Reactive Separation of H_2S from Fuel Process Streams Using Ionic Liquids

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Problem Background

- Renewable energy deriving from biomass sources has great potential for growth to meet our future energy demands.

- Biogas is produced in many different environments, including landfills, sewage sludge, and during anaerobic degradation of organic material.

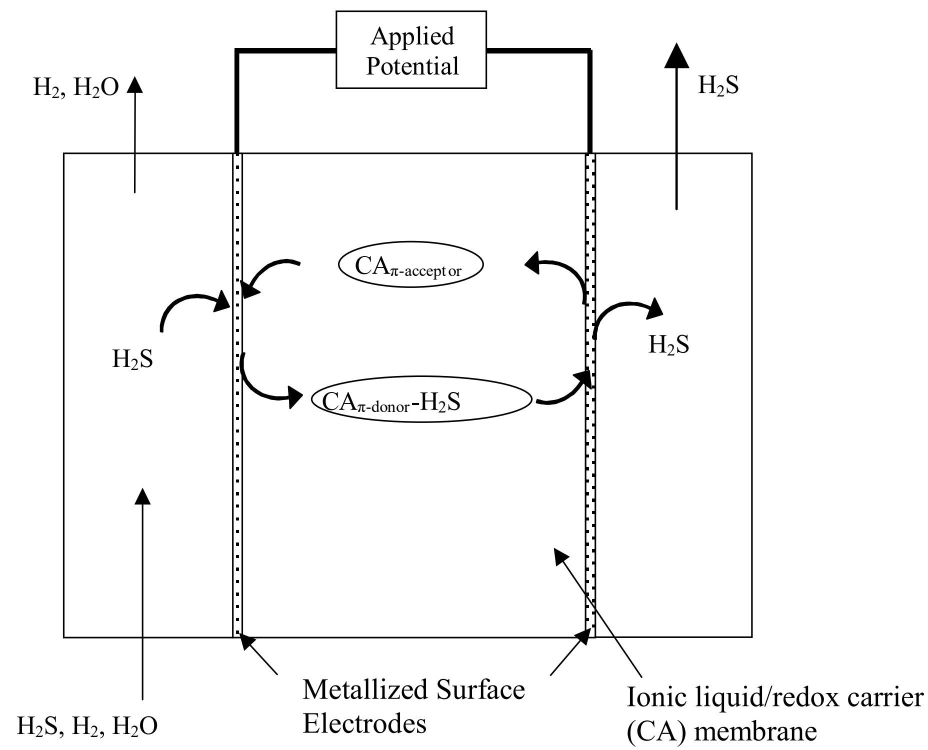
- Biogas is comprised of methane (45-75% by volume), carbon dioxide (25-55%) and other compounds including hydrogen sulfide (100-10000 ppm) and *volatile methylsiloxanes (50 ppm and less)*

- Biogas can be converted to electricity through combustion processes or fuel cells, but must be purified:
  - CO_2 acts as a diluant, reducing energy content
  - H_2S is corrosive

- Separation processes are required to remove H_2S, CO_2 and siloxanes from Biogas to enable more widespread use of this alternative fuel.

Electrochemically Facilitated Transport Separation Approach

- In this approach, a sulfur compound such as H_2S or SO_2 forms a charge-transfer complex with a redox molecule (such as 4,5-dicyano-2,7-dinitrofluorenone) that is immobilized within an ionic liquid imbibed membrane
- A small potential is applied across the electrochemical cell which facilitates binding sulfur on one side of the cell and releasing it on the other side
- This process lends itself to an effective method for removing sulfur from process streams forming separated streams of H_2S or SO_2
- Process continuously regenerates the redox carrier

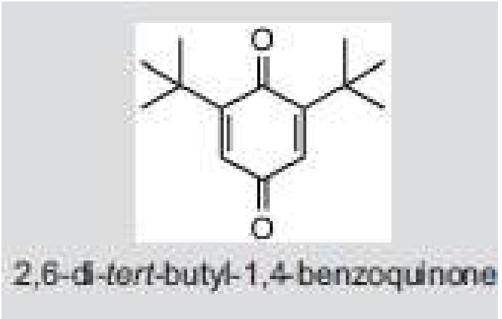


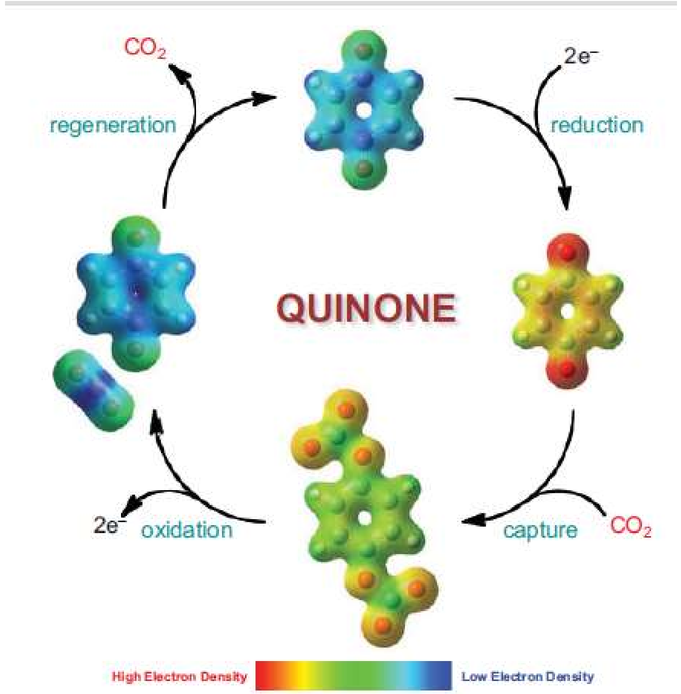
Technical Approach

- The immobilized ionic liquid membrane will embody metallic electrodes deposited on both sides to form a membrane and electrode assembly (MEA)
- These electrodes might function catalytically, but mainly serve as electron donor and acceptor current collectors
- Thus, we can select metals that have known corrosion resistance to hydrogen sulfide that include
  - tantalum, molybdenum, tungsten, aluminum, and magnesium
- Prior precedence for extractive desulfurization in fuels using ionic liquids based on
  - 1-alkyl-3-methylimidazolium [Amim] and either tetrafluoroborate [BF_4] or hexafluorophosphate [PF_6]
  - Trimethylamine hydrochloride ($AlCl_3$-TMAC), ethyl-[$MIMBF_4$], butyl-[$MIMPF_6$], and butyl-[$MIMBF_4$] also have shown sulfur selectivity
  - Regeneration steps had to be used with these ionic liquids making their use limited in a continuous manner unless multiple beds are used
- Proposed facilitated transport process aims to overcome the regeneration difficulties culminating in a continuous process

