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Membrane Characterization for a Sulfur-Dioxide Depolarized Electrolyzer (SDE)

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HyS Electrolyzer Workshop and Information Exchange

SRNL-STI-2009-00268

Outline

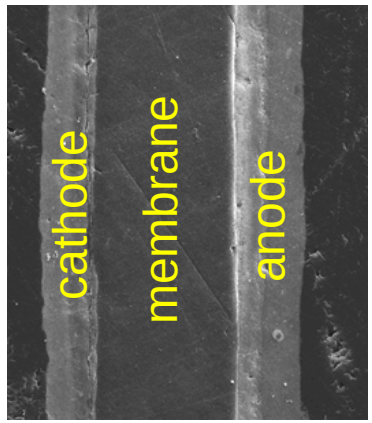
- **Background**
- **Membrane Candidates**
- **Experimental Methods**
- **Results**
  - Durability
  - SO_2 flux, SO_2 transport
  - Ionic conductivity, SDE performance

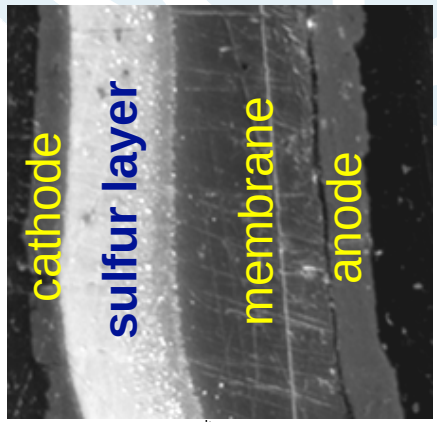
The Problem: Sulfur Layer Formation

GES has shown that the presence of both SO_2 and H_2S is required for sulfur formation (Clause reaction)

$$2H_2S + SO_2 \rightarrow {}^3/_8S_8 + 2H_2O$$

Sulfur formation is evident after multiple hours of SDE operation





Pt: 0.77 wt%
C: 19.63 wt%
S: 75.48 wt%
F: 4.12 wt%

Methods for minimizing SO_2 transport

- Operating conditions: temperature, pressure, [SO_2]
- Decrease membrane SO_2 permeability
- Minimize cathode reactivity towards SO_2 through catalyst selection

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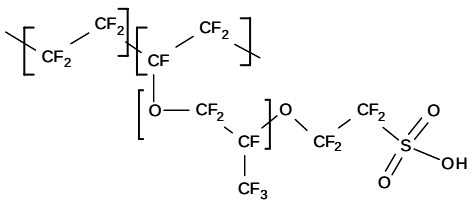
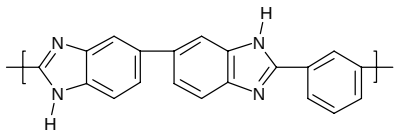
Membranes Tested

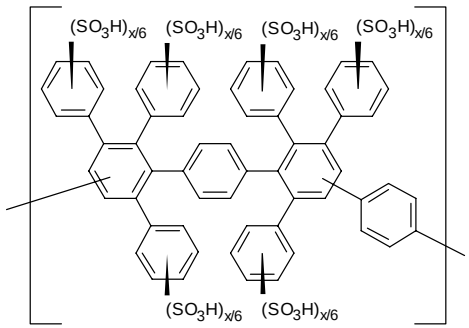
Perfluorinated sulfonic acid (PFSA) . . . . . Dupont
Polybenzimidizole (PBI) . . . . . BASF
Sulfonated Diels-Alder polyphenylenes (SDAPP) . . . . . SNL
Stretched recast PFSA . . . . . Case
PFSA/fluorinated ethylene propylene (FEP) blends . . . . . Case
Treated PFSA . . . . . GES
Perfluorocyclobutane-biphenyl vinyl ether (BPVE) . . . . . Clemson
Perfluorocyclobutane-biphenyl vinyl ether hexafluoroisopropylidene (BPVE-6F) . . . . . Clemson



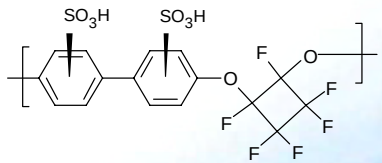
PFSA



PBI



SDAPP



BPVE-6F

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Experimental Methods

- **Chemical durability**
  - Record FTIR spectrum of membrane before and after contact with hot H_2SO_4 solution
- **SO_2 transport under non-polarized conditions**
- **Ionic conductivity**
  - Electrochemical impedance spectroscopy (EIS)
- **SDE performance**
  - Constant potential (1 V) HyS electrolyzer performance

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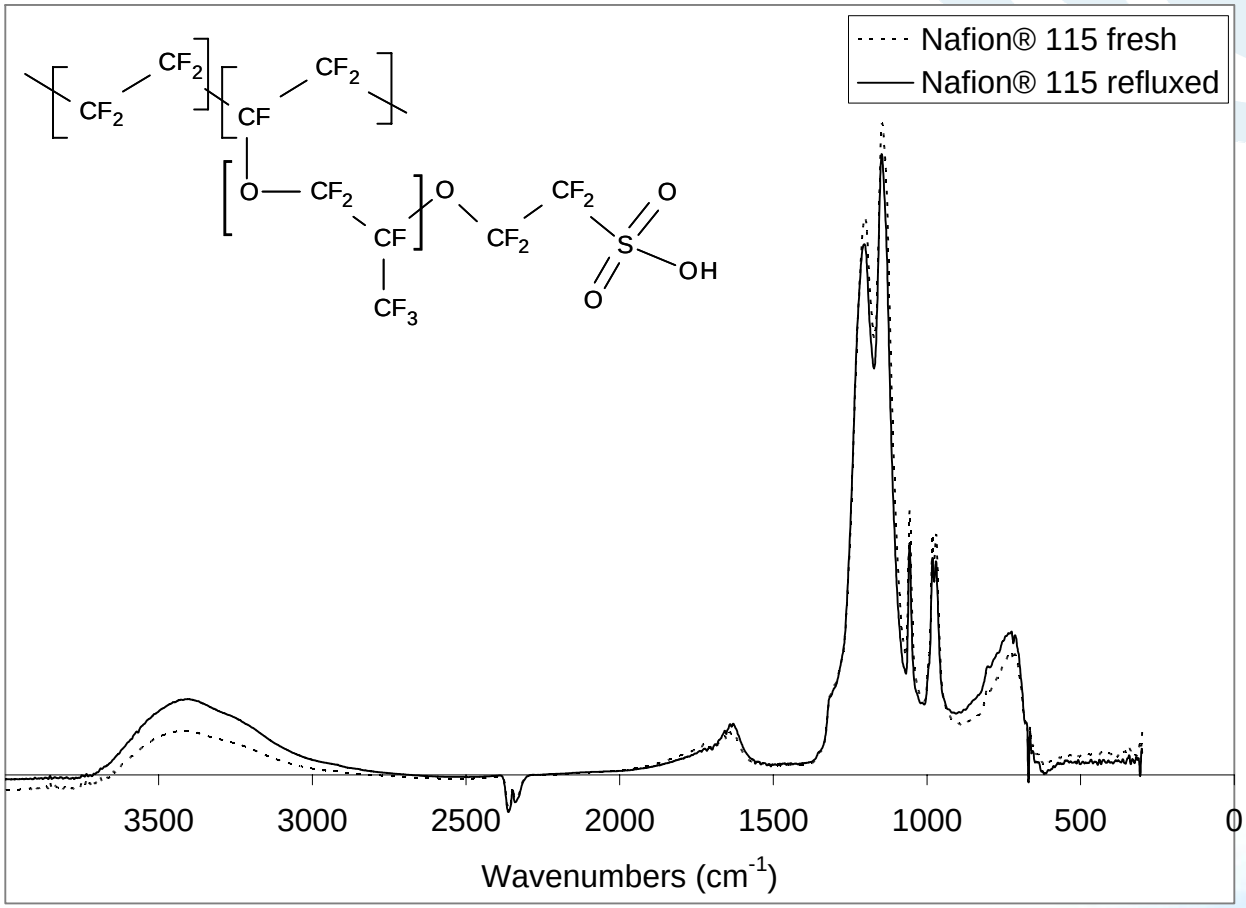
Membrane Durability Studies

