electrolyte is made ultra-thin, a SOFC can operate at “low temperature” (LT) under 500°C [60-65].
Operating in the LT regime has many disadvantages, not the least of which is the poor cathode-reaction kinetics which require specialty cathode materials or platinum to overcome. Fuel reforming also becomes more difficult to achieve internally, and anode coking is more likely with unreformed carbonaceous fuels. Fleig et al. [66] pointed out that as the electrolyte thickness dips below ~1.5× the electrode particle size, mass transfer resistance at the electrode/electrolyte interface becomes dominant over Ohmic resistance, and this puts geometric constraints on the benefits achieved by going ultra-thin.

So why go ultra-thin, then? One major opportunity for IT-SOFCs is the use of flexible, porous metallic supporting structures. In the LT regime thin, flexible polymer supports are available [67]. The possibility of operating SOFCs on flexible supports opens up continuous processing methods, fast start-up and ramp-down times, and space-efficiencies unimaginable for HT-SOFCs. Estimations put the stack volume/active area ratio of spiral-wound SOFC stacks at 10-100× that of flat HT-SOFC stacks [68]. As will be shown in Chapter 5 and Chapter 6 of this thesis, using colloidal syntheses, dip-coating and rapid thermal processing, electrode particle size can be reduced to <20nm, which puts the lower thickness boundary well below 100nm for the electrolyte. At these length scales, slow reaction kinetics due to low temperature is less likely to dominate performance. It is well established in the literature that power densities can be achieved at operating tempera-

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**Figure 1.7:** SOFC temperature regimes.
tures as low as 350°C that rival those achieved at $T > 800^\circ\text{C}$ [65], but so far the greatest successes have been reported for micro-fabrication techniques such as MEMS, and successes with active areas $>1\mu\text{m}^2$ have been few [60,62]. This thesis will show that such successes are likely to proliferate in the near future.
CHAPTER 2

GAS SORPTION ON ZEOLITE NAY, 1: EQUILIBRIUM

The first step in modeling the transport and performance of zeolite NaY membranes was a systematic study of the equilibrium gas sorption behavior of the material. In this chapter, the equilibrium sorption of CO₂, H₂O, and N₂ on the interior surface area of zeolite NaY is discussed, and gravimetric data sets are presented.

2.1 Introduction

2.1.1 Membrane synthesis and performance

As discussed in Chapter 1, high CO₂ permeance and CO₂/N₂ selectivities were achieved by White et al. [20] with a membrane of FAU-type zeolite, with the promise of meeting DOE targets given reduced transport resistance in the supporting structure. The Zeolite Y (ZY) characterized in this work was prepared by Michael Severance (see acknowledgements) using a method similar to that described by White et al. [20] and Li et al. [69]. According to Li, Zeolite Y synthesis was accomplished by autoclaving at 100 or 130°C a homogenized mixture of two solutions, A and B. Solution A consisted of aluminum isopropylate dissolved in aqueous tetramethylammonium hydroxide (TMAOH) and sodium hydroxide (NaOH). Solution B consisted of tetraethylorthosilicate (TEOS) dissolved in aqueous TMAOH. The relative amount of each precursor was as required to achieve the formula 2.46 (TMA)_2O:0.032 Na₂O:1.0 Al₂O₃:3.40 SiO₂:370 H₂O:13.6 EtOH.

Li et al. found that adding the full amount of NaOH at the beginning of the synthesis resulted in the formation of Zeolite A (ZA), whereas adding the NaOH in parts during the synthesis achieved 9 - 100% ZY (versus ZA) depending on the amount of and the time
between each addition [69]. In [20] the reported yield was >95% ZY / ZA. After ~7 days, the particle diameter was 80 - 200nm in [20], 75 - 130nm in [69].

At this processing stage, the ZY particles were referred to as seeds, and were dip-coated on supporting structures such that 1.6µm seed layers were formed. The supported seed layers were placed in growth solutions and hydrothermally treated at 80-90°C for hours (Composition A) or days (Composition B).

Growth composition A did not contain the templating agent (TA), whereas composition B did contain the TA and was essentially the same as the original synthesis solution. The rapid growth that occurred for composition A did not allow the seed layer to be reincorporated into the solution and yielded a 2.5...25 µm membrane with a CO₂ permeance of ~10⁻⁹ mol/(m²·s·Pa). The N₂ permeance was below the detection limit of the GC and so the CO₂/N₂ selectivity was reported as >550. Membranes grown slower, with composition B, exhibited a dense layer of 350-600nm thickness, with a ~25 µm porous layer on top. The porous layer was regarded as insignificant to the membrane permeance and selectivity. CO₂ permeance for membrane B was ~10⁻⁷, and CO₂/N₂ selectivity was 40...500. The lower permeance for membrane A was shown to be mainly due to the thickness, as the CO₂ permeabilities (f_i × X) were only 2-3× lower for A than for B [20].

The absence of the TA in the growth solution, and thus the retention of the templated seed-crystal layer, was shown to have consequences for the membrane morphology, but the role of the TA in gas transport was not investigated.

The TA could be removed from the seed-layer by heat-treatment (ZY_NoTA), or could be left in place (ZY_TA). In previously unpublished experiments, the presence or absence of TA had a profound effect on the CO₂/N₂ and CO₂/H₂ performances of the membranes. As will be shown in more detail in chapter 4, the ZY_NoTA membranes were selective for H₂ over CO₂, whereas in retaining the templating agent, the ZY_TA membranes were selective for CO₂ over H₂.

To explain these observations, the competing phenomena of thermodynamics and diffusion in the zeolite micropores will be investigated. The gas occupancies in the micropores are the subject of this chapter, while diffusion will be investigated in chapter 3.
2.1.2 Gas sorption thermodynamics

Though the difference is not always apparent, physisorption as opposed to chemisorption involves relatively weak and thermodynamically reversible bonds [70]. A gas-phase molecule that physisorbs to a solid surface reduces the local chemical potential by an amount known as the sorption energy. In equilibrium the chemical potential is the same between adsorbate and adsorbent; $\mu_g = \mu_s$. The value of $\mu_g$ is a function of the temperature, pressure and composition of the bulk gas phase. As illustrated in figure 2.1, the solid surface, simply modeled as a flat grid of equidistant sorption sites, has a certain equilibrium concentration of adsorbate molecules of species $l$, $C_l$, relative to the saturated state, $C^\text{max}_l$, in which all sorption sites have been filled. The ratio of the equilibrium concentration to the saturated concentration is known as the sorption site occupancy: $\theta_l = C_l/C^\text{max}_l$. $\theta_l$, like $\mu_g$, depends on the state of the bulk gas phase. $C_l$ is alternatively referred to in the literature as the loading, and $C^\text{max}_l$ the sorption capacity.

![Figure 2.1: Solid surface, modeled as grid of equidistant sorption sites, some occupied by CO$_2$ molecules. Here, $\theta_l = C_l/C^\text{max}_l = 4/18 \approx 0.22$.](image)

The pore size of the FAU structure ranges from $\sim 0.74$nm in the windows to $\sim 1.2$nm at the centers of the $\alpha$-cages. Only a few CO$_2$, N$_2$, or H$_2$O molecules can fit at any given time
and so the sorption behavior with temperature and pressure follows the Generalized Langmuir (GL) monolayer model as formulated by [71]:

\[
\frac{C_i}{C_{i,sat}} = \theta_i = \left( \frac{K_i(T, p_i)^n }{p^0 + (K_i(T, p_i)^n} \right)^{\frac{m}{n}}
\]  

(2.1)

In (2.1), \(K_i(T)\) is the unitless Langmuir constant and \(m\) and \(n\) are unitless modifiers that represent the broadening of the energy distribution along the surface as discussed below.

If \(m = n = 1\), then (2.1) simplifies to the classic Langmuir (L) model:

\[
\frac{C_i}{C_{i,sat}} = \theta_i = \frac{K_i^L(T) p_i}{p^0 + K_i^L(T) p_i}
\]  

(2.2)

The classic Langmuir sorption model assumes one value of sorption energy for each sorption site across the solid surface for a given bulk gas phase state. The temperature dependence in (2.2) is then given by

\[
K_i^L(T) = K_i^{0,L} \exp \left( -\frac{h_i^{a,L}}{RT} \right) = \frac{\theta_i}{1-\theta_i} \frac{p^0}{p_i}
\]  

(2.3)

The molar sorption affinity, \(h^a\), in J/mol, can be found by determining \(\theta_i\) for a range of temperatures and pressures, and calculating the slope of linearized (2.3):

\[
\ln \left( \frac{\theta_i p^0}{1-\theta_i p_i} \right) = \ln K_i^{0,L} - \left( \frac{1}{RT} \right) h_i^{a,L}
\]  

(2.4)

If the sorption affinity is not the same for all sorption sites on the surface, e.g. is heterogeneous, then the classic Langmuir isotherm may not be adequate to describe the sorption behavior, particularly in the case of H\(_2\)O. If the energy distribution broadens but is symmetric about one mean value, then \(0 < m = n < 1\), and (2.1) simplifies to the Langmuir-Freundlich (LF) isotherm:

\[
\theta_i = \left( \frac{K_i^{LF}(T, p_i)^n }{p^0 + (K_i^{LF}(T, p_i)^n} \right)^{\frac{m}{n}} \Rightarrow \ln \left( \frac{\theta_i}{1-\theta_i} \frac{1}{p_i} \right)^{\frac{1}{n}} p_i = \ln K_i^{0,LF} - \left( \frac{1}{RT} \right) h_i^{a,LF}
\]  

(2.5)
If the non-uniform surface energy distribution is not symmetric, but is skewed toward lower energies, meaning there are more lower-energy sorption sites than higher-energy sorption sites, then \( m = 1 \) and \( 0 < n < 1 \), and (2.1) simplifies to the Toth isotherm [72]:

\[
\theta_i = \left( \frac{K_i^T (T) p_i}{p^0 + (K_i^T (T) p_i)^n} \right)^{\frac{1}{n}} \Rightarrow \ln \left( \frac{\theta_i^n}{1 - \theta_i^n} \right) \frac{p^0}{p_i} = \ln K_i^{0,T} - \left( \frac{1}{RT} \right) h_i^{\gamma,T} \quad (2.6)
\]

(2.5) and (2.6) assume that \( K_i^{\text{LF}} \) and \( K_i^T \) exhibit the same Arrhenius temperature dependence as \( K_i^{L1} \), which can only be justified by the linearity of the experimental results. The implications of (2.5) and (2.6) for the simplified solid surface model are diagrammed in figure 2.2.

![Symmetric energy distribution](image1)

![Asymmetric energy distribution, skewed to lower energy](image2)

**Figure 2.2:** Solid surface, modeled as grid of equidistant sorption sites with heterogeneous sorption energy. Lower energy sites are more likely to be occupied by adsorbate.
For a membrane in isothermal conditions, the state of species \( l \) in the bulk gas phase depends on the partial pressure in the feed stream, \( p_f^l \), and the permeate stream, \( p_p^l \). Maintaining local equilibrium across the membrane, an occupancy gradient \( (\nabla \theta_l) \) develops as sketched in figure 2.3 which is proportional to the chemical potential gradient \( \nabla \mu_l \). Macroscopically the gradient simplifies to the 1-dimensional case of decreasing chemical potential across the membrane thickness \( X \) perpendicular to the surface. Thus, \( \Delta \mu_l / X \) is the thermodynamic driving force for the transport of \( l \) across the membrane. To achieve type II \( l_1/l_2 \) transport as discussed in section 1.3.2, \( \Delta \theta_l \) should be large for \( l_1 \) and small for \( l_2 \). For \( \text{CO}_2/\text{N}_2 \) selectivity, this is often the case for microporous materials. \( \text{CO}_2/\text{H}_2\text{O} \), however, is a different story.

![Figure 2.3](image)

**Figure 2.3:** CO\(_2\) occupancy gradient develops in response to difference in feed and permeate partial pressures.

### 2.1.3 The \( \text{H}_2\text{O} \) problem, part 1

As stated in section 1.3.3, to be practical for carbon capture a membrane must meet \( \text{CO}_2 \) permeance and selectivity targets in the presence of \( \text{H}_2\text{O} \). The affinity of \( \text{H}_2\text{O} \) for FAU zeolites increases as the Si/Al ratio decreases. Wang [45] measured isosteric \( \text{H}_2\text{O} \) sorption heats of \( \sim 55 \text{ kJ/mol} \) for zeolite 13X (Si/Al < 1.5), which far exceeded those of \( \text{CO}_2 \) at low loading, \( \sim 30 \text{ kJ/mol} \) as reported by Hocker [75]. Ferreira et al. [85] observed significant deactivation of both \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) adsorption capacities in mixed-gas vacuum-
pressure swing breakout curves using commercial 13X, but the effect was smaller for H₂O. Lee et al. [86] measured CO₂ adsorption capacities at 3000 ppm concentration, and the data sets showed that 20% moisture in the gas flow lowered the CO₂ sorption capacity by ~20% on commercial 13X zeolite at 1 atm. Molecular simulations conducted by Beauvais [87] and Joos [44] showed considerable shifts in molecular configuration and CO₂ sorption isotherms in the presence of 1% water in the FAU micro-pores. Thus, ample evidence exists that even small H₂O concentrations in the feed can have a significant impact on the CO₂ sorption in a 13X membrane, and large concentrations may be enough to block out CO₂ completely. This is clearly a concern for carbon capture efforts, and no investigation into sorption behavior of materials for this purpose is complete without data for H₂O.

2.1.4 Sorption capacity and the templating agent

By geometric argument the sorption capacity of the FAU structure is 9,520 mol/m³ for both CO₂ and N₂ with hard sphere diameters of 3.9 and 3.5 Å respectively, while for H₂O, \(C_{\text{max}}^{\text{H₂O}} \approx 26,000 \text{ mol/m}^3\) for a hard sphere diameter of 2.8 Å [88]. The effect of TA on the sorption capacity is to lower it by however much space the tetramethylammonium ion occupies. Given a C-N bond length of 0.1499 nm, a C-H bond length of 0.1094 nm, a hydrogen ionic radius of 0.035 nm, and an angle of 111.17° between the C-N and C-H bonds, a TMA ion radius of 0.250 nm can be calculated. Values given in the literature, however, are as high as 0.322 nm [89,90]. The discrepancy could be in the bond angle, which was taken from ethane for the geometrical argument and may be significantly higher in TMA due to a shorter C-N bond (as opposed to C-C in ethane) and steric from the presence of four methyl groups.

Considering the geometric radius as a minimum and the literature value as a maximum, each TMA molecule would remove 1 or 2 CO₂ molecules, 4 or 6 H₂O molecules from the saturated FAU micro-pores. If each cage is assumed to have 1 TMA molecule, the respective saturation value is expected to be 8,700 or 7,800 mol CO₂ / m³ ZY_{TA}, and 23,000 or 20,300 mol H₂O / m³ ZY_{TA}. These represent reductions of 9 or 18% CO₂, 12 or 22%
H₂O from the expected saturation values of ZY₇₀TA. N₂ sorption capacity reduction was expected to be similar to CO₂.

### 2.2 Experimental

#### 2.2.1 Powder samples

The powders were provided by Michael Severence and Dr. P.K. Dutta. ZY₇₀TA was heat-treated at 400°C for 12 hrs to be sure the templating agent had been removed, but ZY₇₁TA was never heated beyond 250°C to preserve the templating agent. Characterization was done before and after the sorption measurements, including: pore size distribution by N₂ at 77K on a Micromeritics ASAP 2020, X-ray diffraction (XRD) patterns taken on a Rigaku Miniflex, and Si/Al ratios were determined by energy-dispersive x-ray spectrometry (EDX) on an FEI Quanta 200 SEM.

The seed crystal particle size, determined for the supported seed layer by SEM and DLS by White [20], was 80-200 nm. For spherical particles, this translates to external, mass-specific surface areas (SAₑₓ) of 55 – 22 m²/g. The internal surface area (SAᵢⁿ) of the FAU structure has been reported to be 550 – 900 m²/g [73,76].

SEM images were taken on ZY₇₀TA and ZY₇₁TA to determine how the agglomeration during drying and subsequent heat-treatments affected the zeolite particle sizes. The images were translated to binary black/white and >5000 agglomerates of each sample were analyzed for particle size by Image J software.

#### 2.2.2 High-pressure thermo-gravimetric analysis (HP-TGA)

Isotherms of CO₂, N₂, CH₄, and H₂ were measured on a ThermoCahn Thermax 500 HP-TGA, diagrammed in figure 2.4. The instrument was equipped with a quartz sample holder with 18.9 mm OD, 16.8 mm ID, and 20 mm depth. The sample holder was suspended inside a tubular furnace, insulated from the furnace elements by a quartz tube, in a space between baffles 162mm long with 29.25 mm ID. Gas flow from the bottom of the furnace was regulated by mass-flow controllers at the inlets and the gas pressure was maintained by a regulator at the outlet, set to 150 sccm during the experiments. The mechanical balance was kept in an inert atmosphere at the same pressure as the sample by
purge gas, which entered the balance at the top of the instrument and met the sample gas at the outlet. The purge gas flow was 5-8% lower than the sample gas flow to avoid mixing within the furnace.