Facilitated Transport Chemistry

- Primary transport is through redox carrier that can reversibly bind to CO_2/H_2S
- For example: acid/base reaction of dianionic quinones with CO_2
  - electron rich oxygens donate and share electron pairs with electrophilic carbon of CO_2
  - Forms stable carbonates
  - dtBBQ studied extensively*





*Paul Scovazzo, Univ. of Miss.
Carl Koval, Richard Noble, Univ. of Colorado
Daniel Dubois, PNL
Alan Hatton, MIT
Karen Jayne, Reactive Innovations

Electrolyte Development

- Considered ionic liquids that included
  - 1-ethyl,3-methylimidazolium bis-trifluoromethylsulfonylimide [emim-bis(tFSI)]
  - butylmethylpyrrolidinium bis(trifluoromethylsulfonyl)imide [bmpdim-bis(tFSI)]
  - 1-ethyl-3-methyl imidazolium trifluoromethanesulfonate [emim-tFMS]
  - 1-butyl-3-methylimidazolium octylsulfate [Bmim-$OcSO_4$]
  - 1-ethyl-3-methyl-imidazolium ethylsulfate [Emim-$EtSO_4$]
- Considered redox carriers that included
  - di-tertiary butyl benzoquinone [dtBBQ]
  - 2-t-butylanthraquinone (TBAQ)
  - Ethanolamine
  - Ethylenediamine
  - Aminobutyric acid salt/poly(allylamine)
  - Fe-CDTA
  - Coenzyme-Q-10

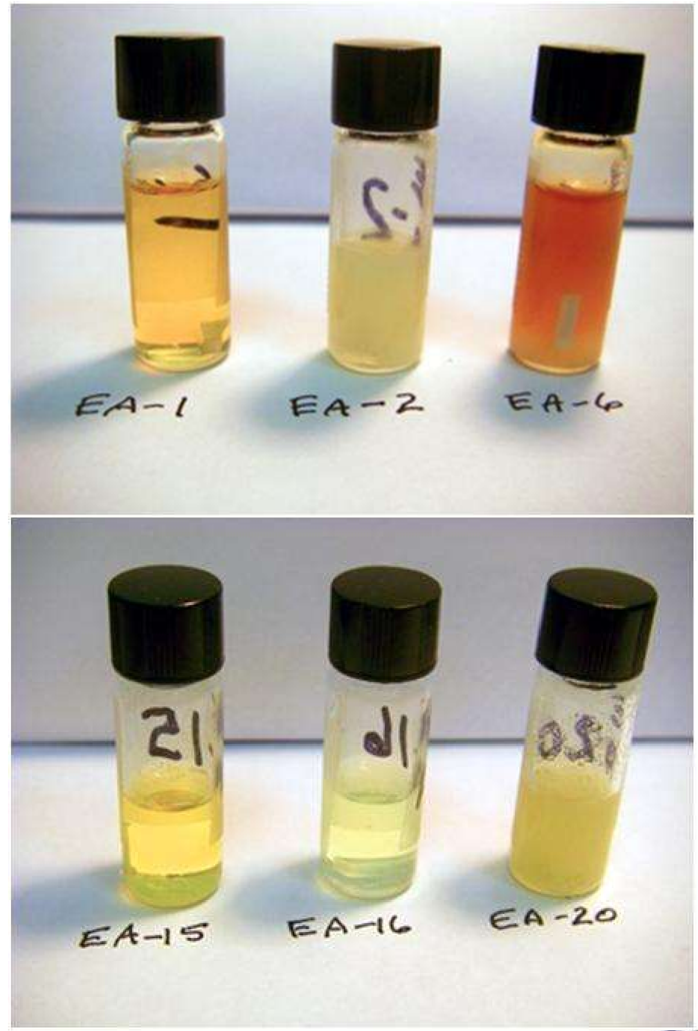
Electrolyte Evaluation

- Used three-step evaluation process
  1) determine if the redox carrier is soluble in the ionic liquid, then
  2) use cyclic voltammetry to show the redox carrier has reversible behavior, then
  3) evaluate the ionic liquid/redox carrier with and without H_2S being present to show which ones bind and release sulfur