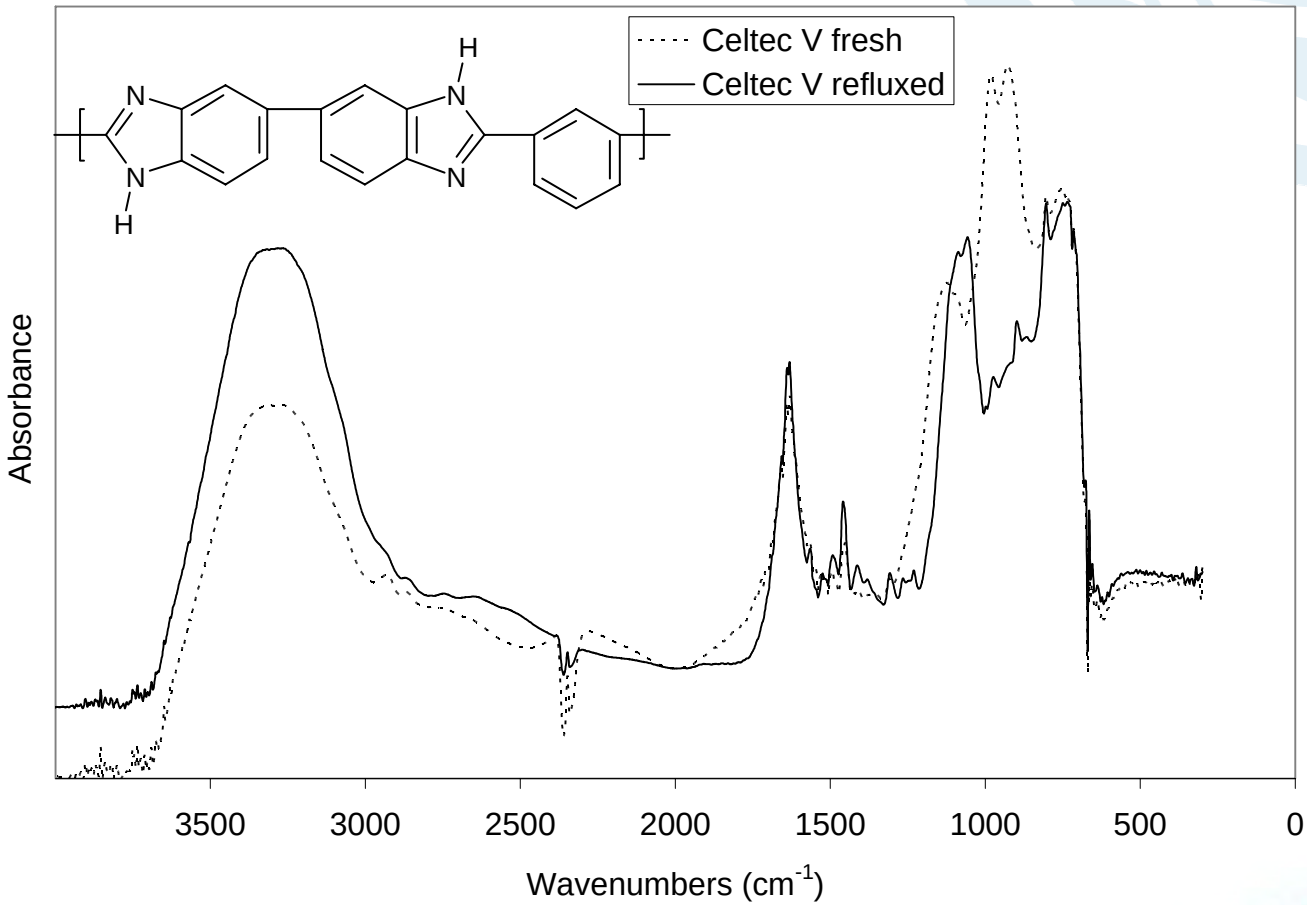
- Expose Membrane samples to 60 wt% H_2SO_4 at 80 °C for 24 hours
- Record FTIR spectra before and after acid exposure using an ATR cell
- Inspect FTIR spectra for evidence of degradation

Ir Spectra for Nafion® 115 (Dupont)

No evidence of membrane degradation



Ir Spectra for PBI Membrane (BASF)



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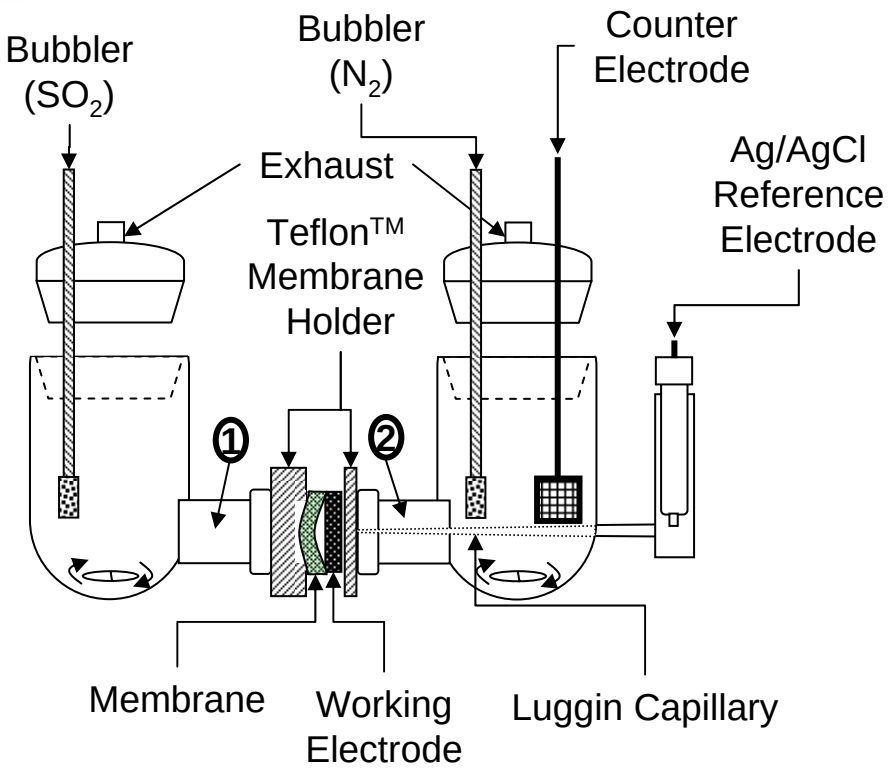
Membrane Durability Study Summary

- PFSA, SDAPP, BPVE and BPVE-6F membranes showed little or no degradation
- PBI membrane showed no degradation of the polymer backbone, however loss of H_3PO_4 was observed with simultaneous uptake of H_2SO_4

SO_2 Transport characterization Cell

Original SO_2 transport characterization cell



Original Cell Design Limitations

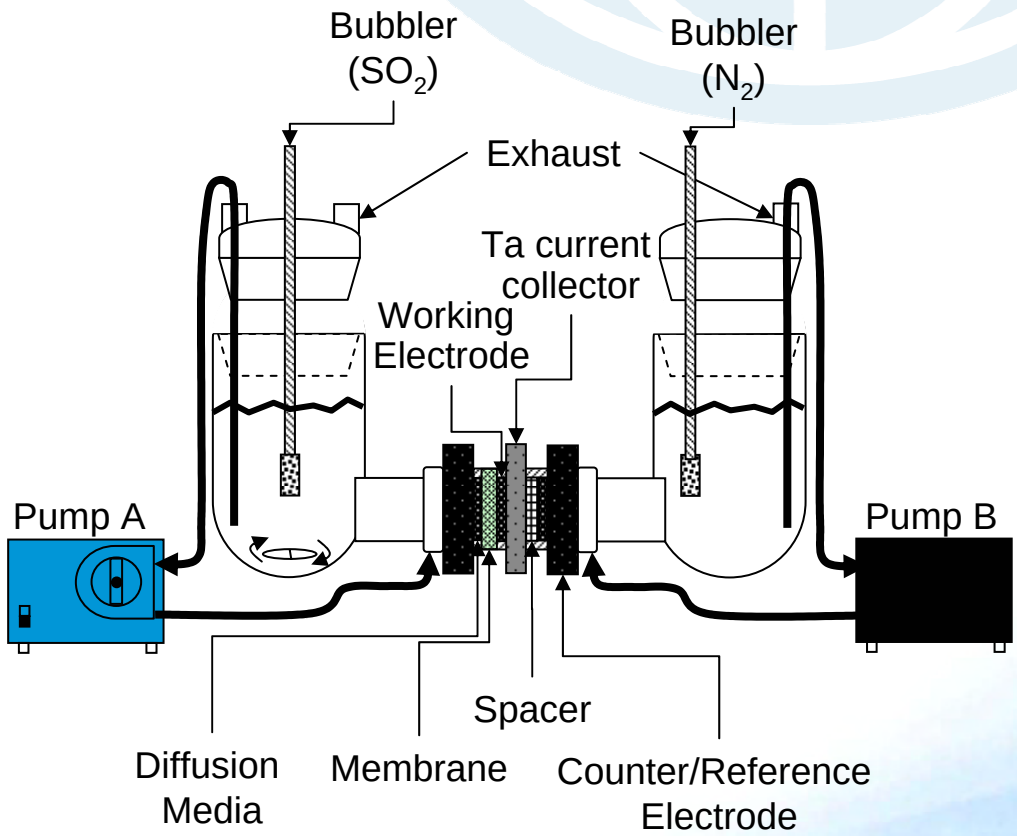
- SO_2 concentration gradient is formed in region 1
- Hygroscopic membranes can wrinkle and/or not lay flat
- H_2SO_4 generation at working electrode results in a H_2O concentration gradient in region 2