**Figure 2.4:** HP-TGA setup. Bubbler was only used in time-transient measurements discussed in chapter 3.

Gas sorption by the sample holder was determined using blank runs at measurement conditions. “Background” corrections for non-sorption-related weight effects were determined from measurements in pure argon following a similar data analysis method to Gao [76], except with argon in place of helium, and gas density data from the NIST webbook [91]. Background weight effects include buoyancy and viscous drag. To verify the use of argon in our background corrections, equilibrium isotherms were measured up to 5 MPa on Ar, N$_2$, and CO$_2$ on 1g of 5mm balls of dense zirconia (Ortech), and thus the material was not expected to adsorb a detectable amount of any of the gases. Our background correction method successfully produced nearly zero values at all pressures, with an error of 0.02%. Room temperature N$_2$ and CO$_2$ sorption of Zeolite NaY, Zeolite 13X and a sample of amorphous silica were also measured on both the Thermax 500 and the ASAP 2020, and the values were comparable within 5%. Proper instrument operation was veri-
fied by measurements of a standard sample of calcium oxalate hydrate from RT to 850°C, at 0.1 and 3.5 MPa, to results provided by Thermo-Fisher Scientific. The 1 atm results were also within 0.05% error compared to the same material measured on a Perkin Elmer TGA7.

2.2.3 Volumetric sorption by Micromeritics ASAP2020

Though the Thermax 500 could be outfitted with a humidifier at the gas inlet, as discussed in section 2.2.2, the setup was not properly equipped to accurately measure H₂O sorption at a range of pressures with good statistical confidence. Isotherms of H₂O were instead measured on a Micromeritics ASAP 2020 equipped with a humidifier at the gas inlet, using argon as the carrier gas. Pressures from 2 — 2000 Pa were measured at 25, 40, 50, and 75°C. 75°C was the highest temperature measured because the sample temperature was controlled by circulating water bath.

2.3 Results and discussion

Sorption capacities and associated energies, affinities, K⁰ values, and heats of adsorption are tabulated in Appendix A.1. Isotherms and other illustrative plots are given and discussed here.

2.3.1 PSD, XRD, SEM and EDX

Figure 2.5 shows the PSD and XRD results on the two powders taken after the sorption studies were conducted. The pre-analysis results were similar. The PSD data, analyzed by the Horvath-Kawazoe method using the Saito-Foley cylindrical pore correction [73,74], showed peak pore sizes of 7.9 and 7.8 Å, median pore sizes of 8.1 and 8.4 Å, and total pore volumes of 0.192 and 0.233 cm³/g for ZY_TA and ZY_NoTA respectively. The reduction in pore volume due to the TMA ion was 17.5%. The XRD patterns were very close for the two powders, showing small deviations in orientation, and the small peak at 2θ ≈ 7°, corresponding to <5% zeolite A impurity, was present in both samples, matching the powder spectrum discussed by White [20]. EDX spectra taken before and after analyses showed Si/Al ratio of 1.59 +/- 0.06 for both samples. This put the Si/Al ratio on the low
end for what is considered to be zeolite Y, and between the structures studied by Hocker, Si/Al = 1.23 [75], and Gao, Si/Al = 2.55 [76].

Figure 2.5: XRD and PSD results on powder samples.

Figure 2.6: Representative SEM images of powder samples.
Figure 2.6 shows a representative SEM image of the powder samples. The 80…200nm zeolite particles agglomerated during drying and subsequent heat-treatment (200°C, 48hrs). The average agglomerate size was \( \sim 3.0 \mu m \) for \( \text{ZY}_{\text{NoTA}} \), and \( \sim 2.9 \mu m \) for \( \text{ZY}_{\text{TA}} \).

### 2.3.2 Equilibrium Isotherms

The \( \text{CO}_2 \) and \( \text{N}_2 \) isotherms for \( \text{ZY}_{\text{NoTA}} \) and \( \text{ZY}_{\text{TA}} \) are given in figure 2.7. Desorption curves showed no hysteresis in any case. The sorption capacities were significantly lower for \( \text{ZY}_{\text{TA}} \), which was consistent with the ASAP pore volume data given in section 2.3.1 that showed a reduced pore volume due to templating agent present in the zeolite cages. \( \text{N}_2 \) adsorption at low temperature was significant for \( \text{ZY}_{\text{NoTA}} \), particularly at high pressure, while for \( \text{ZY}_{\text{TA}} \) it was barely observable. (Note that for \( \text{ZY}_{\text{NoTA}} \) the y-axis did not need to be rescaled to resolve the \( \text{N}_2 \) adsorption curves, while for \( \text{ZY}_{\text{TA}} \) the y-axis has been multiplied by 1000.) The upward curve to the 80, 150 and 200°C isotherms are indicative of the difficulty in resolving any \( \text{N}_2 \) adsorption in \( \text{ZY}_{\text{TA}} \). The orders of magnitude lower \( \text{N}_2 \) sorption observed in \( \text{ZY}_{\text{TA}} \) suggest that the presence of TA prevented \( \text{N}_2 \) from entering the micropores to a much greater extent than it did for \( \text{CO}_2 \). Both \( \text{CO}_2 \) and \( \text{N}_2 \) data sets fit well to the classic Langmuir isotherm, (2.2), but it should also be noted that the constant slopes observed for \( \text{N}_2 \) in \( \text{ZY}_{\text{TA}} \) suggest that the calculation of the sorption capacity by the Langmuir relation may be highly inaccurate, which is reflected in the errors given in Appendix A.1.
Figure 2.7: Equilibrium isotherms, CO$_2$ and N$_2$ on ZY$_{NoTA}$, ZY$_{TA}$ powders. Note that N$_2$ sorption for ZY$_{TA}$ was rescaled by $10^3$.

The ZY$_{NoTA}$ CO$_2$ isotherms exhibited good comparison to the literature, the sorption capacities between those for FAU structures with Si/Al ratios of 1.23 and 2.55 as shown in figure 2.8. The trend was consistent with the increased hydrophilicity expected as more Si$^{4+}$ framework atoms were replaced with Al$^{3+}$, which had the effect of enhancing the negative surface charge [77]. For example, Rees et al. [78] noted enhancements in sorptive loading from silicalite to NaY (Si/Al = 2.5 +/- 0.2) of 16% for N$_2$ and 5000% for CO$_2$. Other data sets of this type for FAU structures including TMA in the micropores could not be found. Also given in figure 2.8 is the isosteric heat of adsorption at low loading, calculated from the sorption data by [73, 76].
\[ q_{st} = R \left[ \frac{p_{1,1}}{p_{1,2}} \cdot \frac{1}{T_2} - \frac{1}{T_1} \right] \] (2.7)

The isosteric heat of adsorption also fit well between the two published data sets and again was consistent with the expected response of the adsorbate to a higher-charged surface.

**Figure 2.8:** Literature comparison: Sorption capacity, isosteric heat [75,76,79].

**Figure 2.9:** Equilibrium isotherms, H$_2$O on ZY$_{NoTA}$, ZY$_{TA}$ powders.
The equilibrium sorption data for H₂O is given in figure 2.9. The data was fit globally to the Langmuir model with exponential modifications. For ZYₜₐₜ, the best fit was found using the Toth model, (2.6), and for ZYₜₐₐ, the Langmuir-Freundlich model, (2.5). These models indicate that, unlike the cases for CO₂ and N₂, the intrazeolitic surface has a heterogeneous distribution of sites for H₂O sorption, that is, not all sites have the same energy. It may be inferred from the best fit of the Toth model that when the TMA ions are not present the sorption site energy distribution is skewed toward lower energies [72]. The LF configuration indicates that when the TMA ions are present, the energy distribution for H₂O sorption is roughly symmetric in character [71]. This would seem to indicate that the TMA ion is itself adsorbed to the micropore surface, and preferentially occupies sites that exhibit lower-energy bonding for H₂O. This observation is consistent with the preferential adsorption of benzene to sites in proximity to the resident Na⁺ ions observed by Fitch et al. [80]. There were few studies of H₂O equilibrium sorption on this particular zeolite system found in the literature, but for FAU-structured zeolites in general it has been well documented both experimentally [45] and by molecular simulation [44] that isotherms of H₂O do not fit well to the Langmuir model without exponential modification. The Toth model is most frequently used, as is consistent with the ZYₜₐₜ data in this work.

2.3.3 Sorption capacity

The material saturation concentrations on both samples are shown in figure 2.10. For CO₂, the saturation amounts decreased with increasing temperature for both samples at close to the same rate, but for ZYₜₐₐ the effect of temperature on N₂ saturation was very slight. This makes sense given that the amount of N₂ sorption was small in the presence of the templating agent. H₂O and CO₂ were in good agreement in the sorption capacity magnitude, its temperature dependence, and the effect of the templating agent which caused small increases in the saturation energies calculated here from:

\[ C_i^{\text{max}}(T) = C_i^{\text{max},0} \exp \left( -\frac{U_i^{\text{sat}}}{RT} \right) \]  

(2.8)
In (2.8), $C_i^{\text{max}, 0}$ is a pre-exponential term not to be confused with $\Gamma_i$, the geometric maximum concentration discussed in section 2.1. $U_i^{\text{sat}}$ is referred to here as the saturation energy. The deleterious effect of temperature on sorption capacity is well documented [44,45,76,81], and the energies in this work, given in Appendix A.1 are not exceptions. Explanations for the observation however, are not found as frequently. Change in the size of the adsorbate relative to the zeolite structure has been suggested to be the principle factor [82], except in cases such as H$_2$ sorption [83] and the N$_2$ behavior on ZY$_{TA}$ in this work, in which the sorption capacity increased with temperature.

![Figure 2.10](image)

**Figure 2.10:** Sorption capacity of CO$_2$, N$_2$, H$_2$O on ZY$_{NoTA}$, ZY$_{TA}$ powders.

### 2.3.4 Sorption thermodynamics

The equilibrium sorption data are presented in figure 2.11 as the LHS of (2.1) for each species. Thus, the slope and intercepts of the trendlines are $h^a$ (in kJ/mol) and $\ln(K^0)$, respectively. H$_2$O is much more likely to occupy the sorption sites than CO$_2$ at the range of temperatures and pressures studied, which is consistent with the literature discussed in section 2.1.3. Despite the reduction in void volume due to TA, $h^a$ and $K^0$ for CO$_2$ and H$_2$O were not significantly affected over the studied temperature ranges. This is a very important result because the similarity of the affinities implies that the observed im-
Improvements in membrane performance had very little to do with sorption thermodynamics.

Figure 2.11: LHS of (2.1), CO$_2$, N$_2$, H$_2$O on ZY$_{NoTA}$, ZY$_{TA}$ powders.

The reduction in N$_2$ occupation in the micropores due to the templating agent was apparent in the large downward translation of the ZY$_{TA}$ data from the ZY$_{NoTA}$ data. Interestingly, the sorption affinity was not affected so much as the intercept term which is related to the configurational entropy. This is consistent with a steric obstruction rather than a change in the sorbate-sorbent bonding [84]. This is the key selection mechanism at work in the zeolite NaY membranes, to be discussed further in section 4.3.
2.4 **Conclusions**

The equilibrium sorption data presented in this chapter were consistent with data published for related zeolite systems. CO$_2$ occupied far more of the zeolite micro-pores than N$_2$ at all studied temperatures and pressures, but H$_2$O adsorbed much more than CO$_2$. Interestingly, it was not only the sorption affinity that differed between H$_2$O and CO$_2$ but the entropic component of the chemical potential. H$_2$O is smaller, so it fits better and has more configurational freedom than CO$_2$ or N$_2$. The effect of the templating agent on the sorption behavior was relatively small for H$_2$O and CO$_2$, reducing occupation by ~15-25% but having little effect on the affinity. The presence of TA appeared to shut N$_2$ out of the micro-pores such that the N$_2$ occupation was orders of magnitude reduced. Completion of transport/performance modeling for this system requires study of the change in sorption over time. Time-transience will be discussed in chapter 3.
CHAPTER 3

GAS SORPTION ON ZEOLITE NAY, 2: TIME-TRANSIENTS

In chapter 2, equilibrium sorption isotherms were presented from which thermodynamic parameters of gas transport in zeolite membrane materials were derived. In this chapter, time-transient isotherms are presented from which sorption kinetic parameters are derived and their implications are discussed.

3.1 Introduction

3.1.1 Molecular mobility

The data measured and presented in this work are macroscopic in nature, which makes intensive treatments of microporous diffusion models superfluous. Also, given that the membranes have been shown to exhibit type II permeance for the CO$_2$/N$_2$ system favorable to CO$_2$, and for the CO$_2$/H$_2$O system favorable to H$_2$O, it is sufficient to treat the dominant species in each system as the fastest case and compare single-gas conditions to mixed-gas conditions to determine the correlating effects.

If the intrazeolitic surface is modeled as a grid of discrete physisorption sites as in figure 2.1, then the transport of competing species across the surface is analogous to diffusion in a stress-free, binary solid solution. In this case, the molar flux of component $i$ is the product of the molar composition, $C_i$, and the net drift velocity, $v_i$, superimposed on the sum of random jumps from sorption site to sorption site [92]: $J_i = v_i C_i$. A net drift velocity develops in response to a chemical potential gradient, and since the molecules move toward the equilibrium state, the velocity is the product of an infinitesimal difference in chemical potential in the drift direction, $x$, and a factor of resistance to the movement of
molecules, [92]: \( v_i = -b_i \frac{\partial \mu_i}{\partial x} \). The resistance factor, \( b_i \), is known as the molecular mobility. Thus, the flux equation is

\[
J_i = -b_i C_i \frac{\partial \mu_i}{\partial x} \quad (3.1)
\]

So long as the solution of competing gases along the surface is dilute enough to be considered ideal, (3.1) can be related to Fick’s 1st law of diffusion, \( J_i = -D_i \frac{\partial C_i}{\partial x} \), by means of the so-called thermodynamic factor, \( \phi \). The mobility is related to the diffusivity, \( D_i \), by \( D_i = b_i RT \phi \). For the CO\(_2\)/N\(_2\) system it must be shown that the thermodynamic factor is ideal, \( (\phi \approx 1) \), but assuming for now that this is the case, the mobility can be fully characterized by transient gravimetric isotherms provided the absence of significant external mass and heat transfer resistances. A general solution of Fick’s 2nd law

\[
\frac{\partial C_i}{\partial x} = \frac{\delta}{\delta x} \left( D_i \frac{\partial C_i}{\partial x} \right)
\]

gives [92, 93]:

\[
b_i^0 = \frac{\ell^2}{2\tau^T RT} = b_i^0 \exp \left( \frac{-u^m}{RT} \right) \quad (3.2)
\]

In (3.2), \( \ell \) and \( \tau^T \) are the characteristic length and temperature-dependent time of diffusion, respectively, and \( u^m \) is the transport activation energy mentioned earlier. To maintain consistency with the literature, the activation energy is also reported for the thermally activated diffusion constant:

\[
D_i(T) = D_i^0 \exp \left( \frac{-u^D}{RT} \right) \quad (3.3)
\]
3.1.2 The H$_2$O problem, part 2

Qausi elastic neutron scattering (QENS) experiments by Demontis [94] yielded H$_2$O diffusivities of $10^{-10}$-$10^{-11}$ m$^2$/s from low-high loading at 77°C on zeolite 13X, supported by MD simulations by Shirono [95], while MD simulations by Krishna [96] and permeation/sorption experiments by Hasegawa and Kusakabe [48,97,98] yielded calculations of CO$_2$ diffusivities of $10^{-9}$-$10^{-10}$ m$^2$/s at 27 and 35°C. From these data sets it appears that CO$_2$ is considerably more mobile than H$_2$O in the FAU micropores. This could be promising for CO$_2$/H$_2$O selectivity given a small concentration of H$_2$O, but for larger concentrations it appears that H$_2$O will not only dominate the micropore occupation, but will move very slowly through the membrane structure.

The effect of any H$_2$O concentration on the CO$_2$/N$_2$ performance of membranes of the vast range of possible Si/Al ratios could not be found in the literature, in particular NaY Si/Al = 1.6 as reported in [20]. Galhotra et al. [100] studied CO$_2$ adsorption by FTIR on nano-crystalline zeolite NaY (Si/Al = 1.8) in the presence of co-adsorbed H$_2$O, and concluded that extra-framework alumina on the particle surface acted as catalyst sites to form carbonate/bicarbonate ions at room temperature. Given access to the micropores the ions may be immobile and capable of a similarly beneficial effect for CO$_2$ permeance as that achieved by the templating agent [99]. As will be shown in chapter 4, some limited amount of immobile water in the supercages also has the potential to imitate the effect of the templating agent. Mobile water may have its uses as well: given a higher Si/Al ratio than 13X and higher temperature, FAU membranes have been investigated for H$_2$O separation from alcohol mixtures (pervaporation) [101,102,103], so it may be possible to tailor zeolite properties for H$_2$O removal from the gas stream. With so many possible scenarios, detailed studies of the transport and sorption behavior of CO$_2$ and H$_2$O are needed on a range of Si/Al ratios to determine the optimal membrane systems for carbon capture from coal flue-gas.
3.2 Experimental

3.2.1 Powder samples

The same batches of powder zeolite seed-crystal samples, ZYNATA and ZYTOTA, discussed in chapter 2 were used in these experiments. The sample weight, however, was as low as 0.1 +/- 0.05g to better control mass and heat transfer. CO2 isotherms were taken at three sample masses, 1g, 0.25g, and 0.1g. Results varied greatly between 1g and 0.25g, but the difference was within 10% between 0.25g and 0.1g. At sample masses lower than 0.1g, instrument noise began to factor largely into the error of the results, so this was considered the lowest possible sample size while maintaining statistical confidence.