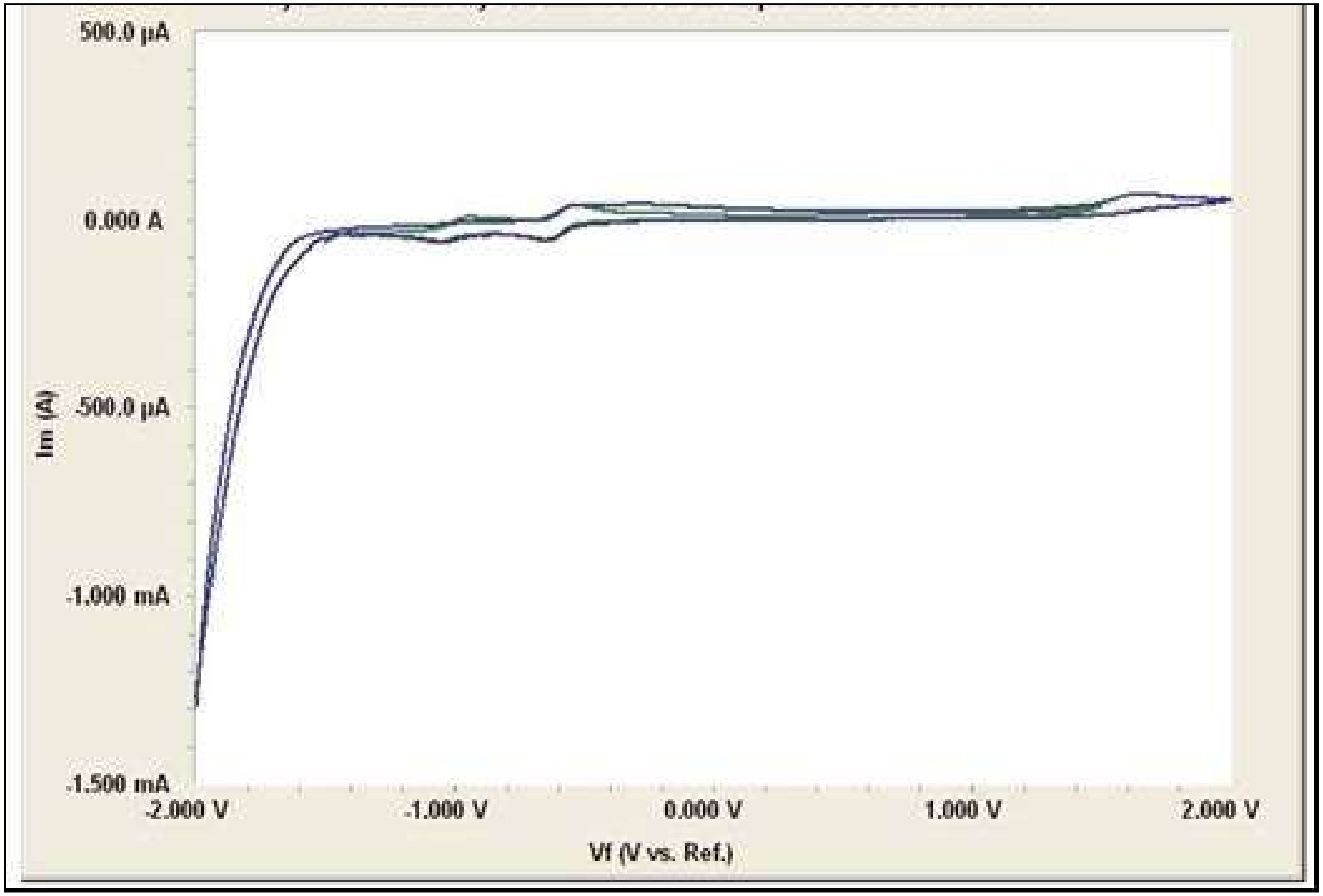
Experiment number	Ionic liquid	Redox carrier	Soluble at 0.05M Or Misc/non-Misc	Redox activity via Cyclic voltammetry
1	[emim(tFMS)]	DtBBQ Ditertiary butyl Benzoquinone	Yes	Yes
6	[emim(tFMS)]	Fe-CDTA	Yes	Yes
16	[emim-bis(tFSI)]	TBAQ 2-t-butyl anthroquinone	Yes	Yes
22	BMIM OcSO4	DtBBQ	Yes	Yes
23	BMIM OcSO4	TBAQ	Yes	Yes
26	BMIM OcSO4	Aminobutyric acid salt/polyallylamine	Misc	No
27	BMIM OcSO4	Fe CDTA	Yes	No
31	EMIM EtSO4	Ethanoloamine	Misc	Yes
32	EMIM EtSO4	Ethylenediamine	Misc	No

Redox Carrier Solubility Assessment

- Solubility of the redox carriers in the ionic liquids qualitatively assessed
- Targeted concentration of 0.05M
- Small samples (1-2 ml) of the redox/ ionic liquid formulations prepared and left stirring for at least 48 hours
- Moderate heating (~50 C) was used in some cases to effect dissolution
- Qualitative Yes/No/Partial solubility metric used for the redox carrier
- For cases where the redox carrier is a liquid, we use a “miscible/ immiscible” characterization