SO_2 Transport characterization Cell

Modified SO_2 transport characterization cell

Modified Cell Design Features

- H_2SO_4 saturated with SO_2 is pumped by pump A to the membrane interface
- Graphite blocks secure and press the membrane flat
- H_2SO_4 with desired concentration is pumped by pump B into the working electrode region



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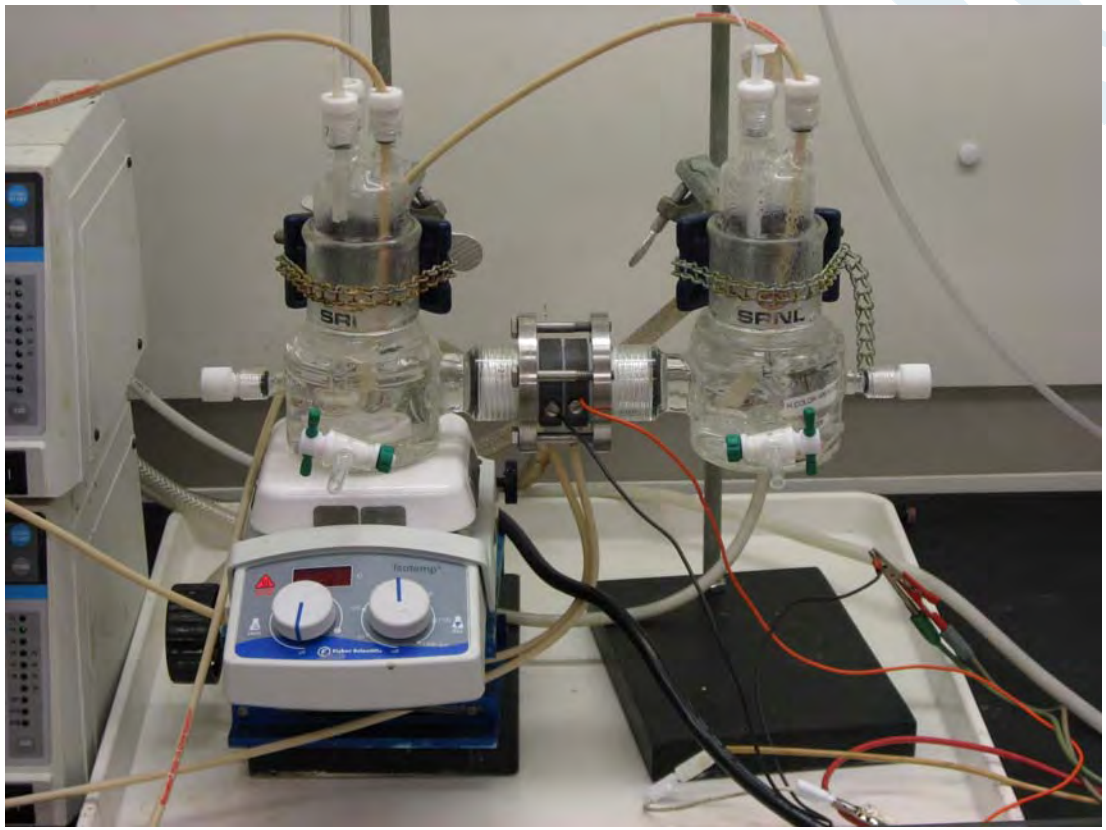
SO_2 Transport characterization Cell

Modified SO_2 transport characterization cell



SO_2 Transport

SO_2 flux/transport experimental design

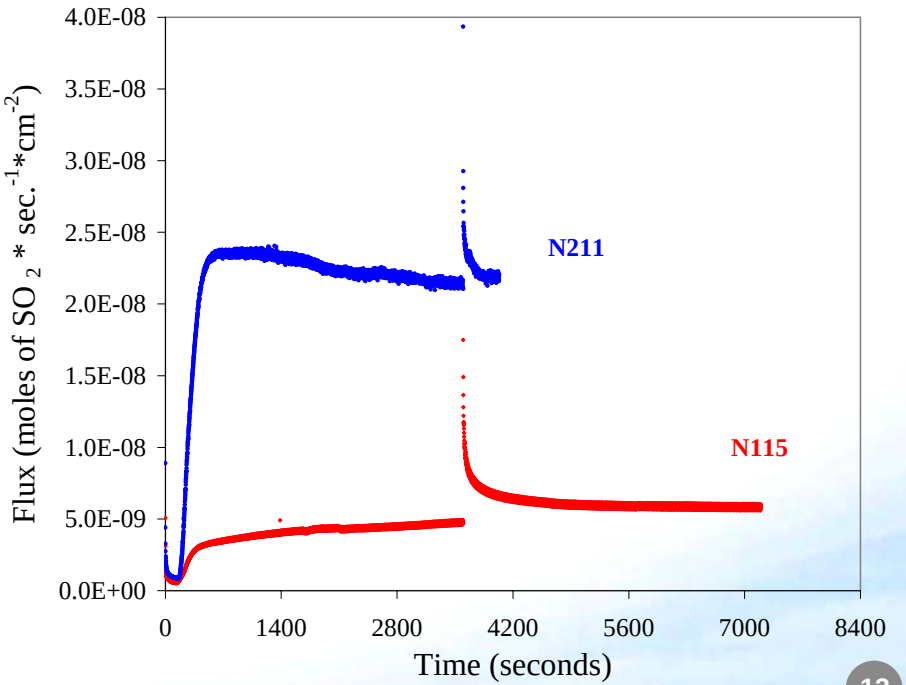
- Constant potential experiment (1 V)
- Current monitored over time in 1 hour segments
- SO_2 flux determined using Faraday's Law

$$J_{SO_2} = \frac{i}{nF}$$

- SO_2 transport can be <u>estimated</u> by Fick's first law of diffusion

$$SO_2 \text{ transport} = \frac{J_{SO_2} L}{C_0}$$

- Nafion® 115 and Nafion® 211 serve as baselines



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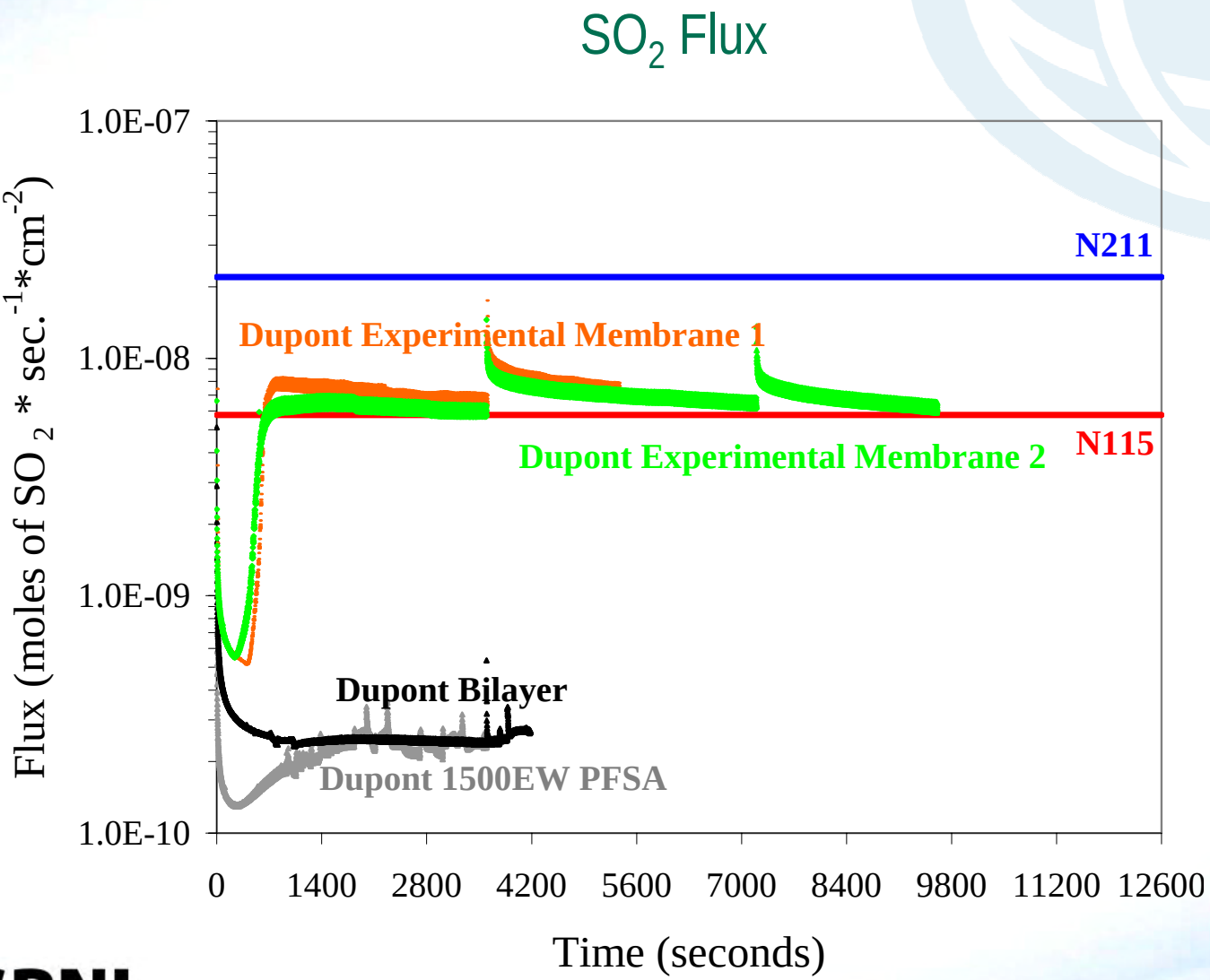
SO_2 Transport: Experimental Membranes (Dupont)