3.2.2 High-pressure thermal gravimetric analysis (HP-TGA)

Time-transient isotherms were measured on the Thermax 500 setup introduced in 2.2.2. A parallel gasline bypassing the bubbler was activated/deactivated with a set of valves to introduce/remove H2O from the inlet gas stream. Prior to each isotherm, the sample was heated to 200°C in vacuum for 12 hrs to be sure that the powder was dehydrated. The dehydrated samples were first weighed in argon, then the sorbate gas was introduced and the adsorption data was taken at 1 point/second sample rate. Once equilibrium was achieved, the sorbate was replaced with argon to measure the sorbate desorption. The chronology of the gas-switching procedure is illustrated in figure 3.1. All measurements were taken at 1 atm total pressure. Turnover of the atmosphere in the instrument was determined by taking samples of the gas stream at the gas outlet and measuring the moisture content by in-line humidifier. Turnover times were ~6s, so this number was factored into the instrumental errors but was only significant for N2, and CO2 adsorption.
3.2.3 Data analysis

The adsorption and desorption isotherms were fitted to exponential models to conform to a general solution to Fick’s 2nd law as discussed in section 3.1.1. The characteristic times were calculated as

\[ \tau_{i}^{\text{Ads}} = \left[ 1 - \frac{1}{e} \right] C_{i}^{\text{Ads}, t \to \infty} ; \quad \tau_{i}^{\text{Des}} = \frac{1}{e} C_{i}^{\text{Des}, t \to \infty} \]  

(3.4)

In (3.3), \( C_{i}^{\text{Ads}, t \to \infty} \) was the equilibrium adsorption concentration. For some of the isotherms, in particular H\(_2\)O, the desorption isotherms did not return to zero wt% gas adsorbed within 48hrs. At low temperature, it did not appear that many of the isotherms would return to zero in infinite time. In these cases a residual parameter, \( C_{i}^{\text{Des}, t \to \infty} \), was included in the fitting model and is reported in Appendix A.2.

3.3 Results and discussion

Mobility and diffusivity parameters are given in Appendix A.2. In this section, the relevant data are plotted for discussion.
3.3.1 Isotherms

The CO₂ and N₂ equilibrium concentrations in the time-transient experiments were in good agreement with the 0.1 MPa data points on the equilibrium isotherms, which was expected as the procedure was the same. The H₂O equilibrium concentrations, at ~3000 Pa in the time-transient experiments, matched fairly well with the ASAP 2020 isotherms extrapolated from 2000 Pa.

![Isotherms Graph](image)

**Figure 3.2:** CO₂ time-transient isotherms on ZYₕ₉TA and ZYₜₐ. (Top) adsorption, (bottom) desorption). Pressure was 1 atm.

The CO₂ time-transient isotherms shown in figure 3.2 yielded characteristic times on the order of 20-70s for adsorption and in the hundreds of seconds for desorption. These dif-
ferences were most likely due to heating/cooling effects during ad/desorption. The discrepancy was not likely due to mass transfer limitations. For a powder sample 4.45 mm in height, the CO$_2$ and N$_2$ isobaric intermolecular diffusion coefficient [104] is $1.7 \times 10^{-5}$ m$^2$/s at 30°C. Thus, the diffusion rate exceeded the storage rate (tortuosity = 1.5) with a 2.7s characteristic time, which was factored into the error. Furthermore, external film resistance would have impeded the adsorption as much or more than the desorption rates [93]. Many of the adsorption times were within error, particularly considering the environment turnover time within the sample chamber, ~6s, as mentioned previously.

Regardless of hysteresis, the derived adsorption diffusivity of $2.4 \times 10^{-13}$ m$^2$/s at 50°C on ZY$_{NaT}$ was comparable to that of Yi et al. [105] at the same temperature from column breakthrough curves on what they referred to as zeolite NaY (no Si/Al ratio given): the result of which gave $D \approx 2.6 \times 10^{-13}$m$^2$/s at $r_c = 3\mu$m. Molecular simulations [106,107,108], microscopic analyses such as QENS [94,109], and nuclear magnetic resonance (NMR) [110,111,112] give diffusivities for various alkanes ~100× higher than those reported for CO$_2$ here. However, there are few studies on the particular material and gas system studied here. On related materials such as silicalite there is a well-documented discrepancy between the results of such microscopic determinations of diffusion constants, and macroscopic techniques such as frequency response (FR) [113,114,115,116] that indeed spans several orders of magnitude [93,112,117,118]. Such a known discrepancy by no means invalidates the results of these experiments, but it does show that lower diffusion constants are expected for macroscopic methods.
Hysteresis was even more pronounced in the H$_2$O data, given in figure 3.3, than in the CO$_2$ data. Desorption characteristic times were on the order of tens of thousands of seconds, even hundreds of thousands at 30°C. It came as no surprise, then, that calculated H$_2$O mobilities were orders of magnitude lower for H$_2$O than for CO$_2$, a result which is strongly supported in the literature as discussed in 2.1.3. The isosteric adsorption heats as functions of loading, calculated from the equilibrium sorption models presented in chapter 2, are given in figure 3.4. The larger H$_2$O sorption heat values reinforce the heating/cooling effects as the cause for hysteresis. Further, the disadvantage of this method of diffusion measurement is apparent in the shifts in adsorption heats as the micropores filled.
Normalized adsorption and desorption isotherms for N₂, CO₂, and H₂O are plotted in figure 3.5. N₂ isotherms were taken at 30, 40, and 50°C. Isotherms above 50°C are not included since the error was >10%. The CO₂ and N₂ adsorption isotherms exhibited sudden changes in adsorption rates that appeared as elbows in the normalized isotherms. The most likely cause of these shifts was mass transfer resistance that built up as the micropore loading increased [70]. The path of incoming gas from the environment into the pore windows was from less restriction to greater restriction. The reverse occurred as the gas was released back into the environment, and so no such resistance was resolvable in the desorption data. To eliminate the effects of transfer resistance $\tau_{ads}^t$ was calculated by fitting the exponential function to the initial stage of adsorption, before the transfer resistance dominated the sorption rate. N₂ was slower than CO₂ in adsorption, but faster in desorption. This is likely due to heat transfer effects, which affected CO₂ far more than N₂, speeding up adsorption and slowing down desorption.
Figure 3.5: Normalized time-transient isotherms. Adsorption isotherms normalized to the saturation amount (wt% adsorbed at $t = \infty$). Desorption isotherms normalized to the adsorption saturation and residual amount (wt% remain at $t = \infty$).

3.3.2 Activation energy

Figure 3.6: Mobility activation plots in Ar: a) CO$_2$ and b) H$_2$O. Slope of the lines are activation energy, $u^m$. Intercepts are $\ln(b^a)$. Figure 3.6 shows the effects of TA on $u^m$ and $b^a$. For CO$_2$ the presence of TA increased the overall mobility but the activation energy was essentially unchanged. H$_2$O adsorption did not appear to be largely affected by TA, though there was a small shift in activation energy in desorption. The activation parameters are given in Appendix A.3.
Preliminary measurements of H$_2$O desorption used N$_2$ and CO$_2$ as the carrier gases in place of argon. CO$_2$ sorption was also measured in N$_2$, and the results are shown in figure 3.6. Characteristic times were 30-110% longer in N$_2$ than in Ar, and the residual amounts of H$_2$O/CO$_2$ after desorption were smaller, overall. This is likely due to an exchange of adsorbed N$_2$ with the incoming gas which did not occur with the less-adsorbed Ar. There did appear to be some correlation between N$_2$ and the other gases in this case. In the case of H$_2$O desorption in CO$_2$, desorption times appeared to be far shorter, <1hr in some cases. The CO$_2$ saturation amount was taken to be zero for H$_2$O, assuming that CO$_2$ was replacing H$_2$O in the micropores. If this were true, it would amount to a drying effect that would drastically change the dynamics of permeance in the membrane. To further investigate this phenomenon, an experiment was conducted in which, after H$_2$O desorption appeared to be complete in CO$_2$, the gas stream was switched to argon. The adsorbed
amount immediately dropped to a lower level, and stayed relatively flat for hours onward. In figure 3.7, the entire experiment at 30°C is plotted over time. The H₂O desorption isotherm in Ar is superimposed (in blue) to show that the level to which the adsorbed amount dropped was the same level to which the H₂O curve reached in argon over the same time period. Thus, while CO₂ may have occupied what volume H₂O left vacant, CO₂ did not seem to hasten the departure of H₂O.

![Graph showing desorption isotherm](image)

**Figure 3.8:** Multiple-gas trade-off experiment on ZY₅OA at 1 atm to determine the effect of CO₂ on H₂O desorption. (Buoyancy corrected.)

### 3.4 Conclusions

The molecular mobilities of H₂O, CO₂, and N₂ were investigated by time-transient gravimetric isotherms. CO₂, with average $u^m$ of 5.7 and 7.7 kJ/mol for ZY₅OA and ZY₅TA, was far more mobile in the zeolite micropores than H₂O, with average $u^m = 29$ and 35 kJ/mol respectively. N₂ activation energies were close to CO₂, 8.4 and 17 kJ/mol.
Hysteresis was observed between adsorption and desorption curves, which was likely due to heating/cooling effects in ads/desorption. These effects were stronger for CO$_2$ than for N$_2$, and considerably stronger for H$_2$O than for CO$_2$. For further investigation it is therefore recommended that additional mass flow controllers are added to the gravimetric set-up so that gas mixes can be altered, rather than switching between gas cylinders. If this is done, much smaller pressure increments can be tested in which heat transfer may be made negligible.

The effect of N$_2$ on CO$_2$ and H$_2$O was also studied, and N$_2$ appeared to slow CO$_2$ and H$_2$O desorption significantly. In the presence of CO$_2$, the H$_2$O isotherms dropped to the CO$_2$ equilibrium sorption level and remained there indefinitely. However, further study strongly suggested that CO$_2$ was not significantly altering the desorption of H$_2$O regardless of the shape of the CO$_2$ + H$_2$O isotherm. The implication for membrane performance is that CO$_2$ may not have much of an effect on H$_2$O transport, and the very same blocking mechanism which yields such high CO$_2$/N$_2$ performance may work against CO$_2$ permeance if H$_2$O is added to the gas stream. The problem of H$_2$O will be presented in this context in chapter 4.
CHAPTER 4

GAS SORPTION ON ZEOLITE NaY, 3: PERFORMANCE

Equilibrium sorption studies of H₂O, CO₂, and N₂ on zeolite NaY were discussed in chapter 2, and respective mobility studies were presented in chapter 3. In this chapter, the previous data sets are synthesized into a micro-pore permeance model, and the model is evaluated by comparison to membrane performance data.

4.1 Introduction

4.1.1 Permeance model

The molar flux of gas \( l \) across the membrane is most generally given by \( j_i = F_i \times b_i \times \hat{f} \) \[92,93\], in which \( F \) is the driving force for transport, \( b \) is the molecular mobility of the gas and \( \hat{f} \) is a correlation factor that compensates for the increased probability that a molecule, after hopping from one site to another, will return to that original site rather than hop to a third site, \( 0 \leq \hat{f} \leq 1 \). At \( \theta > 0.6 \), \( \hat{f} \) will be close to 1 for a surface-diffusing gas like CO₂ but at \( \theta < 0.3 \) \( \hat{f} \) will be near zero for less-active gases such as N₂ \[119\].

As discussed in section 2.1.2, the driving force for transport is oriented down the chemical potential gradient, which mobile species will migrate to eliminate. The mobility was discussed in 3.1.1, and combining these concepts with (1.1), the permeance for gas A transporting in competition with gas B across the microporous membrane is \[79\]

\[
f_A = \frac{j_A}{\Delta p^{F}} = -\frac{RT}{\Delta p^{F}} C_{A}^{\max} b_A^{\theta} \hat{f} \left[ \left(1 - \theta_B \right) \nabla \theta_A + \theta_A \nabla \theta_B \right] \tag{4.1}
\]
For non-dilute mixtures, (4.1) must be integrated over the membrane thickness. In the case of high concentrations of A and low concentrations of B, (4.1) simplifies to [79]

\[ f_A = \frac{j_A}{\Delta p_A} = -\frac{RT}{X\Delta p_A} C_{\text{max}}^A b_A \tilde{f} \Delta \theta_A \]

The RHS of (4.1) and (4.2) are color-coded to show which parameter was determined in which experiment. The uncolored factors are constants, geometric properties and operational conditions. In red are equilibrium sorption parameters found in Appendix A.1 and discussed in chapter 2; in blue are kinetic parameters found in A.2 and discussed in chapter 3; and the green parameter \( \tilde{f} \) is undetermined.

### 4.1.2 Previous membrane performance

Some of the interesting data on the Zeolite NaY membranes in [20] was not published at the time, such as the CO\(_2\) permeance in absence of the templating agent, as shown in figure 4.1. The CO\(_2\) permeance was significantly higher for the NoTA membrane at the same feed pressure, which made sense given the absence of the obstructing TA. Also in figure 4.1 is the effect of the templating agent on CO\(_2\)/H\(_2\) true selectivity for a 50/50 gas mixture at 1 atm, which fully illustrates the CO\(_2\) blocking mechanism given the proper pore modification: without the templating agent present, the membrane was selective for H\(_2\) over CO\(_2\). When the TA was retained in the micropores, the membrane was selective for CO\(_2\) over H\(_2\).
White et al. reported that, for the best performing membranes overall, CO₂ was nearly undetectable in the permeate prior to dehydrating the membranes at 150°C [20]. The question remained however if good performance would be observed for the other membranes given pore modification by immobile H₂O in the micropores, and the effect of H₂O in the feed gas stream on CO₂/N₂ selectivity was not formally investigated. Membrane performance experiments with and without H₂O were therefore carried out in this work.

4.2 Experimental

As White et al. reported in [20], the zeolite NaY membranes in this work, kindly provided by J. White and P.K. Dutta, were made by dip-coating seed crystals on disc-shaped, macroporous, α-alumina substrates. Membrane fabrication was discussed in more detail in section 2.1.

CO₂ permeance and CO₂/N₂ selectivity measurements were performed on each type of membrane, A and B. The membranes were made wet using a humidified feed stream of 3000 kPa H₂O in N₂ at 1 atm and 25°C. CO₂ permeance and CO₂/N₂ selectivity were then measured in a dry gas stream at intervals from 25 to 150°C by a Wicke-Kallenbach setup [120] diagrammed in figure 4.2. The membranes were held at 150°C for 12 hrs, and then
measurements were taken again on the dry membrane at intervals down to 25°C. The procedure was repeated with 0.8mol% and 1.6mol% H₂O in the gas stream, the humidity introduced by a bubbler in a chilled water bath and monitored by an in-line humidity sensor. The feed and sweep gas flows were controlled by mass flow controller, and pressure on each side of the membrane was controlled by transducer. The total feed gas flow was 100sccm, and the He sweep flow was 50sccm.

**Figure 4.2:** Zeolite NaY membrane performance measurement setup. Feed and sweep were in crossflow, but are shown in parallel here for simplicity.
4.3 Results and discussion

4.3.1 Templating agent: powders vs. membranes

Figure 4.3: Calculated Zeolite NaY occupancy and mobility for gas composition 70mol% N₂, 14mol% CO₂ and 16mol% H₂O. (Left) ZY₉₉TA, (right) ZY₉₉TA.

The competitive nature of the thermodynamic and kinetic parameters in the permeance model is apparent in figure 4.3, which shows the N₂, CO₂ and H₂O occupancies and average sorption mobilities as functions of temperature. The occupancies given are the ratio of the species concentration to its temperature-dependent saturation amount, \( C_{\text{max}} \), as determined from the equilibrium sorption measurements in chapter 2. The gas composition under consideration was 70mol% N₂, 14 mol% CO₂, and 16 mol% H₂O. Also apparent from figure 4.3 is that, the higher the affinity of a species for the zeolite framework, the less affected its occupancy was by the presence of TA over the practical temperature range of 25-150°C. The N₂ occupancy, small to begin with for ZY₉₉TA, was effectively zero for ZY₉₉TA. The CO₂ occupancy was reduced slightly, while the H₂O occupancy was unchanged. Meanwhile the H₂O mobility, small to begin with, was further reduced by the presence of TA while for CO₂ and N₂ and the mobility was enhanced by factors of 2…4. The most important aspect of figure 4.3 is the near-full saturation of H₂O, particularly at the target temperature of 57°C, because for the application of flue-gas membranes this
means that in mixed conditions there is not likely to be significant CO₂ transport. Further, since H₂O is relatively immobile in all cases, the membrane will not work well for removing H₂O, either. Water vapor will fill the pores, and the membrane will become effectively impermeable. This effect is confirmed in section 4.3.2.