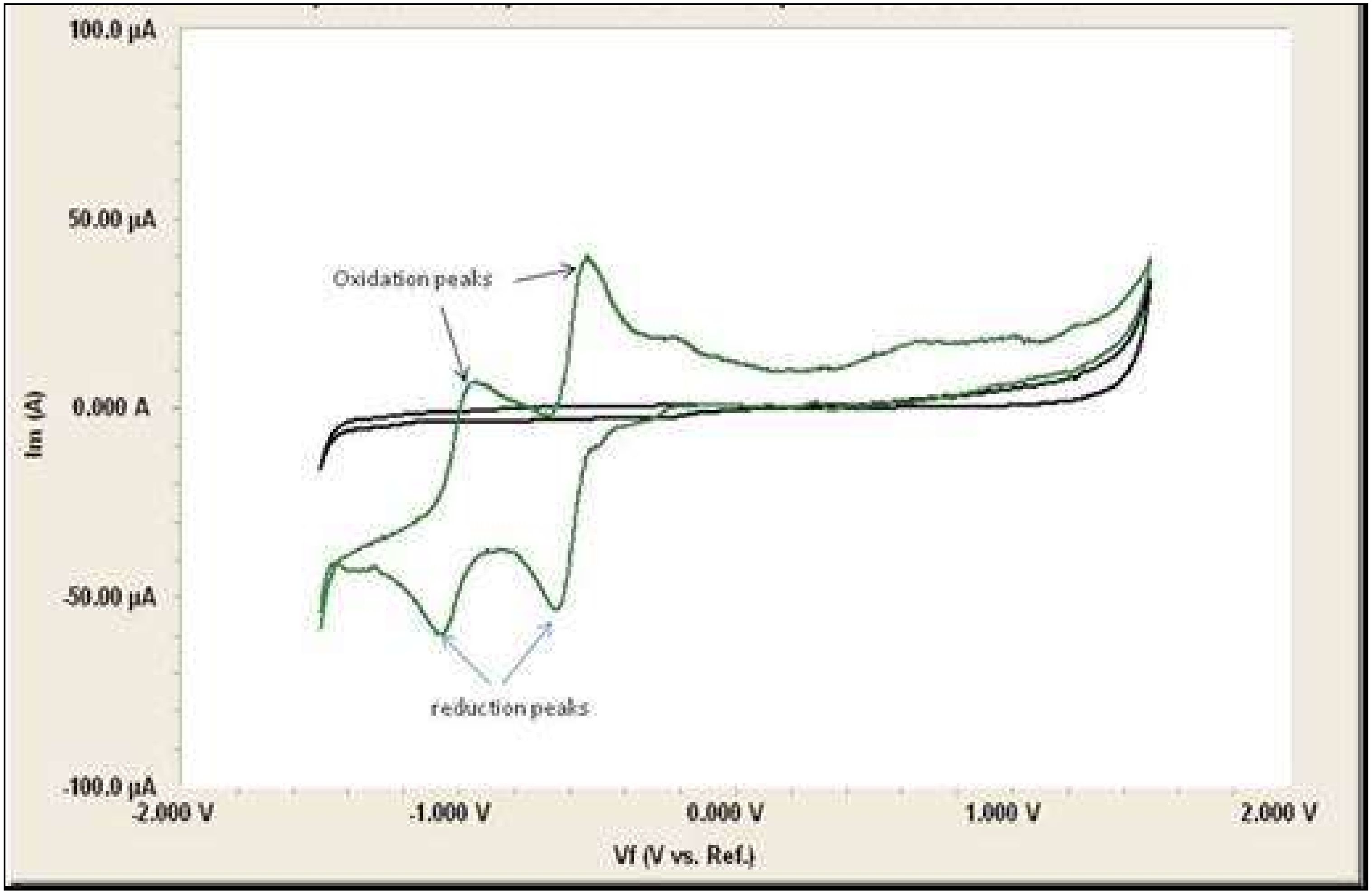


Cyclic Voltammogram of Ionic Liquid Emim-tFMS Showing Featureless Behavior



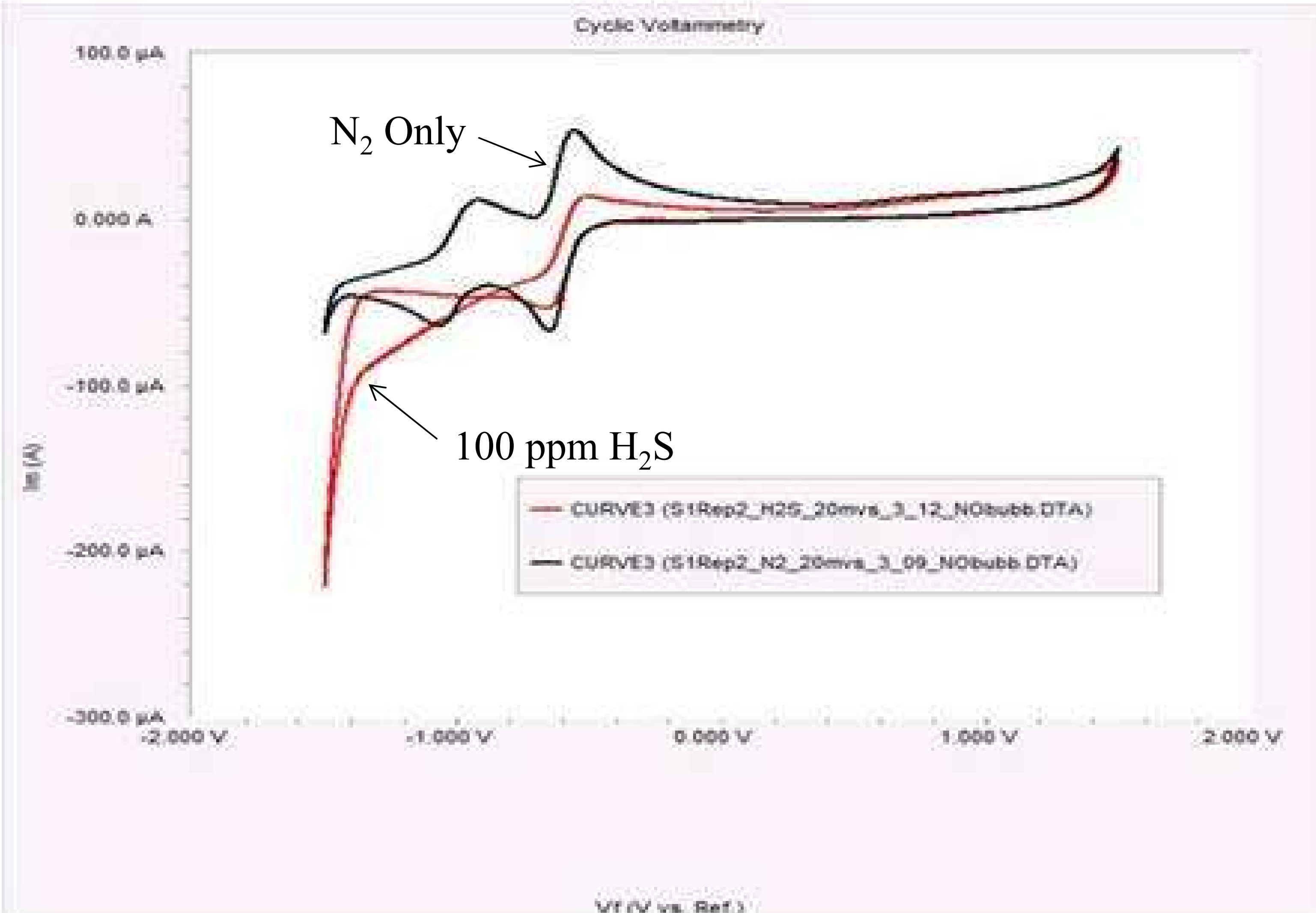
Scan rate 20mV/s, Pt wire working electrode vs Ag/AgCl reference