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SO_2 Transport: Experimental Membranes (Dupont)

Membrane ID	Membrane Type	Thickness	i_{ave} (mA)	SO_2 flux (mol s^{-1} cm^{-2})	SO_2 transport (cm^2 s^{-1}) x 10^{-8}
Dupont Nafion® 115	PFSA	5.0	2.02	5.23×10^{-9}	6.10
Dupont Nafion® 112	PFSA	2.0	5.25	1.36×10^{-8}	6.34
Dupont Nafion® 211	PFSA	1.0	8.43	2.18×10^{-8}	5.09
Dupont 1500 EW PFSA	1500 EW PFSA	4.0	0.055	1.43×10^{-10}	0.13
Dupont bilayer	fluorinated sulfonic/carboxylic acid	5.5	0.042	1.09×10^{-10}	0.14
Dupont experimental membrane 1	treated PFSA	2.0	2.55	6.61×10^{-9}	3.08
Dupont experimental membrane 2	treated PFSA	3.5	2.32	6.01×10^{-9}	4.90

SO_2 Transport: Stretched PFSA, PFSA/FEP blend (Case)

Membrane ID	Membrane Type	Thickness	i_{ave} (mA)	SO_2 flux (mol s^{-1} cm^{-2})	SO_2 transport (cm^2 s^{-1}) x 10^{-8}
Dupont Nafion® 115	PFSA	5.0	2.02	5.23×10^{-9}	6.10
Dupont Nafion® 211	PFSA	1.0	8.43	2.18×10^{-8}	5.09
Case sample 1	streched PFSA	2.2	4.04	1.05×10^{-8}	5.28
Case sample 4	streched PFSA	2.5	7.66	1.98×10^{-8}	11.47
Case sample 60-40-2	PFSA/FEP blend	2.4	2.27	5.88×10^{-9}	3.35
Case sample 50-50-2	PFSA/FEP blend	2.2	2.30	5.96×10^{-9}	3.01
Case sample 45-55-2	PFSA/FEP blend	2.1	1.58	4.09×10^{-9}	1.99

SO_2 Transport: Treated PFSA Membrane (GES)

Membrane ID	Membrane Type	Thickness	i_{ave} (mA)	SO_2 flux (mol s^{-1} cm^{-2})	SO_2 transport (cm^2 s^{-1}) x 10^{-8}
Dupont Nafion® 115	PFSA	5.0	2.02	5.23 x 10^{-9}	6.10
Dupont Nafion® 211	PFSA	1.0	8.43	2.18 x 10^{-8}	5.09
Giner sample 1	treated PFSA	5.0	4.87	1.26 x 10^{-8}	14.70
Giner sample 2	treated PFSA	5.0	3.95	1.02 x 10^{-8}	11.92

SO_2 Transport: SDAPP Membrane (Sandia National Lab)

Membrane ID	Membrane Type	Thickness	i_{ave} (mA)	SO_2 flux (mol s^{-1} cm^{-2})	SO_2 transport (cm^2 s^{-1}) x 10^{-8}
Dupont Nafion® 115	PFSA	5.0	2.02	5.23 x 10^{-9}	6.10
Dupont Nafion® 211	PFSA	1.0	8.43	2.18 x 10^{-8}	5.09
Sandia 519C	SDAPP	3.0	4.30	1.11 x 10^{-8}	7.79

SO_2 Transport: BPVE, BPVE-6F Membranes (Clemson)

Membrane ID	Membrane Type	Thickness	i_{ave} (mA)	SO_2 flux (mol s^{-1} cm^{-2})	SO_2 transport (cm^2 s^{-1}) x 10^{-8}
Dupont Nafion® 115	PFSA	5.0	2.02	5.23 x 10^{-9}	6.10
Dupont Nafion® 211	PFSA	1.0	8.43	2.18 x 10^{-8}	5.09
Clemson B(2)	BPVE	0.71	8.17	2.12 x 10^{-8}	3.50
Clemson B1F1(1)	BPVE-6F (1:1)	0.63	6.24	1.62 x 10^{-8}	2.37
Clemson B2F1(3)	BPVE-6F (2:1)	0.75	6.80	1.76 x 10^{-8}	3.07

SO_2 Transport: PBI membrane, Celtec V® (BASF)

Membrane ID	Membrane Type	Thickness	i_{ave} (mA)	SO_2 flux (mol s^{-1} cm^{-2})	SO_2 transport (cm^2 s^{-1}) x 10^{-8}
Dupont Nafion® 115	PFSA	5.0	2.02	5.23 x 10^{-9}	6.10
Dupont Nafion® 211	PFSA	1.0	8.43	2.18 x 10^{-8}	5.09
BASF Celtec-V	PBI	4.0	0.82	2.14 x 10^{-9}	1.99

SO_2 Transport: Summary

Membrane ID	Membrane Type	Thickness	i_{ave} (mA)	SO_2 flux (mol s^{-1} cm^{-2})	SO_2 transport (cm^2 s^{-1}) x 10^{-8}
Dupont Nafion® 115	PFSA	5.0	2.02	5.23×10^{-9}	6.10
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Dupont bilayer	fluorinated sulfonic/ carboxylic acid	5.5	0.042	1.09×10^{-10}	0.14
Dupont exp. membrane 1	treated PFSA	2.0	2.55	6.61×10^{-9}	3.08
Dupont exp. membrane 2	treated PFSA	3.5	2.32	6.01×10^{-9}	4.90
Case sample 1	streched PFSA	2.2	4.04	1.05×10^{-8}	5.28
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Case sample 50-50-2	PFSA/FEP blend	2.2	2.30	5.96×10^{-9}	3.01
Case sample 45-55-2	PFSA/FEP blend	2.1	1.58	4.09×10^{-9}	1.99
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Clemson B2F1(3)	BPVE-6F (2:1)	0.75	6.80	1.76×10^{-8}	3.07
BASF Celtec-V	PBI	4.0	0.82	2.14×10^{-9}	1.99

Conductivity and SDE Performance

Membrane electrode assembly (MEA) preparation

- Spray deposition method
- Ink: 75 wt% platinized carbon, 25% PFSA
- Anode loading target: 1.8 mg Pt cm^{-2}
- Cathode loading target: 0.8 – 0.9 mg Pt cm^{-2}

Conductivity

- Through-plane conductivity determined for MEAs
- Electrochemical impedance spectroscopy (EIS)

SDE performance experimental design

- Constant potential experiment (1 V)
- Current monitored over time in 1 hour segments

Conductivity and SDE Performance

Membrane ID	Membrane Type	Thickness	Conductivity (S cm^{-1})	Current Density (mA cm^{-2})
Dupont Nafion® 115	PFSA	5.0	0.0241	270
Dupont Nafion® 211	PFSA	1.0	0.0159	393
Dupont 1500 EW PFSA	1500 EW PFSA	4.0	-	0.005
Dupont bilayer	fluorinated sulfonic/carboxylic acid	5.5	-	0.010
Dupont experimental membrane 1	treated PFSA	2.0	0.0036	127
Dupont experimental membrane 2	treated PFSA	3.5	0.0064	123
Case sample 50-50-2	PFSA/FEP blend	2.2	0.0034	155
Case sample 45-55-2	PFSA/FEP blend	2.1	0.0096	228
Sandia 519C	SDAPP	3.0	0.0328	286
Clemson B(2)	BPVE	0.71	0.0048	320
Clemson B1F1(1)	BPVE-6F (1:1)	0.63	0.0063	337
Clemson B2F1(3)	BPVE-6F (2:1)	0.75	0.0109	335
BASF Celtec-V	PBI	4.0	-	344