Figure 4.4 shows the dry CO₂ membrane permeance data in comparison to calculations from the powder experiments. In these experiments, $p_{CO_2} = 20\text{kPa}$, $p_{N_2} = 80\text{kPa}$. Overall the two data sets were very close and many of the trends were consistent. The calculations predicted an increase in permeance with removal of the TA, which was observed in the membranes but not with such consistency. The TA effect on CO₂ permeance was exaggerated by the differences in membrane thickness, but this applies to both membrane and powder data sets. In each case the membrane CO₂ permeance peaked between 50…100°C, decreasing above and below that interval. Calculations from the powder data predicted a continuous decrease in CO₂ permeance. These discrepancies may have been due to multiple transport mechanisms that were not accounted for in the microporous transport calculations. The quality of the powder data calculations however is undeniable, and verifies the methods used in this approach.
The dry CO\textsubscript{2}/N\textsubscript{2} selectivity predicted by the powder data at 30°C was \(~100\) for ZY\textsubscript{NoTA}, and \(~10,000\) for ZY\textsubscript{TA}, while for the membranes the values were 40 and \(>550\), respectively. Also, the ZY\textsubscript{NoTA} powder data calculations predicted an increase in CO\textsubscript{2}/N\textsubscript{2} selectivity up to 150°C (~1400), while the membrane selectivity peaked at \(~55\) at 100°C and then decrease at higher temperatures. These discrepancies may be due to the large errors in the N\textsubscript{2} sorption data, since the overall sorption amounts were close to the detection limit of the HP-TGA. Also, the error was so large above 50°C that the N\textsubscript{2} isotherms were not used at all in the analysis, so selectivity data at T \(> 50°C\) is extrapolated from the data set.
4.3.2 The H$_2$O problem, part 3

Figure 4.5: (Left) NoTA membrane CO$_2$ permeance. (Right) NoTA membrane CO$_2$/N$_2$ selectivity. Gas composition: $p_{CO_2} = 20$ kPa, $p_{N_2} = 80$ kPa, $p_{H_2O} = 800...1600$ Pa

Microporous transport calculations, particularly from macroscopic, single-gas equilibrium and transient sorption data, are much more difficult to solve and are less reliable when gas mixtures are not dilute. This is the certainly the case with CO$_2$/H$_2$O mixtures. From the powder data calculations of occupancy and mobility in section 4.3.1, it was qualitatively deduced that H$_2$O would dominate in competitive transport given its very high occupancy in operating conditions. In figure 4.5 it is shown that the membrane data was in agreement: the presence of even 0.8...1.6 mol% of H$_2$O in the gas stream, (10$^\times$ less than that in the flue gas stream,) reduced the CO$_2$ permeance by 100$^\times$, and the CO$_2$/N$_2$ selectivity by 10$^\times$. A humidity sensor in the permeate gas stream at 30, 50, and 57$^\circ$C showed an initial spike in H$_2$O concentration but decreased to near zero after 2...5hrs. This indicated that the membrane had become effectively impermeable. Therefore, it is indeed the case that the presence of H$_2$O is severely detrimental to membrane performance in this application. However, in light of that, the effect of a small amount of H$_2$O is still not so catastrophic. As the membrane data in figure 4.5 shows, residual water in the membrane does act similarly to the templating agent in terms of CO$_2$/N$_2$ selectivity,
but it also has the effect of increasing CO₂ permeance, even 72hrs after membrane humidification. The TA effect demonstrates the enhanced performance of these membranes by zeolite pore modification, and figure 4.5 shows that other methods of pore modification may yield more improvement over tetramethylammonium.

4.4 Conclusions

In this work it was shown that retention of the templating agent in the zeolite micropores enhanced the selectivity of CO₂ over N₂, with some sacrifice to CO₂ permeance. Quantitatively, comparisons to the membrane data showed that the CO₂ permeance predictions of the TA effect from the sorption studies were close to the observed effect in the membranes. The CO₂/N₂ selectivity in the absence of TA was exaggerated by calculations from the powder data, likely due to error in the N₂ sorption measurements. Qualitatively, it was deduced from the powder data that H₂O would dominate membrane transport in mixed gas conditions due to its much higher occupancy even at low concentrations. This was indeed observed in membrane experiments. However, residual H₂O after membrane humidification enhanced CO₂ permeance and CO₂/N₂ selectivity simultaneously.

The implication of the study results for zeolite NaY membranes in coal flue-gas carbon capture applications is that, while pore modification works well for improving CO₂/N₂ separation performance, it is unlikely to have much effect on the blocking of CO₂ from the micropores by H₂O. Dehumidification of the gas stream is therefore required to use these membranes for carbon capture, and the permeance of H₂O will likely be far too low in practical conditions to use these membranes for that purpose as well.
CHAPTER 5

COLLOIDAL PROCESSING OF SOFC MATERIALS

Thin-films for solid oxide fuel cells and other catalytic or sensor devices are typically made by chemical vapor or pulsed laser deposition. In this chapter, aqueous, colloidal syntheses and processing techniques are introduced that could be scaled up for continuous, cheap fabrication of thin, defect-free Pt/GDC composite, GDC, and YSZ membranes.

5.1 Introduction

A colloid is a multiple phase system in which fine particles are uniformly dispersed in a fluid medium. The minor phase, with linear dimensions $10^{-9} - 10^{-6}$ m, can be solid particles or liquid drops, and the medium can be liquid or gas [121]. Examples include fog (water droplets dispersed in air) and milk (fat particles dispersed in water). Colloids consisting of metal and/or metal-oxide particles suspended in water or organic liquids will form uniform compacts and layers when the liquid medium is removed in a controlled way [122]. These compacts and layers can be made reproducibly with a range of geometries and thicknesses, with few macroscopic irregularities and microstructural defects, and this makes colloidal processing attractive for fabricating defect-sensitive devices such as oxygen separation membranes [123,124] and solid oxide fuel cells [125, 126].

The fuel cell design in consideration is described in chapter 6. The electrolyte is a dense layer of gadolinium-doped ceria (GDC) or yttria-stabilized zirconia (YSZ) and the symmetric electrodes are porous composites of GDC and platinum metal. In this work, stable colloids of GDC, YSZ, and Pt were developed for the fabrication of symmetric, ultra-thin SOFC modules on porous alumina substrates as well as flexible metallic and organic
supporting structures. Dip-coating suspensions were optimized to produce defect-free membranes on each of the substrates, and the total conductivities of the membranes were measured by 4-point van der Pauw method.

### 5.1.1 Particle Synthesis

Colloidal processing begins with the synthesis of fine metal or metal-oxide particles from molecular precursors. This can be achieved with combustion and gel-type syntheses, which yield nanoparticle powders that must be heat-treated, then dispersed in liquid [122,127], or with low-temperature reactions such as aqueous metal salt reduction [128] and sonochemical synthesis [129]. In the latter two methods, particle synthesis and liquid dispersion are carried out in the same step without heat treatment and are thus simpler and faster than combustion techniques [130].

Stable, aqueous platinum-particle colloids are synthesized by reduction of chloroplatinic acid hexahydrate, \( \text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O} \), with methanol in an aqueous solution of polyvinyl alcohol (PVA). The two-stage reaction was suggested by Duff et al. [128] as

\[
\begin{align*}
\text{PtCl}_6^{2-} + \text{CH}_3\text{OH} & \rightarrow \text{PtCl}_4^{2-} + \text{HCHO} + 2\text{H}^+ + 2\text{Cl}^- \\
\text{PtCl}_4^{2-} + \text{CH}_3\text{OH} & \rightarrow \text{Pt}^0 + \text{HCHO} + 2\text{H}^+ + 4\text{Cl}^- 
\end{align*}
\]

The PVA acts as a colloidal stabilizer as well as controlling the size (1-5 nm) and morphology (~spherical) of the platinum particles. The reaction takes place at 84°C.

Cerium oxide (\( \text{CeO}_2 \)) colloids with particle size of 10-20 nm can be synthesized at room temperature by a sonochemical method [130,132]. In the first step, cerium ammonium nitrate, \((\text{NH}_4)_2\text{Ce(NO}_3)_6\), is dissolved in water by stirring. This method is particularly advantageous in that to dope the ceria with gadolinium, one simply needs to dissolve the correct stoichiometric amount of gadolinium nitrate hexahydrate, \( \text{Gd(NO}_3)_3\cdot6\text{H}_2\text{O} \), with the cerium precursor in the first step. Ammonium hydroxide is added to the solution under ultrasonic agitation along with a dispersant, and the reaction is complete within ~20 min. The steps of this reaction have yet not been proposed, but in addition to \( \text{CeO}_2 \), there is significant production of ammonium, \( \text{NH}_4^+ \), and nitrite, \( \text{NO}_3^- \) ions in the final dispersion. To achieve a stable colloid, these must be removed by dialysis.
5.1.2 Colloid stabilization

The primary concern in colloidal processing is controlling the aggregation and sedimentation of fine particles. The most accurate description of colloidal stability is one in which the free energy is minimized. This section, however, will take a less rigorous approach and define a “stable” colloid is one in which the forces of gravity and the attractive forces between particles are effectively balanced by counter-forces for an adequate period of time [121]. An “adequate” period of time is before the liquid medium is purposefully removed to form the compact or layer, meaning that colloid stability does not have to be permanent, but merely sufficient for use.

Sedimentation

Gravity acts on a particle with an Earthward force of \( F_g = mg \), where \( m \) is the mass of the particle and \( g \) is the acceleration due to gravity, \( \sim 9.8 \text{ m/s}^2 \) near the Earth’s surface. In the case of particle sizes below \( \sim 1 \text{ nm} \), the gravitational potential energy of a particle is minor compared to its kinetic energy due to Brownian motion, \( KE_{\text{Brown}} \approx \frac{3}{2} k_B T \) [132]. \( F_g \) is stronger for heavier particles, but is somewhat counteracted by the forces of buoyancy and drag. Considering these counteracting forces and assuming laminar fluid flow, the approximate time that it will take a free-falling, spherical particle in a fluid medium to fall from height \( h \), \( t_h \), can be derived using Stokes’ Law [121]:

\[
t_h = \frac{9}{2} \frac{h \eta_f}{g r_s^2 (\rho_s - \rho_f)}
\]  

(5.2)

In (5.2), \( r_s \) is the radius of the sphere in meters, \( \rho_s \) and \( \rho_f \) are the respective densities of the sphere and fluid in \( \text{kg/m}^3 \), and \( \eta_f \) is the fluid dynamic viscosity in \( \text{Ns/m}^2 \). By this approximation, if the average 20 nm-diameter CeO\(_2\) particle (\( \rho_{\text{CeO}_2} = 7200 \text{ kg/m}^3 \) [133]) in an aqueous colloid is 1 cm from the bottom of a container, it will take \( \sim 84 \) days for the particle to fall completely out of the dispersion. If the compact or layer is to be formed within a few weeks this may be an adequate time period, but particle aggregation can de-
stabilize the colloid long before that by dramatically increasing the effective radius of the particles. Thus, measures must be taken in colloidal processing to prevent aggregation.

**Aggregation**

Particles aggregate due to attractive van der Waals forces between particle surfaces [121]. These forces weaken considerably with distance between particles, \( F_{vdw} \propto \frac{1}{d^2} \), but thermal vibrations in the liquid will cause the particles to frequently come within effective range of one another. The formation of a so-called double-layer under certain conditions can prevent aggregation by introducing a repulsive force between regions of excess charge near the particle surfaces [122]. This is known as electrostatic stabilization of colloids.

In an aqueous colloid, the surface of a metal-oxide particle can physically or chemically adsorb water molecules. Depending on the size and surface properties of the oxide, this water adsorption may or may not be enough to effectively hide the particles from one another and prevent aggregation. Physical adsorption involves a relatively weak, rapidly reversible bond. Chemical adsorption is a significantly stronger and irreversible process that results in a monolayer of excess charge on the particle surface. In low pH conditions, positively-charged hydrogen ions are chemically adsorbed to the surface. In high pH conditions hydrogen is desorbed from the surface, leaving an exposed layer of negatively-charged oxygen atoms. These two phenomena can be written as reactions with associated coefficients, \( K_{(+)} \) and \( K_{(-)} \) [122]:

\[
\begin{align*}
\text{MOH}^+_{(surf)} & \rightleftharpoons K_{(+)} \text{MOH}^-_{(surf)} + H^+_{(solution)} \\
\text{MOH}^-_{(surf)} & \rightleftharpoons K_{(-)} \text{MO}^+_{(surf)} + H^+_{(solution)}
\end{align*}
\]

(5.3)

The negative logs of these reaction coefficients give \( pK_{(+)} \) and \( pK_{(-)} \), and the average of these values gives the “point of zero charge”, or PZC, at which the net charge at the surface is neutral [122]. The pH value at which there is no excess charge at the surface is known as the “isoelectric point” or IEP. For ceria, the IEP is between 6.7 and 8.6 [134]. An electrically neutral surface does not free the particles from attractive forces because
van der Waals, compressive and other interactions can be induced by the proximity of particles to one another, but it does mean there is no double-layer to act in repulsion. For colloidal stability, then, the IEP is to be avoided. As the pH of the liquid moves away from the IEP and the surface is covered with a charged monolayer, the excess charges attract oppositely charged ions in the liquid medium. This is a form of physical adsorption, so the bonding is weak relative to the chemisorbed layer and the region of oppositely charged ions can diffuse. Two particles with diffuse layers that overlap will be subjected to a repulsive force that resists aggregation. The magnitude of this repulsive force, $F_{\text{Repulse}}$, has many determining factors [121]:

$$F_{\text{Repulse}} \propto T \exp \left( -\frac{2d}{\kappa^{-1}} \right) ; \quad \kappa^{-1} \propto \sqrt{\sum \frac{\varepsilon_i T}{N_i Z_i^2}}$$

In (5.4), $d$ is the distance between the particles and $\kappa^{-1}$ is the Debye length. The Debye length is defined as the distance from the particle surface at which the electrical potential of the diffuse layer is $1/e$ of the surface potential (where the exponential terms goes to one). However, the precise value of the Debye length is not as important to this discussion as the relationships given in (5.4): Factors that affect the repulsive force resisting aggregation include the dielectric constant of the liquid, $\varepsilon_r$, the temperature, $T$, the number of charged ions in the liquid of species $i$, $N_i$, and the ionization strength of species $i$, $Z_i$.

The dielectric constant of the liquid is a measure of its polarization, and the $\varepsilon_r$ of water is very high compared to various alcohols [121]. The molecular configuration of water, with excess positive charge on one side and excess negative charge on the other, allows interactions with charged molecules such as ions that promote ion dissociation and diffuse layer formation. Increasing $T$ increases the thermal energy of the liquid and ions, and thus also promotes ion dissociation. It should be noted, however, that an increase in $T$ also increases the kinetic energy of the particles, allowing them to overcome the repulsive force and aggregate despite any attempts to stabilize the dispersion. This means that heating up a colloid in order to improve stability may have the opposite effect. Increases in ion concentration and strength in the liquid have a shrinking effect on the diffuse layer, and re-
duce the repulsive force significantly, because what is important is the amount of excess charge. If the bulk of the liquid is charged, then the diffuse layer becomes less distinct from the bulk. Ion concentration and strength can be altered by changes in pH and addition or removal of ions from the liquid. It should also be noted that, while the IEP should be avoided to achieve a stable colloid, so should the far extremes in pH, as the liquid ion concentration is very high in these conditions. In the case of ceria colloids, the synthesis reaction produces significant quantities of ammonium and nitrite ions. These have a destabilizing effect on the dispersion as suggested by (5.4) and must be removed by dialysis.

With many materials, surface charge and diffuse double-layers are not enough to overcome the attractive forces between particles, or to overcome the force of gravity if the particles are heavy. In these cases, colloids may be stabilized using polymer additions, or so-called steric stabilization. Linear polymers with polar and non-polar ends, such as oleic acid, can bind to the charged particle surface with their non-polar ends extending into the fluid [132]. The non-polar ends, while not attracted to water, tend to uniformly disperse in organic liquids because of their thermal energy (enthalpic stabilization) and/or to maximize entropy (entropic stabilization). This has a stabilizing effect because the dispersed ends of the polymers form barriers to contact between particles. Long chain, non-polar polymers have a similar dispersing property while not binding to the particle surfaces, an effect known as depletion stabilization. For large particles in water, the best use of steric stabilization is to use a polymer with two polar ends, as this combines the entropic repulsion of polymer chains with the static repulsion of ions in water.

In the case of the platinum colloid described in section 2.1, the PVA binds to the platinum particle surfaces quickly following the reaction so that the particles do not aggregate to larger than ~5 nm [128]. The term “PVA” is somewhat vague, as polyvinyl alcohol exists in a range of chain lengths. Also, linear PVA cannot be synthesized from monomers because of its ability to branch during polymerization. Thus, PVA is made industrially by hydrolyzing polyvinyl acetate (PVAc). Rheological and solubility properties depend on the extent to which PVAc has been hydrolyzed, and so commercial PVA is sold in a range of hydrolysis percents. For the reaction described in 5.2.1, the PVA is ~100kD.
and >98% hydrolyzed. This means that the chains are flexible and, fully extended, ~500 nm long. Each of its ~2000 monomers has a polarizable –OH group which forms hydrogen bonds with water. Thus, the platinum particles, which are much smaller than the PVA chains, may be considered electrosterically stabilized.