Cyclic Voltammogram of Ionic Liquid Emim-tFMS with DtBBQ Showing Dual Oxidation and Reduction Peaks



Scan rate 20mV/s, Pt wire working electrode vs Ag/AgCl reference

Cyclic Voltammetry of DtBBQ in [Emim][TFMS] With and Without H_2S



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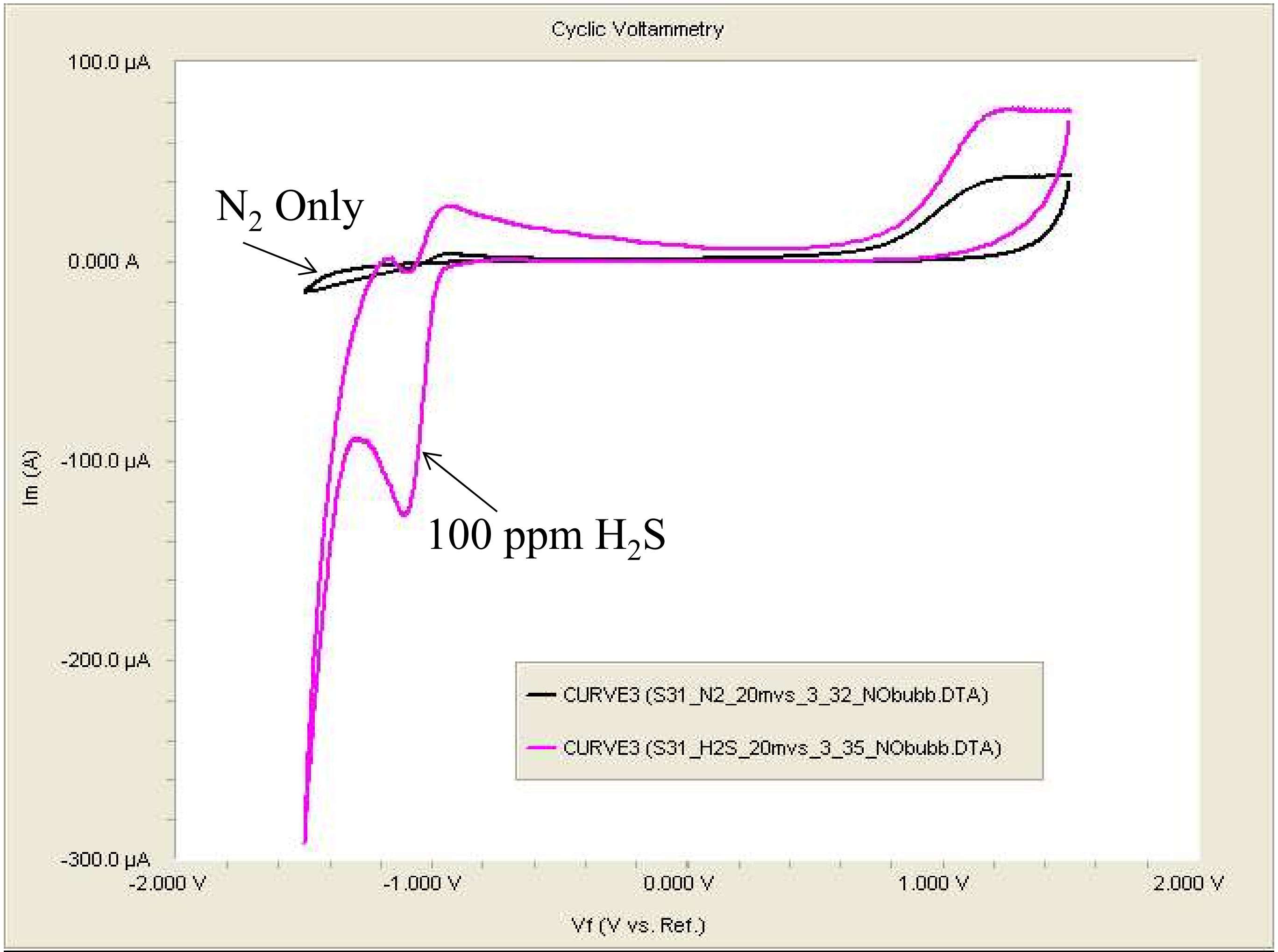
Another Successful Cyclic Voltammogram using Emim $EtSO_4$ in Ethanoloamine With and Without 100 ppm H_2S