SO_2 Transport, Conductivity, and SDE Performance

Membrane ID	Membrane Type	Thickness	SO_2 flux (mol s^{-1} cm^{-2})	SO_2 transport (cm^2 s^{-1}) x 10^{-8}	Conductivity (S cm^{-1})	Current Density (mA cm^{-2})
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Dupont 1500 EW PFSA	1500 EW PFSA	4.0	1.43×10^{-10}	0.13	-	0.005
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Case sample 4	streched PFSA	2.5	1.98×10^{-8}	11.47	-	-
Case sample 60-40-2	PFSA/FEP blend	2.4	5.88×10^{-9}	3.35	-	-
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Clemson B2F1(3)	BPVE-6F (2:1)	0.75	1.76×10^{-8}	3.07	0.0109	335
BASF Celtec-V	PBI	4.0	2.14×10^{-9}	1.99	-	344

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  Hector Colon-Mercado, Mark Elvington, David Hobbs, William Summers, John Steimke, Timothy Steeper, David Herman, Maximilian Gorensek, Edward Danko, Martin Scott
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- BASF
- Giner Electrochemical Systems
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- Sandia National Laboratory
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- Clemson University
  Dennis Smith, Jiyoung Park
- University of South Carolina
  John Staser, John Weidner, Brian Benicewicz
- Case Western Reserve University
  Peter Pintauro

SO_2 Transport: Stretched PFSA, PFSA/FEP blend (Case)

Manufacturer and ID	Membrane type	Thickness (mil)	I_{ave} (mA)	SO_2 flux (mol SO_2 s^{-1} cm^{-2})	**SO_2 transport(cm^2 s^{-1}) x10^{-8}**
Dupont Nafion® 115	PFSA	5.0	2.02	5.23E-09	**6.10**
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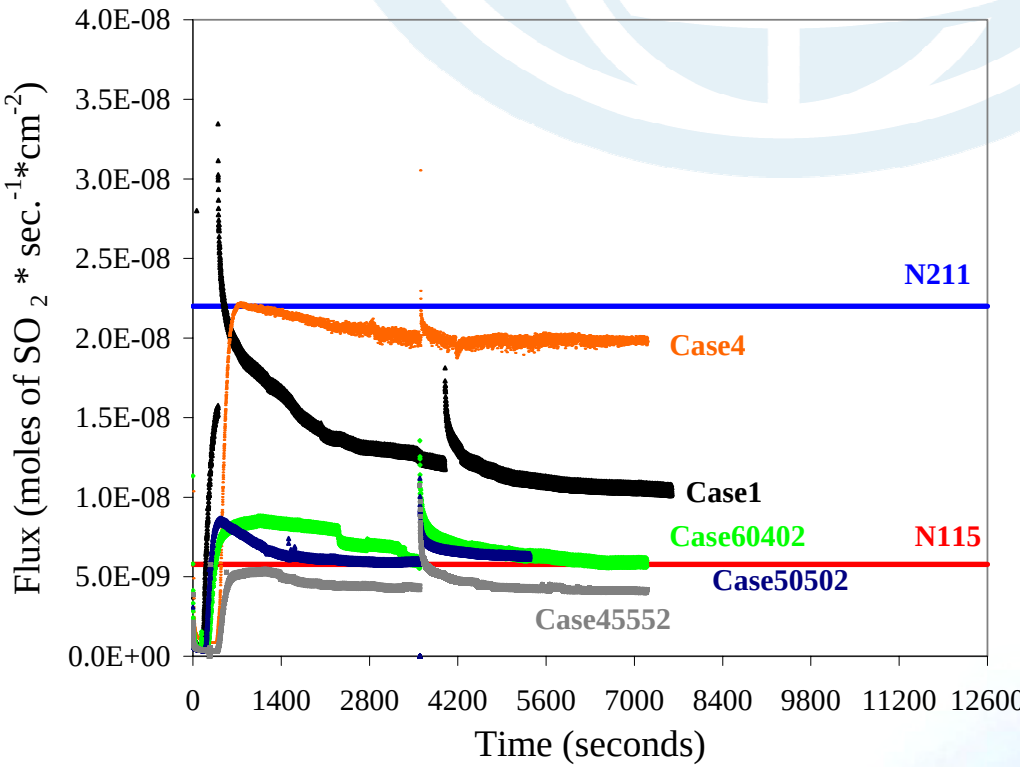
SO_2 Flux



SO_2 Transport: Treated PFSA Membrane (GES)

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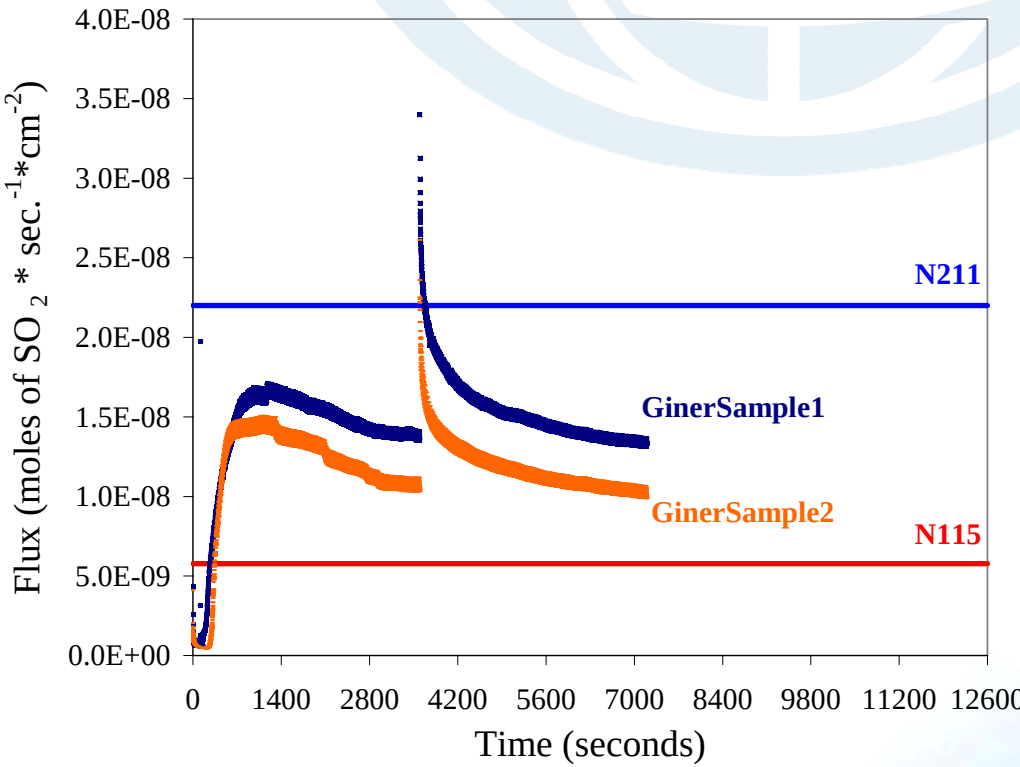
SO_2 Flux



SO_2 Transport: SDAPP Membrane (Sandia National Lab)

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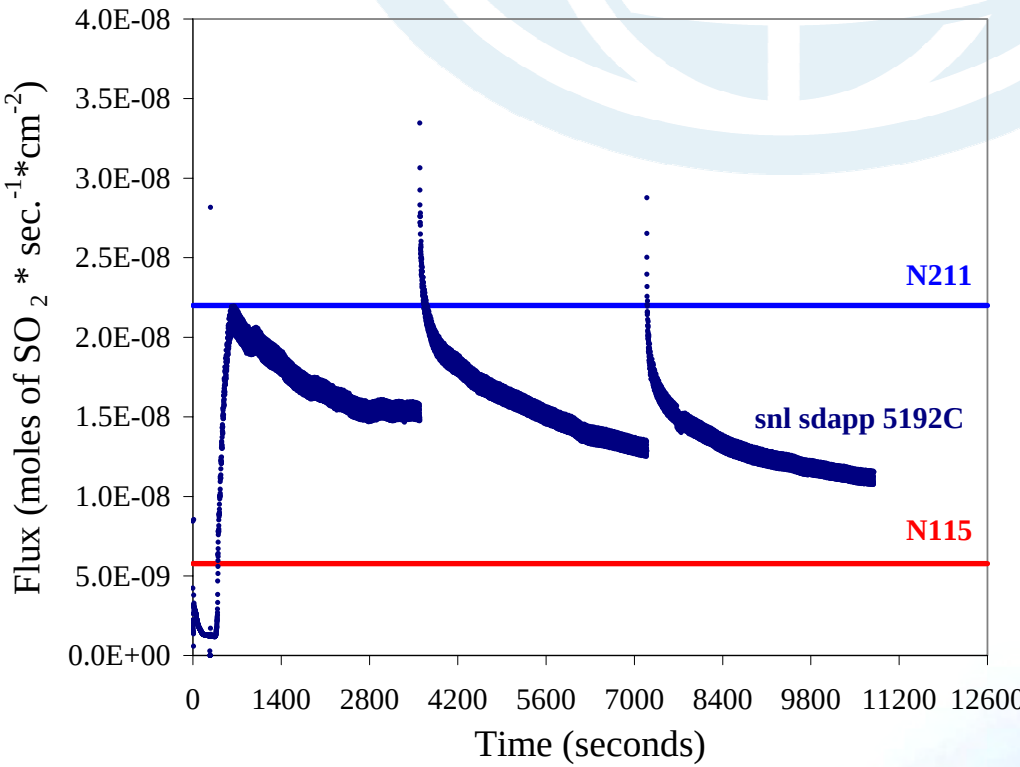
SO_2 Flux