5.1.3 Thin-film conductivity: 4-pt van der Pauw method

Resistance, \( R \), is a measurable quantity with units of voltage (volts) over current (amps), or \( \Omega \). The conductivity, \( \sigma \), and resistivity, \( \rho \), of a material are defined as

\[
\frac{1}{\sigma} = \rho = R \frac{A}{\ell}
\]  

In (5.5), \( A \) is the cross-section of the sample of material measured and \( \ell \) is the length between measurement electrodes. The conductivity of a material is typically measured using a bar or rod of known cross-section, two current-source electrodes and two electrodes for voltage measurement. But irregular shaped samples such as discs have non-uniform cross-sections across their length. For thin-films, van der Pauw [135] argued that as long as the sample is continuous and uniform in thickness, since any shape can be translated on a complex-plane to any other shape [136], the shape is arbitrary. This holds true for very small electrodes located on the edge of the sample. Real electrodes, however, tend to be big and are painted or welded to the top of a thin-film rather than the very small edge, even encroaching on the interior of the sample [137]. Thus, van der Pauw recommended the clover shape diagrammed in figure 5.1 (or a square [138] with the electrodes attached in the corners) to minimize the errors in measurements due to electrode size and position. The current source and voltmeter are set up in two configurations as shown in figure 5.1, and voltage measurements are taken at a range of applied current increments. The van der Pauw equation is solved numerically to find the sheet resistance, \( R_{sh} \):

\[
\exp\left(-\pi \frac{R_{PQ,RS}}{R_{sh}}\right) + \exp\left(-\pi \frac{R_{QR,SP}}{R_{sh}}\right) = 1
\]  

(5.6)

For the sake of accuracy, the current source and voltmeter in the two configurations are swapped (\( R_{RS,PQ} \) and \( R_{SP,QR} \)) and the average taken between the two measurements for each configuration.
5.2 Experimental

5.2.1 Platinum colloid

Chloroplatinitic acid hexahydrate (H₂PtCl₆·6H₂O) was dissolved in water while stirring in an oil bath. Anhydrous methanol and an aqueous, 5wt% solution of organic polymer were added after the Pt-precursor had dissolved. Batches of the mixture were heated at 80, 85, and 90°C under reflux for four hours. The suspension turned from orange to black during reduction of platinum and formation of the colloid. The colloid was filtered to 0.45μm with a syringe filter.

Several types of organic polymer were attempted for use in the procedure, including Selvol 125 and 325 from Sekisui, 40 and 72kD PVA and 40 and 360kD polyvinylpyrrolidone (PVP) from Sigma-Aldrich. The wt% of polymer and methanol was adjusted from ~35-45 and ~2.6-2.9 respectively to achieve the best stability for each system.

For the platinum concentration, the important parameter for the SOFC electrode was the conductivity, which was found to correlate with the wt% of Pt vs. GDC in the final dip suspension. Thus, 10ml colloids with five platinum concentrations were synthesized at 3, 10, 99, 140 and 187mM such that a 1:1 mixture with a 10wt% GDC dispersion would yield 1, 3, 15, 20, and 25wt% Pt vs. GDC once the water and organics were all removed.
5.2.2 GDC and YSZ colloids

A sonochemical method was developed to synthesize aqueous CeO$_2$ and Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ colloids from molecular precursors. Stoichiometric amounts of cerium ((NH$_4$)$_2$Ce(NO$_3$)$_6$) and gadolinium (Gd(NO$_3$)$_3$$\cdot$6H$_2$O) precursors were dissolved in water while stirring. The dissolved precursor solutions were agitated by an ultrasonicating horn set to 45W. During ultrasonication, 25wt% aqueous tetramethylammonium hydroxide (TMAOH) was added to the solution dropwise. After 35min of ultrasonication, bicine was added, and the dispersion was ultrasonicated for another 5min. The total ultrasonication time was 40 minutes. Successful colloid synthesis was found to depend on the molar ratios of TMAOH to the total molar concentration of the cations, as well as the molar ratio of bicine to the total molar concentration of the cations.

The yields of 10wt% GDC formulations were uncontrolled. In later experiments, the target concentration was reduced to 8.5wt% to stabilize the procedure.

The GDC colloid synthesis procedure was adapted for the synthesis of Zr$_{0.84}$Y$_{0.16}$O$_{1.92}$ colloids. The precursors in this case were ZrO(NO$_3$)$_2$$\cdot$H$_2$O and Y(NO$_3$)$_3$$\cdot$H$_2$O. The IEP of nanoparticulate ZrO$_2$ is at pH 4-5 [139], significantly lower than that of ceria, which had the consequence that high precursor concentrations and fast additions of base resulted in irreversible agglomeration and sedimentation. So to maintain stability the solid load was kept below 5wt% and the TMAOH solution was diluted to 5wt% prior to addition.

Immediately following ultrasonication, the GDC and YSZ colloids were dialyzed with a 6-8kD dialysis bag in 3L of pH 2 HNO$_3$ for 3hrs with the goal of removing excess precursor ions from the dispersion.

5.2.3 Dip-coating

Supporting structures

Supports with uniformly flat and defect-free surfaces are critical in fabricating ceramic thin-films, particularly to dense and leak-tight electrolytes. The disc-shaped, 42mm diameter $\alpha$-alumina supports in this work were made in-house with ~40% porosity, made from powders of 300nm diameter by a vacuum-filtration technique in which quality and
reproducibility depend on stable ambient humidity and temperature control during filtration and drying. The fabrication procedure for these substrates has been well documented [140,141,142], so the full protocol will not be included here. In summary: α-alumina powders purchased from Sumitomo Inc., were weighed 50g:50g with aqueous HNO₃, pH~2.25. The resulting alumina suspension was ultrasonicated by horn at ~57W in a chilled glass container for ~12min, then filtered to 20μm and ethanol was added. The suspension was mixed and deaerated in a biaxial mixer, then transferred into cylindrical plastic cups lined with PTFE tape, each with a 0.45μm filter on the bottom, and each attached to a vacuum manifold in an atmospheric control chamber. The humidity and temperature were kept constant at 15% RH (STP) and 25°C through the filtration and drying processes. 70mbar was applied to the bottom-side of the cups via the manifold for 2hrs such that the ceramic compacts had formed, then was decreased to <1mbar for drying overnight. Once dried, the compacts were removed from the cups and heat treated in a furnace at 950°C for 10hrs with 2°C/min ramp rates.

The keys to support fabrication were the ethanol additions and lining of the filtration cups with PTFE. Ethanol additions reduced the surface tension and eliminated bubbles [143] that caused pin-hole types of surface defects [144] as well as reduced the meniscus that formed due to the cup walls. The use of PTFE further reduced the meniscus, producing adequately flat surfaces for membrane coating and, as discussed in chapter 6, hermetic sealing.

**Dip dispersion formulations**

To make a dip-coating suspension for the Pt/GDC composite electrode, the Pt and GDC suspensions were mixed 1:1, filtered to 5μm by syringe filter, and placed in an ultrasoni-

ating bath for 0.5hr. The only organic additive in the GDC and YSZ suspensions prior to dip-suspension preparation was bicine. When dip-coated in these suspensions without further additions, no significant coating was achieved on the alumina supports. Thus, PVA was added to the suspensions, as well as ethanol for wetting improvements and bubble suppression.
In each case, the dip-coating suspension was transferred into a watch glass. Alumina supports were loaded onto a vertical rotary arm by means of a plastic-pronged chuck. The rotary arm swung the supports a maximum of 2, 1, or <0.1mm into the suspension for approximately 5s.

**Heat treatment**

The dipped supports were dried for 1hr at 110°C, and then heat-treated by conventional thermal processing (CTP) in a furnace with 2°C/min ramp rates and 5hr soak times, or rapid thermal processing (RTP) in a Modular Process RTP-600x [145] with 10°C/s ramp rates and 3 min soak times. To investigate the effect of CTP and RTP on GDC membrane microstructure, two membrane samples were dipped at each depth, 2, 1 and <0.1mm. One sample from each dipping depth was fired by CTP, the other by RTP, at 100°C intervals up to 900°C. After each heat treatment the thicknesses of the membranes were measured by spectroscopic ellipsometry [146].

**5.2.4 Characterization**

**Colloids**

The GDC and YSZ colloids were measured for particle size by dynamic laser scattering (DLS) in the liquid state. The GDC colloid and the dialysate before and after GDC colloid dialysis were measured for relative nitrate content by Raman spectrometry [147]. The colloids were then dried at 70°C, washed with DI water and milled to powders in a mini-ball mill. The powdered samples were measured for weight loss by TGA up to 750°C, heat flow by differential scanning calorimetry (DSC) [148] up to 600°C; and x-ray diffraction (XRD).

**Membranes**

The membranes were measured for thickness by spectroscopic ellipsometry and/or SEM. The van der Pauw method as described in section 5.1.3 was used to determine the effect of Pt concentration and heat-treatment temperature \(T_{HT}\) on electrode conductivity at
room temperature. The total conductivity of electrode, GDC, and YSZ membranes were also measured up to 650°C in air.

Cross-sections of GDC and electrode membranes were prepared by focused ion beam (FIB) and analyzed by scanning electron microscopy (SEM). GDC membranes were also examined by transmission electron microscopy (TEM). For the electrode in particular, this was the only means of accurately measuring membrane thickness, as the black and silver colors of the membrane rendered spectroscopic ellipsometry ineffective.

5.3 Results and discussion

5.3.1 Colloids

Formulations

Table 5.1 shows the results of the survey of organic additives for use in the platinum colloid synthesis and subsequent membrane formation. Included are thicknesses found by SEM and conductivities by 4-pt van der Pauw (vdP) method at room temperature after heat treatment by RTP at 650°C. Duff et al. [128] reported synthesis successes with PVP, but in this work the platinum coated the inside of the container during heating in a manner consistent with electroless deposition [149], which suggested that the polymer did not properly stabilize the platinum particles. After concentration optimization, all of the types of PVA tested yielded stable dispersions and crack-free membranes. Selvol 125 was chosen for further investigation due to the higher membrane thickness and conductivity achieved, which eliminated the need for a third layer as 300-500 nm was sufficient for each of the electrodes.
Table 5.1: Success of organic additives for 120mM platinum colloid synthesis.

Table 5.2 shows the optimized formulations for the 120mM Pt colloid synthesis, and the GDC colloid addition to make the electrode dipping suspension.
Table 5.2: Optimized formulations for Pt-colloid synthesis and Pt/GDC composite dipping suspension.

<table>
<thead>
<tr>
<th>Material/reagent</th>
<th>140mM Pt colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂PtCl₆·6H₂O</td>
<td>0.70 ± 0.05g</td>
</tr>
<tr>
<td>5wt% PVA</td>
<td>5.4 ± 0.1 ml</td>
</tr>
<tr>
<td>Methanol</td>
<td>4.1 ± 0.05 ml</td>
</tr>
<tr>
<td>GDC suspension</td>
<td>9.5 ± 0.2 ml</td>
</tr>
</tbody>
</table>

Though 3, 10, 99, 140 and 187mM Pt suspensions were successfully synthesized, composite electrode membranes made from the 140mM colloid showed the highest conductivity, the easiest adaptability with a range of GDC/YSZ concentrations, and the most compatibility with subsequent layers, as discussed in section 6.3.1. Therefore, only the 140mM suspension was optimized for membrane reproducibility. It should be noted that 140mM is nearly 50x the Pt concentration reported in the literature [128].

Table 5.3 shows the GDC/YSZ formulations optimized for reproducibility in terms of stability and particle size. To synthesize CeO₂, the Gd precursor was left out and the ceria precursor appropriately adjusted. The dip suspensions were made by adding 0.7 – 1.4 wt% PVA and 0.7 – 1.0 wt% EtOH to the GDC/YSZ suspensions.
Table 5.3: Optimized formulations for GDC/YSZ suspensions.

<table>
<thead>
<tr>
<th>Target product</th>
<th>$\text{Ce}<em>{0.9}\text{Gd}</em>{0.1}\text{O}_{1.95}$</th>
<th>$\text{Zr}<em>{0.84}\text{Y}</em>{0.16}\text{O}_{1.2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% inorganic</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>Ce/Zr precursor</td>
<td>$20.3 \pm 0.1 \text{ g}$</td>
<td>$4.95 \pm 0.01 \text{ g}$</td>
</tr>
<tr>
<td>Gd/Y precursor</td>
<td>$1.85 \pm 0.01 \text{ g}$</td>
<td>$1.1 \pm 0.01 \text{ g}$</td>
</tr>
<tr>
<td>Water</td>
<td>$28.0 \pm 0.1 \text{ g}$</td>
<td>$32.7 \pm 0.01 \text{ g}$</td>
</tr>
<tr>
<td>TMAOH</td>
<td>$20.1 \pm 0.05 \text{ml}$</td>
<td>$16.8 \pm 0.05 \text{ml}$</td>
</tr>
<tr>
<td>Bicine</td>
<td>$0.34 \pm 0.01 \text{g}$</td>
<td>$0.15 \pm 0.01 \text{g}$</td>
</tr>
<tr>
<td>pH of dissolved precursors</td>
<td>$0.10 \pm 0.05$</td>
<td></td>
</tr>
<tr>
<td>pH after ultrasonication</td>
<td>$1.30 \pm 0.05$</td>
<td></td>
</tr>
<tr>
<td>pH after dialysis</td>
<td>$2.10 \pm 0.05$</td>
<td></td>
</tr>
</tbody>
</table>

Colloid characterization

In nano-particulate thin-films, crystallization of amorphous to cubic ceria has been reported in the literature to occur between 500 and 900°C [150]. Figure 5.2 shows that in the dried-colloid powders in this work, crystallization of GDC was nearly complete below 500°C, with estimated grain size 20-25 nm. The differential TGA results (5°/min) for the dried GDC powder show three peaks, the first two of which were likely complexed water given that the DSC results went (slightly) negative. But the third peak, at 330-
350°C, was large, sharp, and positive in the DSC results. This was likely the release of nitrate and ammonium ions from the dried powder [151], and such intense localized heating may explain the extent to which crystallization was complete by 500°C as evidenced by the XRD spectra in figure 5.2. As a ratio of the area under the spectra peaks of the 50°C to that of the 750°C heat-treated powder, a crystallinity of 22% is calculated for the dried GDC colloid. The TGA results for YSZ showed a peak in the 300°C range as well as some weight loss around 475°C, and were cubic and well crystallized by 750°C, estimated grain size similar to that of GDC, 20-25 nm.

**Figure 5.2:** TGA, DSC, and XRD on GDC and YSZ powders dried from aqueous suspension.
The large release of energy from the GDC powder occurred despite dialysis, the aim of which was to remove the highly volatile ions from dispersion, which would suggest that ion removal was not complete. However, as seen in figure 5.3, ion removal was nearly as complete as it would get after 3hrs of dialysis. Conductivity measurements on the dialysate during GDC colloid dialysis were above 99% of the total change after 3hrs. After replenishing the dialysate, no further charge was recorded. Using the dialysate as background, Raman spectra on the aqueous GDC colloid showed an 82% reduction in the peak around 1050 cm\(^{-1}\), which is associated with N-O bonds [147]. The implication was that the remaining nitrates were in some way complexed with the colloidal particles, though the nature of the complex was not known other than that it released very quickly at temperatures <350°C when heated at 5°C/min. Bicine and nitric acid also contained these bonds so the peak would not be expected to be completely eliminated in any case.

**Figure 5.3:** (Left) Dialysate conductivity data during dialysis. (Right) Raman spectra on GDC colloid, pre- and post-dialysis.

The GDC colloidal particle size distributions by DLS after synthesis and dialysis were roughly symmetric around peaks of 3 - 5nm. Over time, the distributions shifted to higher diameters but tended to retain symmetry. Figure 5.4 shows that the GDC colloids were stable over many months, but aggregated over time to close to 10nm peak diameter after
5 months. The YSZ colloidal particles tended to be broader in distribution and smaller overall, with peaks at 1.5 – 2.5 nm but were skewed to higher diameters.

![Figure 5.4](image)

**Figure 5.4:** DLS spectra. (Left) Aged GDC colloid. (Right) GDC vs. YSZ colloids, each aged ~1 week.

The molar ratio of Gd to Ce in the $T_{HT} = 500$ and 750°C GDC powders (target 10mol% Gd) determined by EDX were 9.1 +/- 0.3%. GDC colloids made with targets of 20mol% Gd were only 12.4 +/- 0.8.