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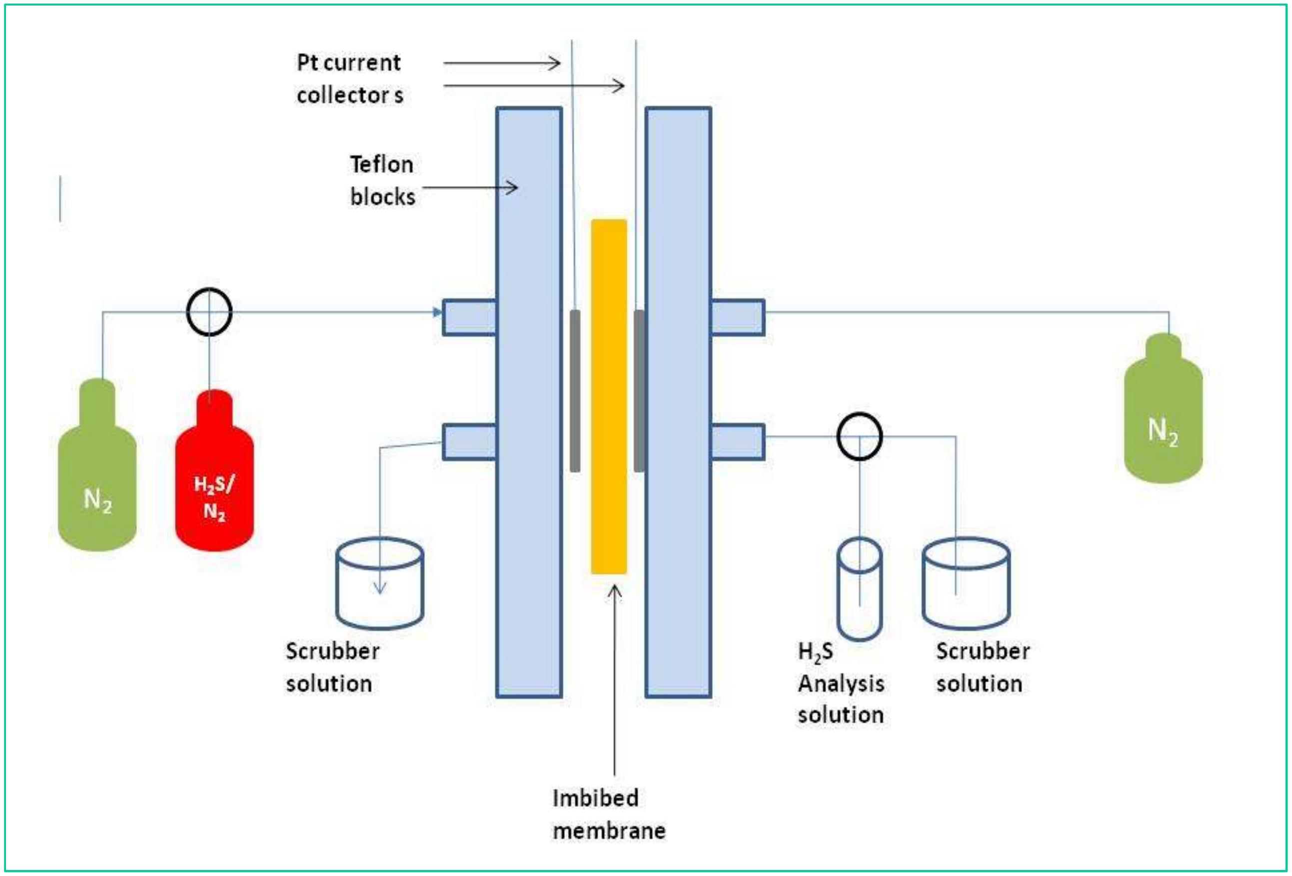
Membrane and Electrode Assembly Development

- Fabrication of MEA
  - Membrane:
    - Uncoated Nafion, Catalyzed Nafion,
    - Microporous membranes
  - Catalyst: Electrolessly deposited Pt
  - Electrodes: corrosion resistant materials
    - Metals: molybdenum, tungsten, aluminum, and magnesium
    - *Carbon fiber: recently developed 3-dimensional carbon-fiber braided electrode*
  - Imbibe ionic liquid/redox carrier in the membranes
- Component arrangement
  - Planar and Tubular Cell Designs
    - Constructed as electrode/separator/electrode
    - Challenge is to improve transport rate: multiple redox carriers, thinner membranes, redox carrier solubility

Evaluate MEAs for H_2S, CO_2 and VMS Separation Using Planar and Tubular Cell

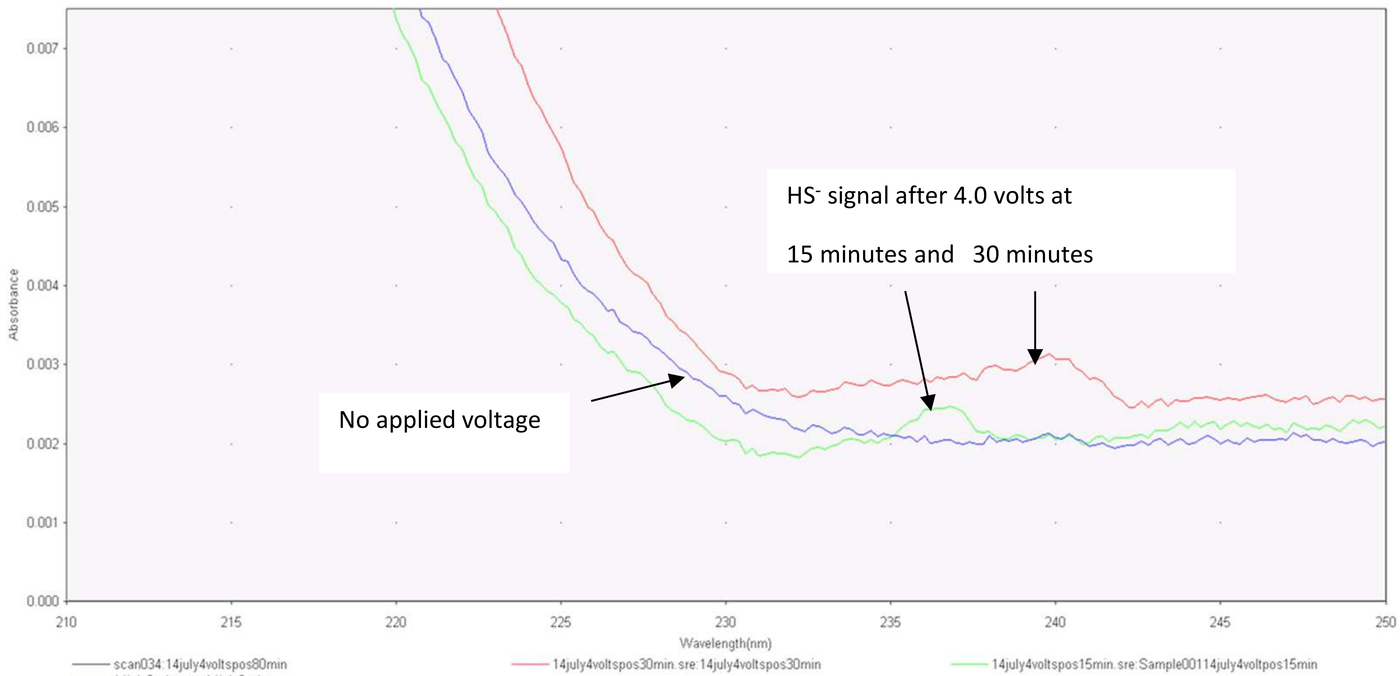


- H_2S detected using UV-Vis spectrophotometry
- Simulated biogas: 100 ppm H_2S/ balance N2 or CH_4