SO_2 Transport: BPVE, BPVE-6F Membranes (Clemson)

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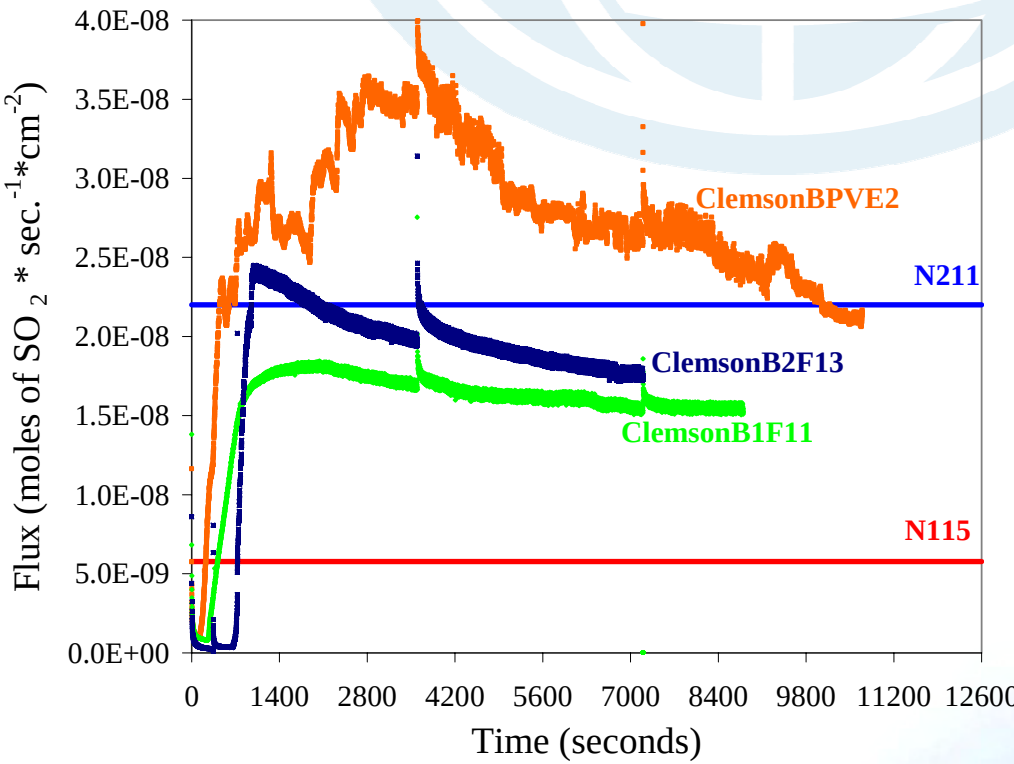
SO_2 Flux



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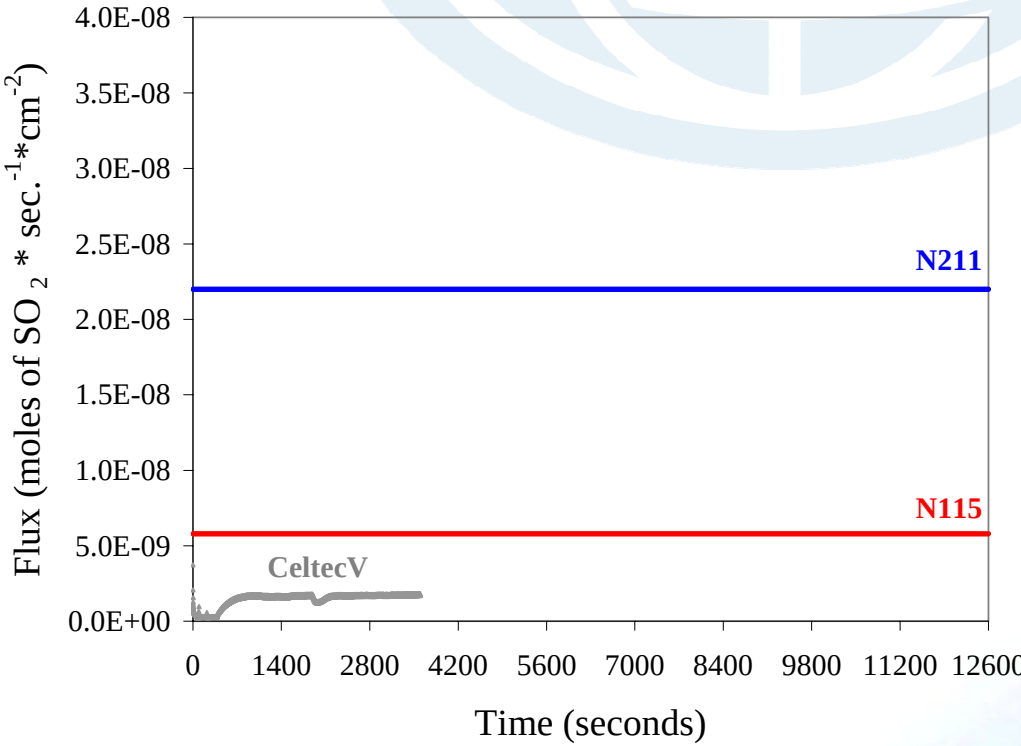
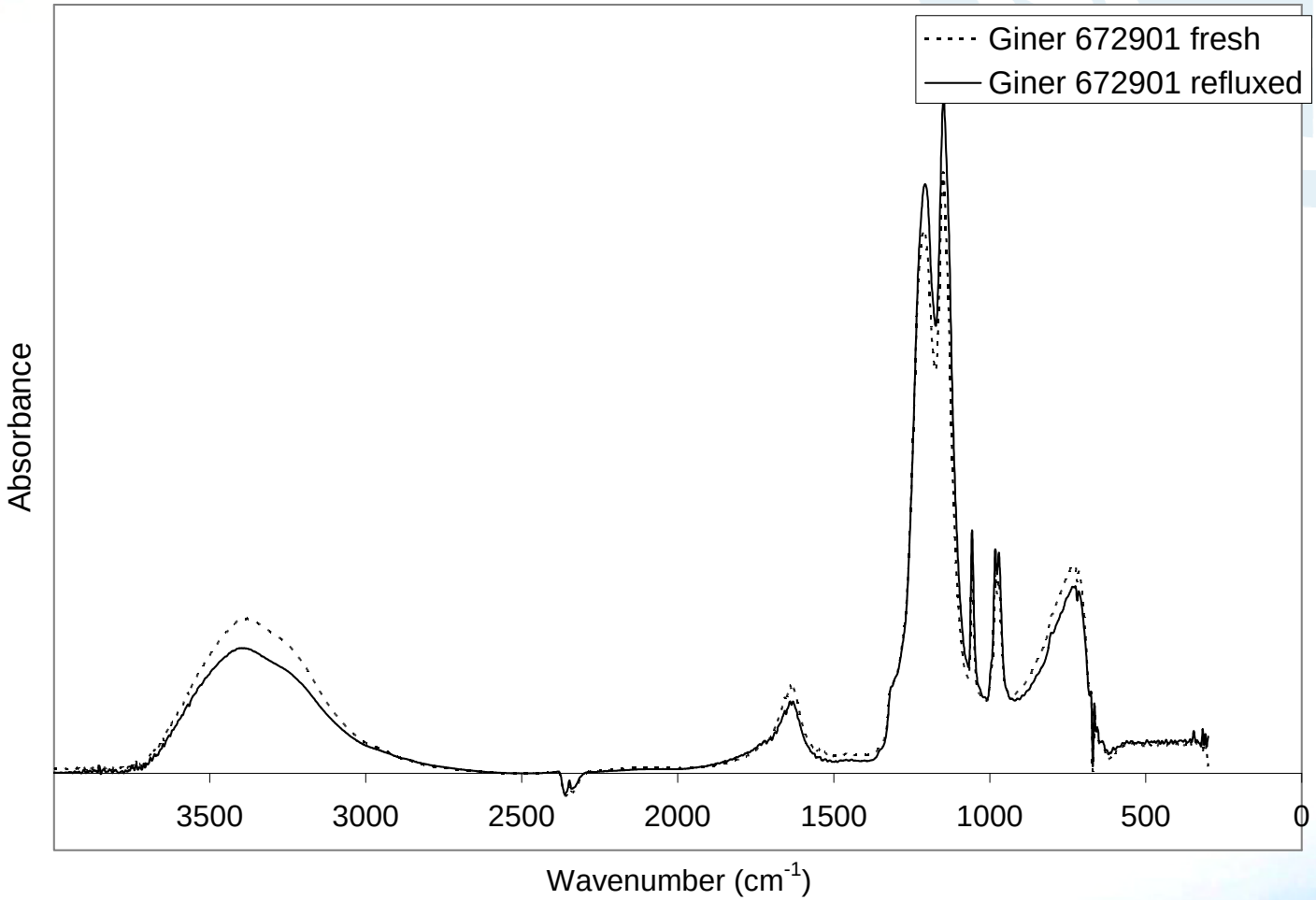
SO_2 Transport: PBI membrane, Celtec V® (BASF)