### 5.3.2 Membranes

**Thickness**

The effects of heat-treatment on GDC membrane thickness are shown in figure 5.5. The thickness values given in nm are the initial values after drying at 110°C. PVA concentrations were 1.0wt%. For dipping depths of 2mm, 1mm, and <0.5mm, membrane thickness was >2000 nm, 700-830 nm, and 110-130 nm, respectively. RTP shrinkage lagged behind CTP up to $T_{HT} = 400°C$, then RTP shrinkage was greater or about the same. Overall, thicker membranes shrank more than thinner ones, but the two higher thicknesses were likely within error of the ellipsometry technique given that the 700-830 nm membranes shrank to 100-150 nm final thickness. This result begged the question if densification was
as high in the mid-range thickness as in the >2000 nm membranes, so N\textsubscript{2} permeances at 30°C were measured on the RTP membranes by non-stationary single-gas permeance (NSSGP) setup as described in [144], after the 500°C heat treatments. The permeances of the thinner membranes were almost indistinguishable from the alumina substrates, but at 700 nm became more significant. At 2700 nm initial thickness (~760nm after 500°C HT) the permeance became very low, \(\sim10^{-9}\ \text{mol/m}^{2}\cdot\text{s}\cdot\text{Pa}\), implying significant densification. Permeances were similar when measured after \(T_{\text{HT}} = 900°C\). So the thickest membranes shrank less but densified more. This result implied that the shrinkage, at least in the thickest membranes, was not uniform from air side to support side and was not a good indicator of membrane density. Membranes which were heat-treated at 900°C in CTP and RTP without step increments, and the shrinkage values were similar to those in figure 5.5.
Figure 5.5: GDC membrane thickness vs. heat-treatment temperature and method. $N_2$ NSSGP permeance at 30°C included for RTP 500°C.
**Microscopy**

*Figure 5.6:* GDC cross-section prepared by FIB, (Left) SEM and (Right) TEM. 

\[ AKP30 = \alpha\text{-alumina, Sumitomo, 300nm particle size.} \]

The micrographs in figure 5.6 show a GDC membrane, RTP 600°C, with ~160 nm thickness. There is considerable penetration of the GDC into the support, ~2 - 2.5x the membrane thickness, though the penetrant is significantly less dense than the membrane.

The fabrication steps from alumina support to dip-coated Pt/GDC electrode membrane to membrane after firing are shown in figure 5.7. The dried electrode coating was initially shiny black, but turned metallic after heat-treatment.
Figure 5.7: Pt/GDC electrode membrane fabrication steps. (Left) Alumina support. (Middle) Dried, dip-coated support. (Right) RTP heat-treated membrane.

Figure 5.8: Pt/GDC electrode (Ode1) on macroporous alumina support: (Left) 1, (Middle) 2, (Right) 3 dipped layers.

Figure 5.8 contrasts the SEM images of FIB-prepared cross-sections of electrode membranes fabricated from 20 wt% Pt/GDC dip suspensions. 1, 2, and 3 dipping layers are shown, which yielded total thicknesses of 70 – 110, 370 – 500, and 650 – 750 nm. Porosity was 35 – 40%.

4-pt vdP conductivity

Effect of Pt. conc. and $T_{\text{soak}}$ on electrode conductivity

A survey was conducted of Pt concentrations (in wt% vs. GDC) in the electrode dipping suspension, as well as electrode heat treatment temperatures, evaluated by the room temperature (RT) conductivity of 2-layer membranes measured by 4-pt. van der Pauw method.
od as contrasted with that of pure platinum. In initial tests for $T_{\text{HT}} = 650^\circ\text{C}$ the 1 and 10% Pt electrode suspensions exhibited no measurable RT conductivity, and so were not investigated further. As shown in table 5.4, the conductivity of the electrode increased from 15 to 20 wt% Pt, but dropped from 20 to 25 wt% Pt. The 20 wt% suspension was then chosen to evaluate the effect of heat-treatment temperature on electrode RT conductivity. The RT conductivity rose significantly from $T_{\text{HT}} = 650^\circ\text{C}$ to 700°C, but improvements above that were marginal. Thus, it did not hurt to go above 700°C but was not necessary for the purpose of forming a well-connected network of Pt in the electrode.
<table>
<thead>
<tr>
<th>Wt.% Pt in dip dispersion</th>
<th>HT Temp. (°C)</th>
<th>Sheet Resistance (Ω)</th>
<th>Room Temp Conductivity (mΩ·m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>650</td>
<td>&gt;10M</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>650</td>
<td>&gt;10M</td>
<td>--</td>
</tr>
<tr>
<td>15</td>
<td>650</td>
<td>197.4</td>
<td>25</td>
</tr>
<tr>
<td>20</td>
<td>400</td>
<td>621k</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>160</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>10.9</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>3.94</td>
<td>1,300</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>3.67</td>
<td>1,400</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>3.35</td>
<td>1,500</td>
</tr>
<tr>
<td>25</td>
<td>650</td>
<td>13.16</td>
<td>400</td>
</tr>
<tr>
<td>Pure Pt [152]</td>
<td>--</td>
<td>0.53</td>
<td>9,500</td>
</tr>
</tbody>
</table>

Table 5.4: Effect of Pt content and heat-treatment temperature on the RT conductivity of 2 layer Pt/GDC electrodes. Red highlights are samples of similar HT temp (650°C).

**Conductivity at high T**

The total conductivity of 150 - 200 nm thick, 2-layer electrodes $T_{HT} = 800°C$ ranged from $1.4 \times 10^6 \ \Omega^{-1}\text{m}^{-1}$ to $8.6 \times 10^6 \ \Omega^{-1}\text{m}^{-1}$ from 22 to 650°C, which was ~1.5 to 3% of the conductivity of elemental platinum [152]. The activation energy was ~0.02eV. For a 35%
porous membrane and assuming the conductivity of GDC was negligible, for an idealized conductor-insulator percolation threshold of 0.17 [153], the volume fraction of Pt in the electrode was calculated [154] to ~25vol% (~65wt% vs. GDC), which gave GDC ~40% of the volume. The linearized plot in figure 5.8 compares the electrode conductivity to a strip of the paint used to attach the current collecting wires to the electrode. The cross-sectional dimensions of the strip of paint, painted on an alumina support, were overestimated to give underestimated values of conductivity, but the underestimated conductivity was still well above that of the electrode. The thermal coefficient of resistivity of the electrode sharply changed around 200°C, but other than that was constant and positive, as expected for metallic, electronic conduction without significant contributions from surfaces or second phases such as GDC. The electrode conductivity did not change discernibly with oxygen partial pressure from air to N₂, which was also consistent with the lack of contributions from the GDC phase.

![Figure 5.9](image1.png)

**Figure 5.9:** Pt/GDC electrode (Ode1) and Pt paint: (Left) Conductivity vs. temperature, (right) thermal resistivity coefficient (slope). Literature values from [152].

In figure 5.10 the conductivity of CEO₂, GDC and YSZ membranes are plotted such that their similar activation energies at low temperature are apparent, and are consistent with the reported values for bulk GDC [155,156] and spray-pyrolyzed YSZ thin-films [157,158]. The total conductivities were overall slightly higher than the literature values.
for GDC. For YSZ the conductivity was lower than the literature values for dense YSZ films on sapphire formed by pulse laser deposition [158,159], and is consistent with ~26% porosity with a percolation threshold of 0.17. The critical temperature for the GDC material at which the activation energy abruptly shifted was 500 - 525°C as opposed to 400°C reported by Steele [156]. The energy change is associated with short-range ordering of oxygen-site vacancies at lower temperature [155], supported by the lack of such a change in undoped CeO₂. It was interesting that the conductivity of CeO₂ was considerably higher than that of the GDC membrane. A tentative explanation for this observation is that the conductivity is grain-boundary dependent, though a thorough study of the grain size in the CeO₂ film has not been conducted.

Figure 5.10: GDC, YSZ conductivity from 4-pt. vdp measurements.
5.4 Conclusions

Methods were developed for the syntheses of aqueous, nano-particulate colloids of platinum, doped and undoped ceria, and stabilized zirconia from molecular precursors. The colloids, with particle sizes <10nm, were stable for several months, and could be easily combined to achieve ceramic/metallic composites with a range of composition. Pt/GDC composite membranes with controllable thicknesses <1μm were dip-coated on porous alumina supports for use as SOFC electrodes. Ceria, GDC, and YSZ membranes were also successfully fabricated for use in liquid and gas separation.

Samples of dried colloidal particles showed high crystallinity at 500°C. When rapid thermal processing was used to heat-treat the membranes, shrinkage lagged behind conventional furnace heat-treatment up to ~500°C, at which point membrane shrinkage in RTP exceeded that in CTP. Membranes with thicknesses ~100-150nm after dip-coating and drying shrank significantly less than those with thickness >700nm.

The total conductivities of the membranes were consistent with the literature given that the membranes were porous, with activation energies ~0.02eV for the Pt/GDC membranes and slightly less than 1eV for ceria, GDC and YSZ.

The colloidal syntheses in this work took ~4hrs for Pt, and ~5hrs for the ceramics. Dip-coating and drying required a total of ~1.25hrs, and HT by RTP ~0.33hrs, for a total of 5.6–6.6 hrs for batches of 6-10 membranes for a single layer, with 1.6 hrs added for each layer. Given automation, these times could be brought down significantly, and this makes the methods discussed in this work exceptionally efficient even for multi-layered systems, such as SOFCs. The fabrication and operation of SOFCs produced using these methods are the subjects of Chapter 6.
CHAPTER 6

SOFC FABRICATION AND PERFORMANCE

6.1 Introduction

6.1.1 SOFC design

The end goal of the project was to realize a low-volume, high-performance solid oxide fuel cell (SOFC) on a polymer or flexible metal support to operate at low temperature on a range of fuels such as hydrogen, methane and ethanol. The design, shown in figure 6.1, combined the efficiency and fuel flexibility of a SOFC – with the mechanical flexibility, cyclic stability and response time of a polymer-electrolyte fuel cell [160]. This enabled a range of compact stack geometries to be proposed for mobile and standalone applications. Fast and continuous colloidal processing techniques would allow SOFCs to be made thinner, cheaper and more space-efficient than state-of-the-art industrial methods.

In a spiral-wound fuel cell stack, as diagrammed in figure 6.1, the circuit is connected to each of the current collectors in caps (not shown) on each end of the cylindrical stack. The current collectors are porous to allow for delivery of the fuel and oxidant, also originating in the end caps. CO₂ and H₂O waste gases escape via the tube in the middle of the stack.

The project was divided into two phases: 1. Development and characterization of an ultra-thin, high-performance SOFC module using aqueous, colloidal material syntheses, dip-coating, and rapid-thermal processing on an alumina supporting structure; 2. Adaptation of SOFC module processing developed in phase 1 to a flexible supporting structure.
as shown in figure 6.1. In this thesis the project progress is presented up to the completion of phase 1.

Figure 6.1:  (Top) Spiral-wound SOFC stack. (Bottom) Proposed SOFC module.
6.2 Experimental

6.2.1 Electrolyte

The electrolyte was dip-coated as described in 5.2.3, over the electrode layer, dried at 110°C for 1 hr and heat-treated by RTP with a 10°/s heating rate, passive cooling rate, and 3 min soak time. Coating experiments using the same formulations as given in chapter 5 yielded cracked and non-uniform layers or delamination, so a survey of polymer and alcohol additives was conducted to achieve electrolyte quality.

Defect elimination

SEM imaging of FIB-prepared cross sections of defects showed that many of the cracks that became visible after electrolyte processing originated between layers of the electrode. The second electrode layer was then reformulated to improve the interfaces between subsequent layers.

One of the principle causes of electrolyte delamination was shrinkage as the volatile ions in the colloid thermalized and the electrolyte crystallized and sintered in the RTP unit. A microwave treatment method of the colloid was then developed to promote crystallization in the suspension as well as to further remove volatile ions from the colloid.

Masking

Current collection from the electrode was not possible from the side or bottom of the module, and so the circuit had to be attached at the top surface. A masking technique using PTFE tape was developed so that the electrolyte did not cover the entire surface. Masking could be accomplished with a range of geometries as shown in figure 6.2. The geometries were accomplished using PTFE donuts as purchased, or cutting the appropriate shapes from circles. The square and clover geometries were the easiest to make and did not promote bubbles to develop during dipping, but a painted ring around the periphery of the module for current collection was preferable in order to take the fullest advantage of the active electrolyte surface area, so the keyhole was chosen as the preferred geometry. The advantage of the keyhole over the circle was that air was able to escape as
the module swung down into the electrolyte dipping suspension, and this improved the yield significantly.

![Figure 6.2: PTFE tape mask geometries for retaining bare portion of electrode for current collection.](image)

### 6.2.2 Electrode 2

The first, support-side electrode (Ode1) was discussed in chapter 5, and is pictured in figures 5.7 and 6.2. The second, air-side electrode (Ode2) was dip-coated over the electrolyte using a PTFE tape mask to avoid overlap of the electrodes. However, the keyhole geometry was not feasible for Ode2 given that the gas-sealing gaskets in the testing apparatus were circular in shape and required a flat surface for hermetic sealing. Thus, bubble formation as the module swung into the dipping suspension had to be alleviated by reformulating the electrode suspension to reduce the surface tension. This was found to be necessary only for the first layer of Ode2. For the second layer, the original electrode suspension given in section 5.3 was used.
6.2.3 Performance testing apparatus

Measuring SOFC performance required current collection from the two electrodes and electrical isolation of the system as well as providing a gas seal between the two electrodes such that a fuel could be applied to one electrode and an oxidant to the other without mixing. Gas sealing at high temperature is the subject of extensive research in the SOFC field since most organics and many metals become unstable, particularly in oxidizing environments. Thermiculite 815 is a machinable gasket material stable up to 950°C, which exhibits up to 40% compression [Flexitallic Group, www.flexitallic.com]. It is also electrically insulating. The gas cell in this work was built around the use of Thermiculite for sealing and Ceramabond 552 [Aremco, www.aremco.com] for electrical isolation from the stainless steel of the gas cell shell, diagrammed in figure 6.3. The Thermiculite gasket and assembled cell are pictured in figure 6.4. The gas cell was equipped with gas inlets and outlets on each side of the module, for fuel and oxidant (not specific). The Ode1 current collector (CC), pictured in figure 6.4, was compressed between gaskets, while the Ode2 CC was shielded with an alumina tube and a thermocouple adapter [High Pressure Equipment Company, www.highpressure.com] as it split from the external gas-line (see figure 6.4-right).
Figure 6.3: Gas cell assembly drawing. Faces, screws, and fittings are SS 316. Gaskets are Thermiculite 815. Additional sealing with Ceramabond where needed, typically between o-ring and SOFC.

Figure 6.4: SOFC and gas cell assembly: (Left) SOFC with Ode1 current collector. (Middle) Thermiculite gasket with Ode2 current collector in center. (Right) Gas cell assembled, positioned in furnace.

The current collectors were connected to either a pair of Keithley 2425C 100W sourcemeters, or to a Solartron SI1287 electrochemical interface and a Solartron 1252A frequency response analyzer. At each temperature tested between RT and 650°C, the OCV was measured for 180s, then, provided a stable signal, the resistance across one of the sourcemeters was reduced stepwise to zero as the current in the circuit was monitored.
by the second sourcemeter, or, on the Solartron, the resistance was reduced in an automated fashion such that the voltage dropped 1 mV/s with 10 mV/data point.
The inlet gas flows were controlled by flow meters, and the outlet gases were monitored by a flow meter and an oxygen sensor.

### 6.3 Results and discussion

#### 6.3.1 Electrolyte quality

There were two fundamental types of defects visible after electrolyte processing: ~5μm pinholes, ~20-50μm pop-outs, and cracks. Figure 6.5 shows both types. Pinholes and pop-outs were caused by bubbles or dust which were already present in the support or electrode or were introduced in the electrolyte dipping suspension. Cracks were typically caused by dipping, drying, or sintering irregularities, and again were sometimes already present in the support or electrode, or developed during electrolyte processing. Eliminating bubbles and dust were matters of filtration (5μm), deaerating using a Thinky biaxial mixer, and adjustments in ethanol content.
Figure 6.5: Examples of electrolyte defects before defect elimination steps. (Left) Optical microscopy. (Right) SEM. (Top) Pop-out defect type, (bottom) crack defect type.

For GDC layers, partial and total delamination occurred in over 80% of the modules regardless of electrolyte processing. These catastrophic failures did not occur with such frequency with YSZ coatings, which indicated that the problems began with the GDC synthesis procedure. The TGA/DSC results in chapter 5 showed intense release of energy upon heating of the GDC, but the energy release was not seen with YSZ. From this it was hypothesized that the intense heat flow was due to remnants of the volatile ammonium and nitrate ions from the precursors, which were likely complexed with bicine and/or the ceria/gadolinia particles in suspension after ultrasonication and thus were not dialyzed.
out. Eliminating these compounds after dip-coating would involve impractically slow heating procedures. To disrupt the molecular complexes in the colloid, a microwave treatment of the GDC suspensions followed by a second dialysis was introduced to the electrolyte processing, (but not the electrode processing, nor in the YSZ processing, in which such steps were unnecessary).

For initial testing of such a microwave treatment, a commercial Westinghouse 750W microwave was used. The consistency of the power output of the microwave was evaluated using 100 and 50ml of deionized water at power settings of 10, 20, 30, and 40%. As figure 6.6 shows, the results were consistent in consecutive trials.