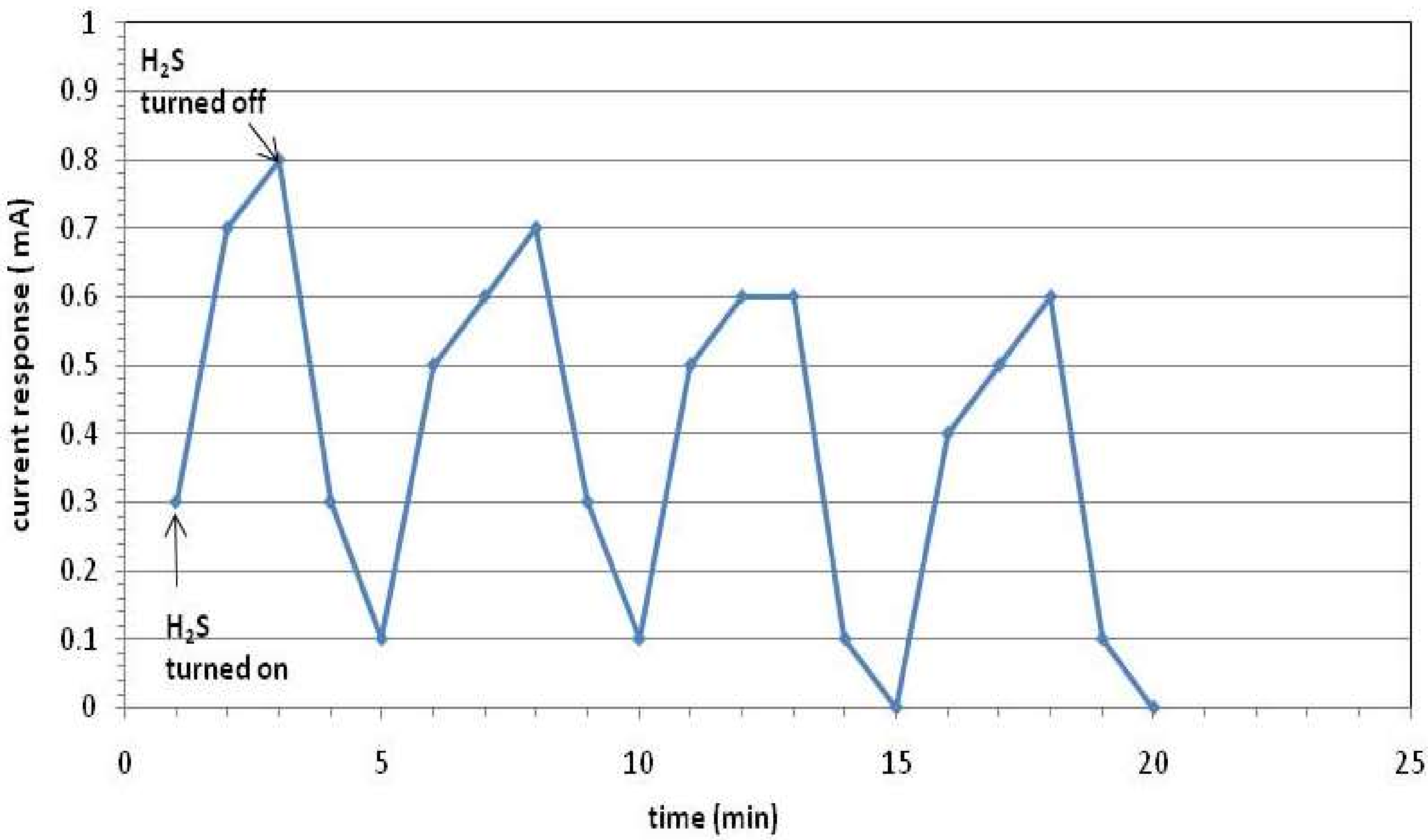
Single Cell Testing Using Down-Selected Electrolytes Shows H_2S Removal

- Prepared imbibed membranes

MEA	Redox carrier	Ionic liquid	Membrane
Nafion-1	dtBBQ	Emim TFMS	Nafion
Nafion-31	Ethanolamine	EMIM EtSO4	Nafion
Celgard-1	Dt BBQ	Emim TFMS	polypropylene



Current Response With Cycling H_2S On/Off



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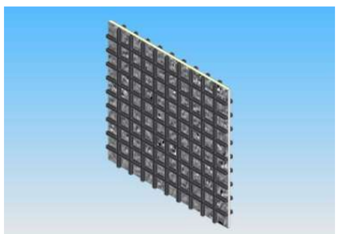
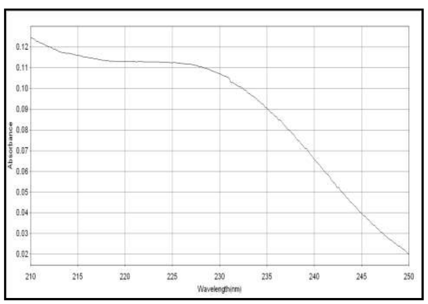
Electrodes: Catalytic or a Current Sink/Source?