Manufacturer and ID	Membrane type	Thickness (mil)	I_{ave} (mA)	SO_2 flux (mol SO_2 s^{-1} cm^{-2})	**SO_2 transport(cm^2 s^{-1}) x10^{-8}**
Dupont Nafion® 115	PFSA	5.0	2.02	5.23E-09	**6.10**
Dupont Nafion® 211	PFSA	1.0	8.43	2.18E-08	**5.09**
BASF Celtec-V	PBI	4	0.824	2.14E-09	**1.99**

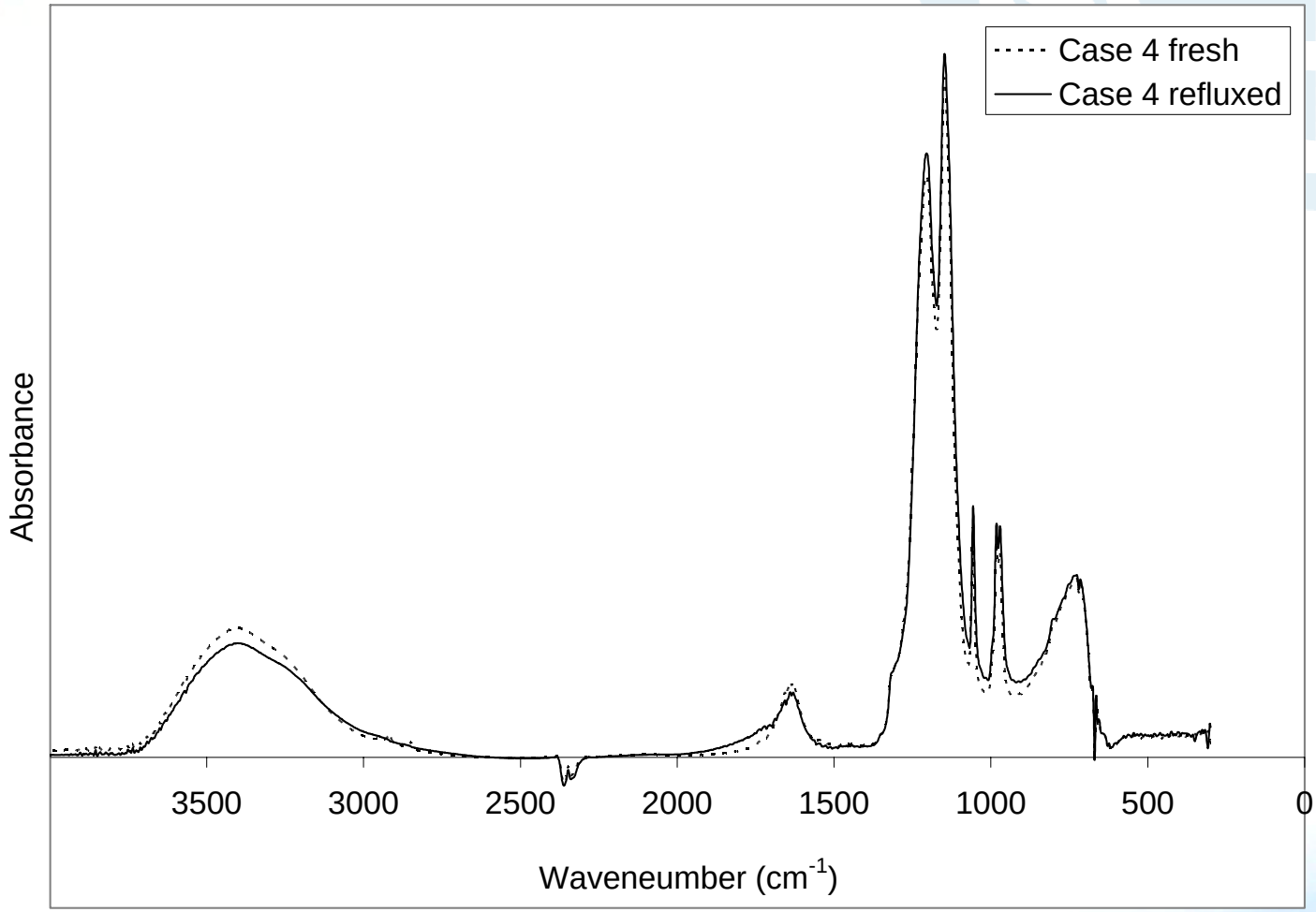
SO_2 Flux



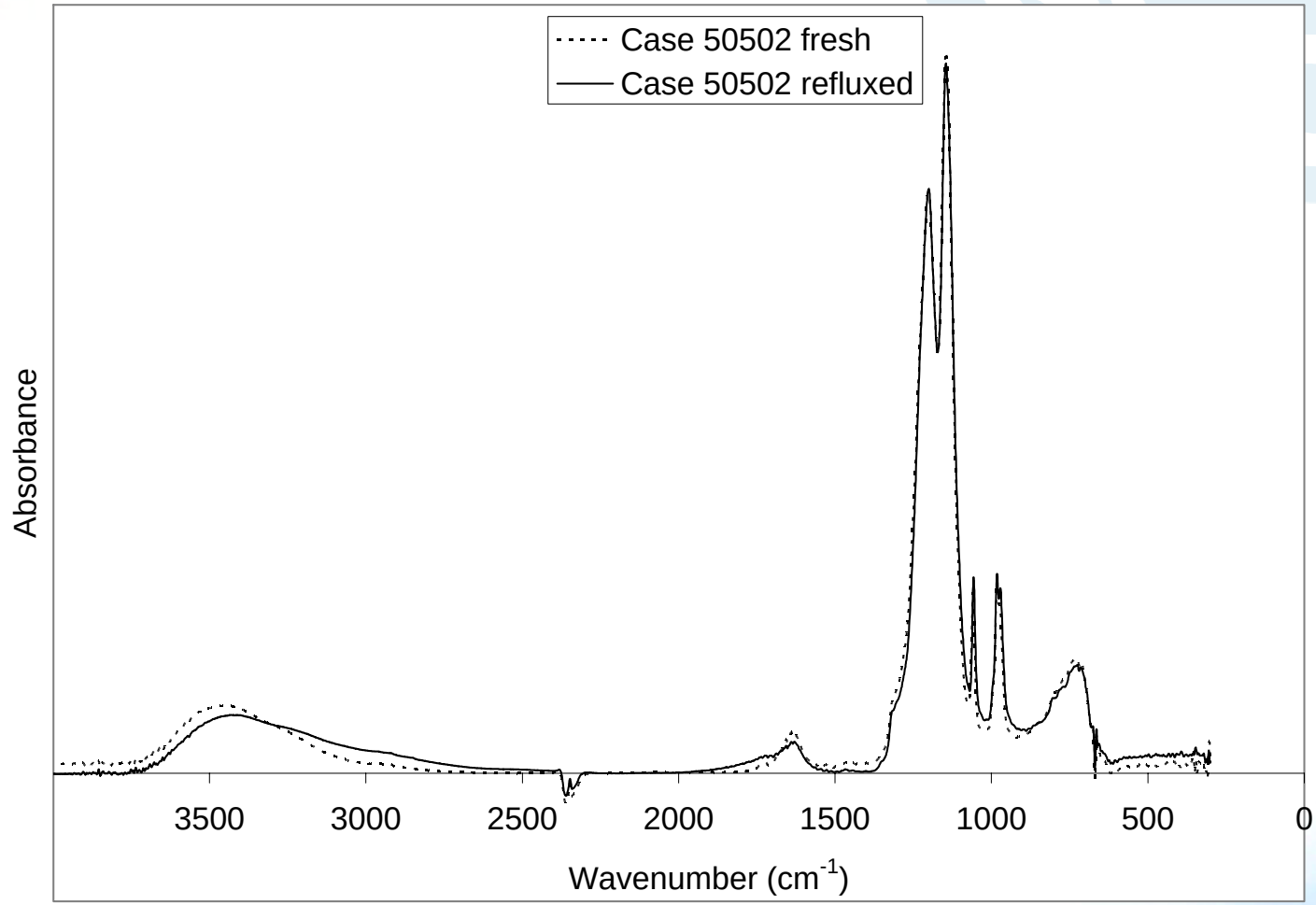
Ir Spectra for Treated PFSA Membrane (Giner)