![Figure 6.6: Selected results from microwave output consistency evaluation. (Left) 100ml, 40% power. (Right) 50ml, 20% power.](image)

The effect of microwave treatment on the particle size of GDC colloids is shown in figure 6.7. Generally, the particle size distributions broadened and the peaks increased. The colloids were diluted to 2wt% GDC prior to treatment, as 5, 6.6, 8.5 and 10wt% dispersions became unstable at treatment times >10 min. Treatment times <10 min did not achieve discernible benefits in electrolyte quality, and power settings >20% caused the colloids to boil at 15 – 20 min. Also in figure 6.7 it is clear that microwave treatments with organic additives (other than bicine) present produced a bimodal distribution including an increase in particle size above 100 nm.
Figure 6.7: Effect of microwave treatments on GDC colloidal particle size.

20% power was selected for colloid treatment due to the more controlled nature of the heating as well as the increased crystallization and reduction in nitrate concentration, as the XRD and Raman spectra in figure 6.8 show. The Raman spectra in particular showed that further reduction in nitrate concentration with increasing microwave power from 20 to 40% were slight.

Figure 6.8: Effect of microwave treatments on GDC. XRD, Raman spectra. XRD was measured on powder dried at 50°C.
The effect of 20%P, 30min microwave treatment on solid yields from dried colloid powders heat-treated at 300 - 550°C is shown in figure 6.9. Without microwave treatment, the solid load dropped nearly 50% during heat treatment, but after microwave treatments, the drop was around 10%. These results confirm the removal of volatile compounds from the colloid.

**Figure 6.9:** Heat treatment of dried colloid powders to show effect of microwave treatments on solid yields.

After microwave treatment of the colloids, the electrolyte quality improved significantly but the yield of good GDC layers over Ode1 was still below 50%. SEM imaging on FIB-prepared cross-sections of crack and pop-out type defects, shown in figure 6.10, showed that many of such defects originated between layers of the electrode.
Figure 6.10: SEM images of FIB-prepared cross sections. (Upper left): Example of trench dug by FIB for analyzing crack. (Upper right): Crack originating between layers of electrode. (Lower left): Cross-section in proximity of pop-out type defect shows delamination between electrode layers. (Lower right): Crack originating from support-electrode interface.

The images in figure 6.10 gave considerable evidence that the problem of delamination had as much to do with electrode microstructure as it had to do with the electrolyte colloid. Figure 6.11 provided even more corroborating evidence that the interfaces between layers of electrode were not seamless, indicating weak layer-to-layer adhesion. The images at the top of figure 6.11 show visible lines where the electrode layers met.
Figure 6.11: SEM images of FIB-prepared cross sections: (Top) *Before* and (Bottom) *after* optimization of electrode dipping suspensions.

The images at the bottom of figure 6.11 show nearly seamless interfaces between electrode layers. This was accomplished by reformulation of the second electrode dipping suspension as given in table 6.1.
<table>
<thead>
<tr>
<th>Material/reagent</th>
<th>Ode1, layer 1</th>
<th>Ode 2, layer 2</th>
<th>Ode 1, layer 2</th>
<th>Ode 2, layer 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$PtCl$_6$·6H$_2$O</td>
<td>0.70 ± 0.05g</td>
<td>0.73± 0.05g</td>
<td>0.73± 0.05g</td>
<td></td>
</tr>
<tr>
<td>5wt% PVA</td>
<td>5.4 ± 0.1 ml</td>
<td>2.9 ± 0.05 ml</td>
<td>2.9 ± 0.05 ml</td>
<td></td>
</tr>
<tr>
<td>DI water</td>
<td>0</td>
<td>2.8 ± 0.05 ml</td>
<td>2.6 ± 0.05 ml</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>4.1 ± 0.05 ml</td>
<td>4.3 ± 0.05 ml</td>
<td>4.5 ± 0.05 ml</td>
<td></td>
</tr>
<tr>
<td>GDC suspension</td>
<td>9.5 ± 0.2 ml</td>
<td>10 ± 0.2 ml</td>
<td>10 ± 0.2 ml</td>
<td></td>
</tr>
</tbody>
</table>

**Table 6.1:** Optimized formulations for Pt-colloid synthesis and Pt/GDC composite dipping suspensions.

TEM images of FIB-prepared cross-sectional foils of full SOFC modules showed excellent electrode and electrolyte microstructure, as seen in figure 6.12. The thickness, particle size, and estimated porosity are given in table 6.2.
Figure 6.12: Full SOFC module: (A) Top-view of module, photograph. (B) SEM image of cross-section. (C) and (D) TEM images of cross-section. The vertical channels were likely damage from FIB.
<table>
<thead>
<tr>
<th>Component</th>
<th>No. of layers</th>
<th>RTP Temp [°C]</th>
<th>Thickness [nm]</th>
<th>Particle Size [nm]</th>
<th>Porosity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ode1 on Sup</td>
<td>2</td>
<td>800</td>
<td>425 ± 8</td>
<td>43 ± 5</td>
<td>38</td>
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<tr>
<td>Yte on Ode1</td>
<td>1</td>
<td>750</td>
<td>80 ± 15</td>
<td>11 ± 3</td>
<td>8</td>
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<tr>
<td>Ode2 on Yte</td>
<td>2</td>
<td>700</td>
<td>354 ± 6</td>
<td>49 ± 2</td>
<td>42</td>
</tr>
</tbody>
</table>

**Table 6.2:** Optimized formulations for Pt-colloid synthesis and Pt/GDC composite dipping suspensions.

### 6.3.2 SOFC performance

Voltage/current and power density plots for the SOFC incorporating an ~80 nm thick GDC electrolyte is shown in figure 6.13. The cell was tested in $\text{N}_2/\text{O}_2$, $p^i_{\text{O}_2} = 0.2$, $p^\text{H}_{\text{H}_2} = 0.001$. The oxygen partial pressure gradient was kept small due to shorting even at small currents, such that $\Delta \Phi_{\text{OC}}^{\text{Nernst}} \approx 84$ mV. Even so the OCV was ~59% of the Nernst voltage at 500°C, which was likely due to defects and/or mixed conduction in the GDC electrolyte. The ion transference number of this particular material has yet to be determined, however.
SOFC modules incorporating YSZ electrolyte ~100 nm thick performed better than the GDC electrolyte discussed above, though the power was still very small. These modules operated in air/(H₂ + 3% H₂O), 100sccm/150sccm flow. The OCVs achieved were >70% of the Nernst voltage, which was consistent with the N₂ NSSGP values of ~10⁻⁸, far from what was recorded for dense membranes (<10⁻¹⁰). Leaks through membrane defects were the most likely cause of the low OCVs and power output given that leaks were not seen in the gaskets with dense samples.
Much higher performance was achieved by incorporating a bi-layer GDC/YSZ electrolyte. The performance of such a SOFC module is shown in figure 6.15. This module incorporated 2 dipped layers of GDC and 2 dipped layers of YSZ, heat-treated at 750°C. Peak power surpassed 1000 W/m² at 450°C, and 5000 W/m² at 600°C. The linear nature of the high temperature V-I curves suggest that the resistance was dominantly Ohmic, while the positive curvature of the lower temperature curves were associated with slow reaction kinetics. This made sense because in thin-films, mass transfer limitations are typically observed at currents above 20 A/m² [60], which were not reached in this case. Thus, resistances at the electrode-electrolyte interfaces were likely insignificant.
These results, particularly at 350-450°C, are unprecedented for thin-film fuel cells of surface area >1cm², with the exception of electrolytes processed by pulse layer deposition [60,62]. The area-specific resistances of the bi-layer electrolyte SOFC are plotted in figure 6.16. The activation energies were ~0.7eV at low temperature, ~0.58eV at high temperature.
Figure 6.16: SOFC module, GDC/YSZ bi-layer electrolyte, area-specific resistance and associated activation energy. Ode1: Air, 100sccm. Ode2: H₂ + 3% H₂O 150sccm.

When the air and fuel were swapped between electrodes, the results were a little better, as Figure 6.17 shows. The module surpassed 900 W/m² at 400°C, and the activation energy from the ASR data was ~0.41eV. Thus, the SOFC module exhibited electrochemical symmetry, which was a promising result for the testing of other types of electrodes, given that either of the electrodes could be switched for another material such as a nickel/GDC anode, or a manganate or cobaltate-type of cathode. The symmetrical results also suggested that the greatest benefit of the GDC part of the bi-layer electrolyte was not electrochemical in nature but was as an interlayer between Ode1 and the YSZ electrolyte, aiding in the reduction of pore size and the ultimate densification of the YSZ layer.
6.4 Comparisons to literature

The power densities of the module measured in this work were ~700 and ~900 W/m\(^2\) at 350 and 400\(^\circ\)C. In table 6.3, these performance values are shown in comparison to the highest published values to date at similar operating temperature. What is remarkable about the performance in this work is that the active surface area of the module was on the order of cm\(^2\), several orders of magnitude higher than that of the published values. Considering the surface area, the power generated by individual cells was significantly higher in this work than that of cells produced by microfabrication methods [64, 65].
<table>
<thead>
<tr>
<th>First Author</th>
<th>Operating temperature [°C]</th>
<th>Power density [W/m²]</th>
<th>Active area [m²]</th>
<th>Cell power [W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shim [64]</td>
<td>350</td>
<td>2700</td>
<td>$10^{-8}$</td>
<td>$3 \times 10^{-5}$</td>
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<tr>
<td>Su [65]</td>
<td>400</td>
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<td>$10^{-5}$</td>
<td>$7 \times 10^{-2}$</td>
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<tr>
<td>Snider [this work]</td>
<td>350</td>
<td>700</td>
<td>$10^{-2}$</td>
<td>$7 \times 10^{0}$</td>
</tr>
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<td>Snider [this work]</td>
<td>400</td>
<td>900</td>
<td>$10^{-2}$</td>
<td>$9 \times 10^{0}$</td>
</tr>
</tbody>
</table>

Table 6.3: SOFC module performance, comparisons to literature.

6.5 Conclusions

The colloidal synthesis and membrane fabrication techniques discussed in Chapter 5 were modified for the formation of GDC and YSZ electrolytes over Pt/GDC electrode membranes. For GDC, a majority of electrolyte layers delaminated during RTP and this was thought to be the result of a massive release of heat as volatile ions from the colloidal dispersion thermalized. This explosive energy release was observed in the TGA/DSC data for GDC, but not as much for YSZ, and YSZ did not exhibit delamination as frequently. In considering solutions to the delamination problem, pre-treatment of the colloid was deemed preferable to treating the membrane layer after dip-coating because of the lengthy times involved in ion removal by heat-treatment, and the complication of the fabrication method introduced by other treatments such as ozone. Also, the high degree of crystallinity observed after heat treatment was thought to be aided by the energy release during ion thermolysis, so a complete removal of nitrates prior to heat-treatment was not preferable. A microwave treatment of the GDC colloid was then introduced to the method post-dialysis. The microwave treatment was meant to promote dissociation of nitrate ions from the oxide particles in the dispersion which were not removed during the first dialy-
sis. Some of these volatile ions may have vaporized, but to be certain of their removal, a second dialysis was implemented. GDC electrolyte yields improved with the microwave treatment, but delamination was still observed in many samples. Examination of FIB-prepared cross-sections by SEM showed that delamination was occurring, not in the electrode-electrolyte interface, but between layers of electrode. The electrode formulation was thus modified for the second layer such that a seamless interface was achieved between electrode layers. After this modification, the only delamination that was observed was in those samples with support defects, which changes to electrode/electrolyte syntheses, dipping, and firing methods could do nothing to alleviate.

Successfully fabricated SOFC modules performed very well in initial performance tests, exhibiting measurable activity at temperatures as low as 275°C and achieving \(\sim 1000\) W/m\(^2\) at 450°C. The best performance was observed YSZ electrolytes with a GDC interlayer, as opposed to GDC or YSZ alone. When fuel/oxidant were swapped between electrodes, the performance of the bilayer electrolyte was similar, and this indicated that the performance enhancement was physical as opposed to electrochemical in nature; that is, the presence of GDC improved the YSZ microstructure by providing an interlayer between the YSZ and the Pt/GDC composite.
CONCLUSIONS

Zeolite NaY for carbon capture

Worldwide fossil fuel consumption is projected to rise significantly in the next thirty years, and thus efficient means of pollution control will become increasingly critical as resource depletion and the progression of climate change will likely translate into social, political, and economic disasters. The centralized nature of carbon emissions from coal-fired power production provides immediate opportunities to implement or upgrade pollution control mechanisms given that carbon can be removed from the flue-gas waste stream cheaply and without significant penalties to plant power output. Gas separation by membrane may be a way to accomplish efficient carbon capture, due to spontaneous mechanisms of gas transport, but only if high CO2 selectivity can be achieved in the presence of trace sulfurous compounds. The instability of many organic membrane materials in the presence of even small amounts of sulfur leads to the consideration of inorganic membranes for this purpose, but fast CO2 selectivity must also be maintained in the presence of large concentrations of H2O.

Dense thin-films of faujasite-type materials such as zeolite NaY can offer high CO2 permeance and CO2/N2 selectivity via a surface-sorption activated transport mechanism. CO2 adsorption on the membrane surface significantly enhances the likelihood that it will enter the micropores, and once CO2 occupies the pores it blocks out the less adsorptive N2. A gradient in CO2 occupancy from feed to permeate sides of the membrane gives rise to transport in the micropores, which is enhanced by retaining the templating agent in the zeolite seed crystals. The templating agent resides in the α-cages of the faujasite structure after synthesis, and its presence reduces CO2 occupancy by as much as 15-25%. A reduction in overall CO2 occupancy would seem to lower the driving force for transport and
therefore slow CO\textsubscript{2} down, but the templating agent has little effect on the gas sorption affinity; it only acts as a physical obstruction. The thermodynamics of the CO\textsubscript{2} separation process are thus nearly unharmed by the templating agent, while the physical obstruction blocks out N\textsubscript{2} almost completely. Despite that the mechanical mobility of CO\textsubscript{2} increases in the presence of the templating agent, the permeance is reduced by \( \sim 10\times \). The CO\textsubscript{2} permeance is even further reduced when H\textsubscript{2}O is present in the gas stream. H\textsubscript{2}O has greater affinity and less mobility than CO\textsubscript{2}. Hence, H\textsubscript{2}O is more likely to occupy the micropores than CO\textsubscript{2}, and moves slowly once it is there. Unfortunately this has a crippling effect on both CO\textsubscript{2}/N\textsubscript{2} selectivity and CO\textsubscript{2} permeance. For a dry gas stream after dehumidification, residual H\textsubscript{2}O in the micropores can act in a parallel way to the templating agent, that is, it can increase CO\textsubscript{2}/N\textsubscript{2} selectivity by providing a limited physical obstruction. Residual water increases CO\textsubscript{2} permeance, though the cause of this effect is still unknown. It also remains to be determined what amount of H\textsubscript{2}O in the gas stream can maintain a certain level of residual micropore occupancy and not reduce the CO\textsubscript{2}/N\textsubscript{2} performance, but with a dense membrane of zeolite NaY with Si/Al ratio of \( \sim 1.6 \), this amount is less than 0.8mol\%.

**Future work**

To use this particular system for carbon capture from coal flue-gas, evidence in this work shows that near-total dehumidification, or some sort of barrier to H\textsubscript{2}O transport, is necessary. Zeolite systems with more hydrophobic structures, such as higher Si/Al-ratio zeolite Y and silicalite, show reduced CO\textsubscript{2}/N\textsubscript{2} selectivity. However, the reduced H\textsubscript{2}O/CO\textsubscript{2} selectivity and increased CO\textsubscript{2} permeance may be worth the penalty. Thus, systematic affinity/transient experiments on higher Si/Al ratio zeolites may reveal systems that well balance these performance parameters.

**Colloidal processing of SOFC materials**

Another way to reduce pollution and slow resource depletion from coal-fired power generation is to combine the steam-turbine system with a more efficient electrochemical conversion process, such as a fuel cell. The elevated operating temperatures of SOFCs make them particularly well-suited for this purpose, but the current state-of-the-art oper-
ating temperatures may be higher than desirable for many applications. On one hand cathode reaction kinetics and ionic conductivities improve at higher temperatures, but these improvements are countered by difficulties in gas sealing and current collection, long ramp times, anode instability, and reduced thermodynamic and volume efficiency. SOFC operation in the range of 350 - 500°C allows for the use of high-performing metal interconnects, and flexible and/or highly conductive supporting structures. To be sufficiently conductive at such low temperatures the YSZ electrolyte must be very thin, and to take full advantage of a thin electrolyte, i.e. to avoid mass diffusion limitations across the electrolyte-electrode interfaces, the electrode microstructures should be very fine.