Stage 1

- Pt-catalyzed Nafion
- Imbibed with redox carrier/IL
- Pt mesh current

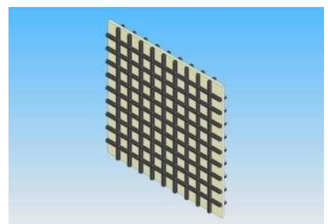


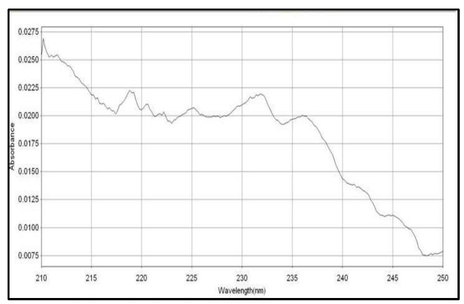


Stage 1. Demonstrated H_2S transport

Stage 2

- Uncatalyzed Nafion
- Imbibed with redox carrier/IL
- Pt mesh current collector

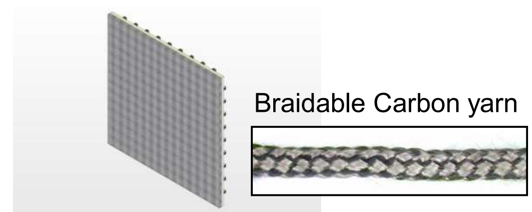


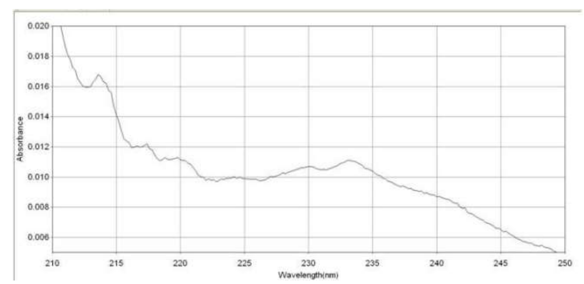


Stage 2. H_2S transport without catalyzed membrane:

Stage 3

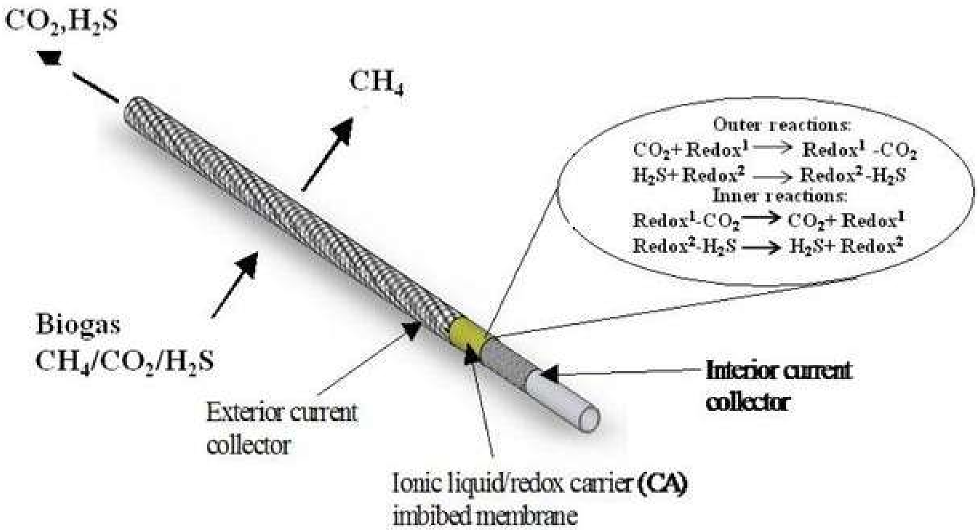
- Uncatalyzed Nafion
- Imbibed with redox carrier/IL
- High surface area, corrosion resistant current collector

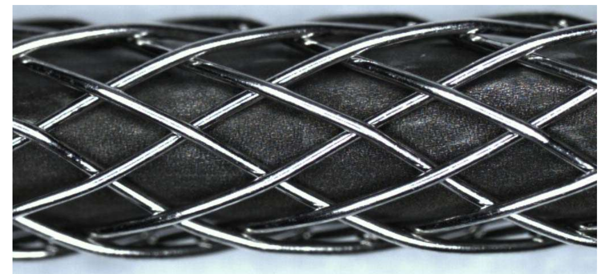




Stage 3. H_2S transport without catalyzed membrane and a carbon yarn electrode

Extension to Reactive's Tubular Reactive-Separator to Increase Membrane Surface Area to Volume Ratio





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Imbided redox carrier/ionic liquid in tubular membrane for H_2S removal

- Tubular Nafion imbibed with dual redox carrier/ionic liquid
- Braided carbon yarn current collectors used

H_2S Removal/Transport Rate

MEA	membrane	Electrodes	H_2S Transport rate (moles/s/cm^2)
100	Nafion	Platinum	7.88×10^{-9}
101	Nafion	carbon yarn	1.08×10^{-8}
300	Celgard (polyproplylene)	carbon yarn	1.32×10^{-8}

- Transport rate is calculated based on current measured at 4 volts
- Using current performance levels, a H_2S separation module would require 65 6-inch tubular MEA cells to remove 1% H_2S from a 7 L/min biogas stream for a 1 kW solid oxide fuel cell
  - Approximate reactor size 2” diameter, 8” long, < 1 lb
  - Power requirement 12 W

Extensions to Other Systems

- Selective separation using the facilitated transport process viable for other systems including
  - CO_2 removal (previously shown by others and Reactive for CO_2 in air/water)
  - H_2S, Cl, F, and Si contaminants from biogas waste-to-fuel processing
  - H_2S and SO_2 selective sensing applications for landfills, animal feeding operations, and oil facilities
- Challenge is in finding optimal ionic liquid/redox carrier selective to the contaminant
  - Successful candidates for H_2S/SO_2 separation include DtBBQ in Emim-(tfms) and Fe-CDTA in Bmim-$OcSO_4$
- Separation transfer rates are low (4 mA/cm^2), thus require large membrane surface area (*e.g.*, tubular MEA arrays)
  - However, for trace contaminant removal, the separator size and power levels are low
- Continued work focusing on minimizing ionic liquid/redox carrier steric hindrance effects in the membranes and minimizing ohmic resistance

Acknowledgment

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