Ir Spectra for Stretched/Recast PFSA Membrane (Case)



Ir Spectra for PFSA/FEP (1:1) Blend (Case)



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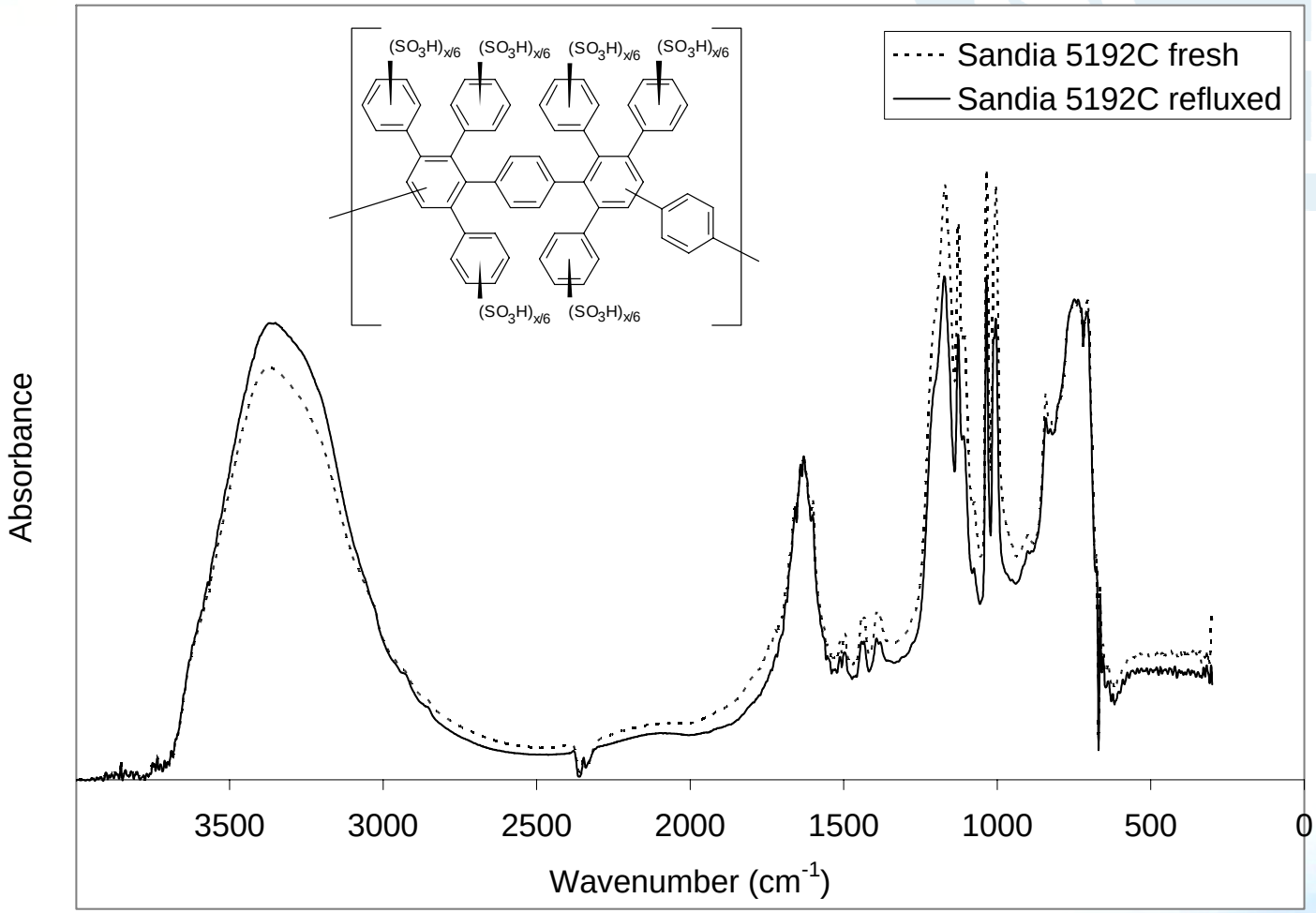
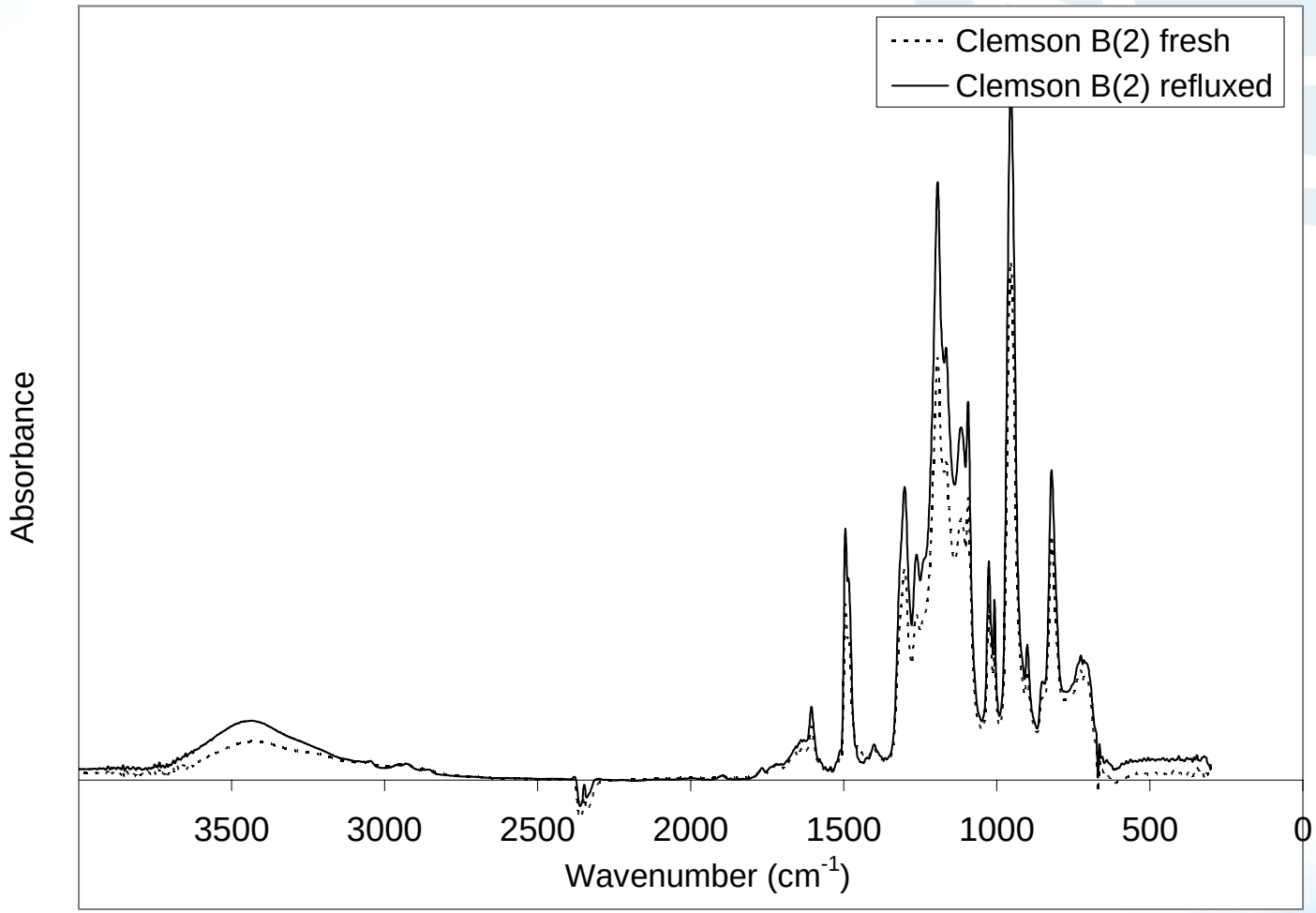
Ir Spectra for SDAPP Membrane (SNL)



Ir Spectra for BPVE Membrane (Clemson)



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Ir Spectra for BPVE-6F Membrane (Clemson)