Thin, fine-particle ceramic films can be fabricated by wet chemical processing methods, beginning with nano-particulate colloids of narrow particle size distribution. This is achieved using ultrasonics to agitate and mix a solution of dissolved molecular precursors as the pH is raised to promote the precipitation of very fine particles. The fine particles are stabilized in suspension with small additions of bicine. Dialysis and microwave treatments remove excess volatiles and promote oxide crystallization in the colloidal state, which allows controlled, low-temperature sintering after dip-coating. Thus, the narrow size distributions of the colloids translate to uniform microstructures in the membranes. Further, small and deliberate changes in the colloid particle size distribution translate to controlled alterations of the membrane pore size distribution. This is useful for fabricating mesoporous electrode membranes, microporous interlayers, and dense electrolytes.

Using rapid thermal processing of dip-coated layers, each layer of each component took ~1.5hrs to apply and heat-treat. Most of this time, 1hr, was used for drying prior to RTP. This means that a SOFC module can be produced on a pre-fabricated support within 8hrs. In addition, dip-coating and RTP are immediately scalable to continuous industrial production.

The colloids produced in this work were aqueous with simple compositions—the only additions being the precursors, nitric acid, TMAOH, bicine, PVA or PVP, and methanol or ethanol. The colloids could be easily destabilized for waste management.
The SOFC module in this work exhibited ~700 and ~900 W/m² power density at 350 and 400°C, which are remarkable achievements considering that the active surface area of the module was considerably larger than the low-temperature SOFCs reported in the literature to date.

**Future work**

The SOFC modules discussed in this work involved sintering steps at >800°C. Experiments on polymer and porous-nickel supports have indicated that heat treatments by RTP are acceptable up to 650°C, with 40°C/s ramp rate and 1s soak time. Thus, improvements to the current fabrication protocol are necessary to bring the sintering temperatures down while maintaining density in the electrolytes and electrical conductivity in the electrodes. There is already some progress in the former. The performance of the electrolyte improved when a GDC interlayer was applied over Ode1 prior to coating the YSZ electrolyte. This is likely because the highly porous electrode constrained the surface-plane shrinkage of the electrolyte. An interlayer between the electrode and the electrolyte not only provided a less porous, defect-free surface onto which to apply a nano-particulate electrolyte, but also facilitated electrolyte shrinkage, and thus densification. Optimization of the interlayer and electrolyte particle sizes will yield higher shrinkages and higher quality, reproducible electrolytes at lower sintering temperature. Initial experiments have indicated that this is true, with the possibility of electrolyte sintering temperatures of 450°C and below.


63. B.-K. Lai, K. Kerman and S. Ramanathan, “Nanostructured La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3/Y_{0.08}Zr_{0.92}O_{1.96}/La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3 (LSCF/YSZ/LSCF) symmetric thin film solid oxide fuel cells,” *Journal of Power Sources* **196** (2011) 1826–1832


91. NIST Webbook, webbook.nist.gov/chemistry/, accessed 7/10/2012.


126


### A.1 Equilibrium sorption parameters

The equilibrium sorption parameters are given by individual isotherm for $ZYN_{oTA}$ in table A.1, and for $ZYT_{A}$ in table A.2. The lumped parameters are given in tables A.3 and A.4.

<table>
<thead>
<tr>
<th>Exp. Gas</th>
<th>Temp [°C]</th>
<th>L / LF / T</th>
<th>$\Gamma_{b}$ [mol/m$^3$]</th>
<th>$C_{sat, T}$ [mol/m$^3$]</th>
<th>$C_{sat, T}$ [mol/kg]</th>
<th>$K(T)$ [-]</th>
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<td>9,520</td>
<td>9320</td>
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*Table A.1: Equilibrium sorption parameters: $ZYN_{oTA}$.  

129
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<th>Exp. Gas</th>
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<td>0.295</td>
<td>2.87E-03</td>
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<td></td>
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<td>L</td>
<td>9,520</td>
<td>411</td>
<td>0.302</td>
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<td>80</td>
<td>L</td>
<td>9,520</td>
<td>417</td>
<td>0.306</td>
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<td>100</td>
<td>L</td>
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<td>417</td>
<td>0.306</td>
<td>1.40E-03</td>
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<td>150</td>
<td>L</td>
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<td>6.95E-04</td>
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</table>

**Table A.2:** Equilibrium sorption parameters: $ZYN_{O/T}$.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>CO₂</th>
<th>+/-</th>
<th>N₂</th>
<th>+/-</th>
<th>H₂O</th>
<th>+/-</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_\nu ) [mol/m³]</td>
<td>9,520</td>
<td>9,520</td>
<td>26,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E^{\text{sat}} ) [J/mol]</td>
<td>6100</td>
<td>2200</td>
<td>35200</td>
<td>40200</td>
<td>5000</td>
<td>90</td>
</tr>
<tr>
<td>( C^{\text{sat},0} ) [mol/m³]</td>
<td>810</td>
<td>120</td>
<td>0.0047</td>
<td>0.29</td>
<td>3400</td>
<td>940</td>
</tr>
<tr>
<td>-( \Delta h ) [J/mol]</td>
<td>16100</td>
<td>2600</td>
<td>8400</td>
<td>1400</td>
<td>30500</td>
<td>2300</td>
</tr>
<tr>
<td>( K^0 ) [-]</td>
<td>0.009</td>
<td>0.035</td>
<td>0.001</td>
<td>0.0008</td>
<td>3.2E-08</td>
<td>6E-09</td>
</tr>
<tr>
<td>( A^0 ) [-]</td>
<td>0</td>
<td>0</td>
<td>111</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n^0 ) [-]</td>
<td>1</td>
<td>1</td>
<td>0.40</td>
<td>0.003</td>
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<td></td>
</tr>
<tr>
<td>( q^{\text{st,Load=0.01}} ) [J/mol]</td>
<td>20800</td>
<td>16400</td>
<td>35700</td>
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**Table A.3:** Equilibrium sorption parameters: \( ZY_{\text{NoTA}} \).

<table>
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<tr>
<th>Parameter</th>
<th>CO₂</th>
<th>+/-</th>
<th>N₂</th>
<th>+/-</th>
<th>H₂O</th>
<th>+/-</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_\nu ) [mol/m³]</td>
<td>9,520</td>
<td>9,520</td>
<td>26,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( U^{\text{sat}} ) [J/mol]</td>
<td>7770</td>
<td>570</td>
<td>-0.44</td>
<td>140</td>
<td>5500</td>
<td>980</td>
</tr>
<tr>
<td>( C^{\text{sat},0} ) [mol/m³]</td>
<td>460</td>
<td>70</td>
<td>650</td>
<td>&lt; 1</td>
<td>2500</td>
<td>260</td>
</tr>
<tr>
<td>-( \Delta h ) [J/mol]</td>
<td>15400</td>
<td>2500</td>
<td>10100.00</td>
<td>2200.00</td>
<td>35000</td>
<td>2800</td>
</tr>
<tr>
<td>( K^0 ) [-]</td>
<td>0.05</td>
<td>0.05</td>
<td>5.1E-05</td>
<td>4E-06</td>
<td>5.6E-09</td>
<td>2.5E-09</td>
</tr>
<tr>
<td>( A^0 ) [-]</td>
<td>0</td>
<td>0</td>
<td>125</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n^0 ) [-]</td>
<td>1</td>
<td>1</td>
<td>0.50</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q^{\text{st,Load=0.01}} ) [J/mol]</td>
<td>21500</td>
<td>9400</td>
<td>34800</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**Table A.4:** Equilibrium sorption parameters: \( ZY_{\text{TA}} \).
A.2 Time-transient sorption parameters with Ar

The time-transient sorption parameters in the gas exchange experiments with argon are given by isotherm in tables A.5 - A.10. In the $C_t^{\to \infty}$ columns, saturation amounts are given for the adsorption isotherms, and remaining amounts are given for desorption isotherms. The lumped parameters are given in table A.11.

<table>
<thead>
<tr>
<th>Ads/Des</th>
<th>Temp [°C]</th>
<th>$C_t^{\to \infty}$ Mass %</th>
<th>$C_t^{\to \infty}$ (mol/m³)</th>
<th>Characteristic Time, $\tau$ [s]</th>
<th>Mobility [mol·s/kg]</th>
<th>Diffusion Constant [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ads</td>
<td>30</td>
<td>20.76</td>
<td>6425</td>
<td>43</td>
<td>8.2E-17</td>
<td>2.1E-13</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>18.59</td>
<td>5754</td>
<td>35</td>
<td>9.8E-17</td>
<td>2.6E-13</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>17.07</td>
<td>5283</td>
<td>34</td>
<td>9.8E-17</td>
<td>2.6E-13</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>12.46</td>
<td>3857</td>
<td>34</td>
<td>8.9E-17</td>
<td>2.6E-13</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>9.22</td>
<td>2853</td>
<td>25</td>
<td>1.1E-16</td>
<td>3.5E-13</td>
</tr>
<tr>
<td>Des</td>
<td>30</td>
<td>0.92</td>
<td>285</td>
<td>638</td>
<td>5.6E-18</td>
<td>1.4E-14</td>
</tr>
<tr>
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<td>40</td>
<td>1.01</td>
<td>314</td>
<td>587</td>
<td>5.9E-18</td>
<td>1.5E-14</td>
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<td>50</td>
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<td>222</td>
<td>459</td>
<td>7.3E-18</td>
<td>2.0E-14</td>
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<tr>
<td></td>
<td>80</td>
<td>1.07</td>
<td>331</td>
<td>336</td>
<td>9.1E-18</td>
<td>2.7E-14</td>
</tr>
<tr>
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<td>100</td>
<td>0.45</td>
<td>140</td>
<td>270</td>
<td>1.1E-17</td>
<td>3.3E-14</td>
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</tbody>
</table>

Table A.5: Time-transient sorption parameters: $ZY_{\text{NoTA}}, \text{CO}_2$. 

132
<table>
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<tr>
<th>Ads/Des</th>
<th>Temp [°C]</th>
<th>( C_{t} \rightarrow \infty ) Mass %</th>
<th>( C_{t} \rightarrow \infty ) (mol/m³)</th>
<th>Characteristic Time, ( \tau ) [s]</th>
<th>Mobility [mol·s/kg]</th>
<th>Diffusion Constant [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ads</td>
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<td>29.14</td>
<td>22050</td>
<td>7020</td>
<td>5.1E-19</td>
<td>1.3E-15</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>24.40</td>
<td>18463</td>
<td>6350</td>
<td>5.3E-19</td>
<td>1.4E-15</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>21.85</td>
<td>16535</td>
<td>3070</td>
<td>1.0E-18</td>
<td>2.9E-15</td>
</tr>
<tr>
<td></td>
<td>100</td>
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<td>13142</td>
<td>2530</td>
<td>1.1E-18</td>
<td>3.6E-15</td>
</tr>
<tr>
<td>Des</td>
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<td>4082</td>
<td>766126</td>
<td>4.7E-21</td>
<td>1.2E-17</td>
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<td>57</td>
<td>3.88</td>
<td>2939</td>
<td>95361</td>
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<td>9.4E-17</td>
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<td>80</td>
<td>3.00</td>
<td>2267</td>
<td>34806</td>
<td>8.8E-20</td>
<td>2.6E-16</td>
</tr>
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<td>1888</td>
<td>17177</td>
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<td>5.2E-16</td>
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</tbody>
</table>

**Table A.6:** Time-transient sorption parameters: \( \text{ZY}_{\text{NoTA}}, \text{H}_2\text{O} \).

<table>
<thead>
<tr>
<th>Ads/Des</th>
<th>Temp [°C]</th>
<th>( C_{t} \rightarrow \infty ) Mass %</th>
<th>( C_{t} \rightarrow \infty ) (mol/m³)</th>
<th>Characteristic Time, ( \tau ) [s]</th>
<th>Mobility [mol·s/kg]</th>
<th>Diffusion Constant [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ads</td>
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<td>0.73</td>
<td>355</td>
<td>76</td>
<td>4.7E-17</td>
<td>1.2E-13</td>
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<tr>
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<td>40</td>
<td>0.69</td>
<td>335</td>
<td>69</td>
<td>5.0E-17</td>
<td>1.3E-13</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.59</td>
<td>286</td>
<td>68</td>
<td>4.9E-17</td>
<td>1.3E-13</td>
</tr>
<tr>
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<td>3.9E-17</td>
<td>9.9E-14</td>
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<td>1.1E-13</td>
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<td>8</td>
<td>59</td>
<td>5.7E-17</td>
<td>1.5E-13</td>
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**Table A.7:** Time-transient sorption parameters: \( \text{ZY}_{\text{NoTA}}, \text{N}_2 \).
<table>
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<th>Ads/Des</th>
<th>Temp [°C]</th>
<th>$c_t^{\rightarrow \infty}$ Mass %</th>
<th>$c_t^{\rightarrow \infty}$ (mol/m³)</th>
<th>Characteristic Time, $\tau$ [s]</th>
<th>Mobility [mol·s/kg]</th>
<th>Diffusion Constant [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ads</td>
<td>30</td>
<td>18.65</td>
<td>5773</td>
<td>22</td>
<td>1.5E-16</td>
<td>3.8E-13</td>
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<td>40</td>
<td>17.40</td>
<td>5385</td>
<td>21</td>
<td>1.5E-16</td>
<td>3.8E-13</td>
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<td>50</td>
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<td>4912</td>
<td>18</td>
<td>1.7E-16</td>
<td>4.4E-13</td>
</tr>
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<td>80</td>
<td>11.18</td>
<td>3460</td>
<td>18</td>
<td>1.5E-16</td>
<td>4.5E-13</td>
</tr>
<tr>
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<td>100</td>
<td>8.53</td>
<td>2640</td>
<td>13</td>
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<td>6.3E-13</td>
</tr>
<tr>
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<td>349</td>
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<td>188</td>
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<td>4.3E-14</td>
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</tbody>
</table>

**Table A.8:** Time-transient sorption parameters: $Z_{Y_{TA}, CO_2}$. 
<table>
<thead>
<tr>
<th>Ads/Des</th>
<th>Temp [°C]</th>
<th>$\mathcal{C} \rightarrow \infty$ Mass %</th>
<th>$\mathcal{C} \rightarrow \infty$ (mol/m³)</th>
<th>Characteristic Time, $\tau$ [s]</th>
<th>Mobility [mol·s/kg]</th>
<th>Diffusion Constant [m²/s]</th>
</tr>
</thead>
<tbody>
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<td>1.8E-15</td>
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<td>3.4E-15</td>
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**Table A.9:** Time-transient sorption parameters: $\text{ZYTA}, \text{H}_2\text{O}$.
<table>
<thead>
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<th>Ads/Des</th>
<th>Temp [°C]</th>
<th>$C^{\rightarrow \infty}$ Mass %</th>
<th>$C^{\rightarrow \infty}$ (mol/m³)</th>
<th>Characteristic Time, $\tau$ [s]</th>
<th>Mobility [mol·s/kg]</th>
<th>Diffusion Constant [m²/s]</th>
</tr>
</thead>
<tbody>
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<td>2.5E-13</td>
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<td>2.9E-13</td>
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</tr>
<tr>
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<td>2.0E-13</td>
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<td>2.8E-13</td>
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**Table A.10:** Time-transient sorption parameters: $ZYT_{TA}$, $N_2$.  

136
<table>
<thead>
<tr>
<th>Gas</th>
<th>Ads/Des</th>
<th>Material</th>
<th>$u^m$ [kJ/mol]</th>
<th>ln($b^*$) [mol·s/kg]</th>
<th>$u^D$ [kJ/mol]</th>
<th>ln($D^0$) [m$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>Ads</td>
<td>ZY$_{noTA}$</td>
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<td>-36.0</td>
<td>-5.4</td>
<td>-27.0</td>
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<td></td>
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<td>-26.2</td>
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**Table A.11:** Lumped time-transient sorption parameters: **all samples, gases.**
### A.3 Time-transient sorption parameters with \( N_2 \)

The time-transient sorption parameters for the experiments in which \( \text{CO}_2 \) or \( \text{H}_2\text{O} \) was exchanged for \( \text{N}_2 \), as opposed to argon, are given in table A.12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas</th>
<th>Temp</th>
<th>Ads/Des</th>
<th>( C^\rightarrow \infty ) Mass %</th>
<th>( C^\rightarrow \infty ) (mol/m(^3))</th>
<th>Characteristic Time [s]</th>
<th>Mobility [mol-s/kg]</th>
<th>Diffusion Constant ([\text{m}^2/\text{s}])</th>
</tr>
</thead>
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<tr>
<td>( \text{ZY}_{\text{NoTA}} )</td>
<td>( \text{CO}_2 )</td>
<td>30</td>
<td>Ads</td>
<td>21.6</td>
<td>492</td>
<td>79</td>
<td>2.01E-19</td>
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<td>404</td>
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<td>516</td>
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<td>( \text{H}_2\text{O} )</td>
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<td>532</td>
<td>159000</td>
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<tr>
<td>( \text{ZY}_{\text{TA}} )</td>
<td>( \text{CO}_2 )</td>
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<td>Ads</td>
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<td>449</td>
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<td>4.67E-19</td>
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<td>15.6</td>
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<td>( \text{H}_2\text{O} )</td>
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<td>257</td>
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</tr>
</tbody>
</table>

| Table A.12: | Lumped time-transient sorption parameters: exchanged with \( N_2 \). |

138
APPENDIX B

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