Mars Propellant Production Using Ionic Liquids

James Captain (KSC/ESC), Tracy Gibson (KSC/ESC), Paul Hintze (NASA/KSC), Laurel Karr (NASA/MSFC), Matthew Marone (Mercer University), Anthony Muscatello (NASA/KSC), Steve Paley (AZ Technology/MSFC) and Jan Surma (KSC/ESC)

Presenter: Prof. Matt Marone

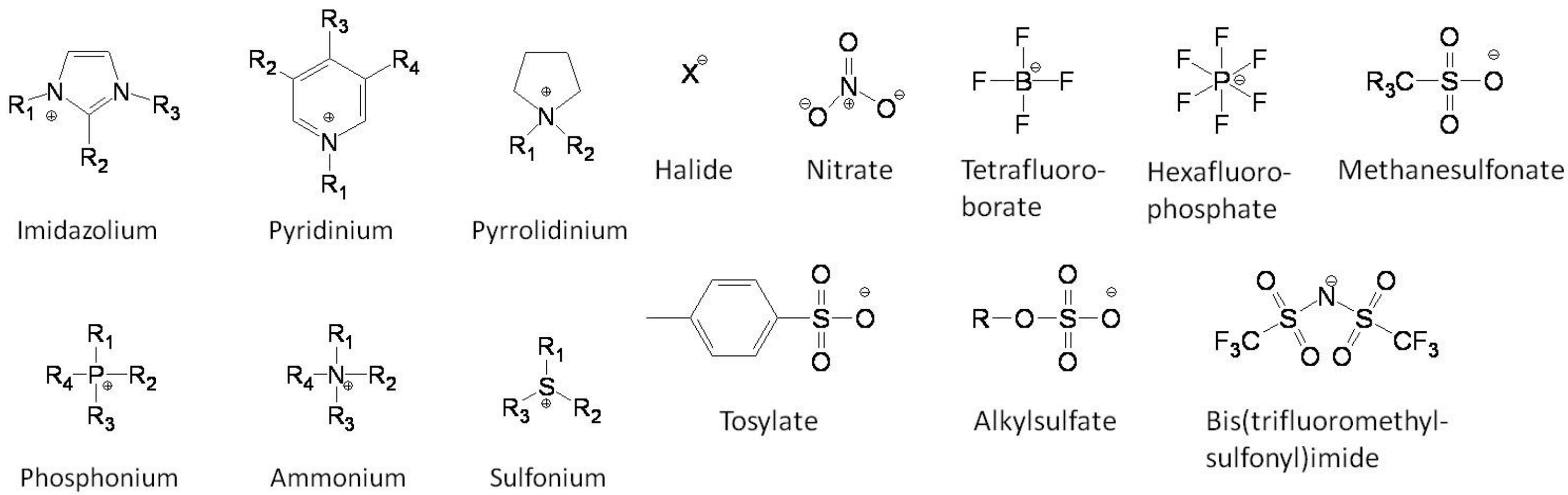
May 13, 2015
Planetary and Terrestrial Mining Sciences Symposium (PTMSS)
Canadian Institute of Mining, Metallurgy and Petroleum (CIM) Convention
Montreal, Canada

Contents

- Introduction
- Technical Approach
- Key Issues
- Current Results
- Summary

Introduction – Ionic Liquids

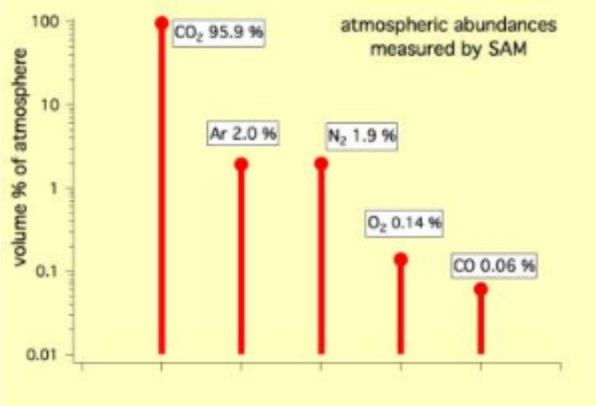
- **Ionic Liquids (ILs) are salts that have melting points near room temperature**
- **Certain ILs adsorb CO_2 at low partial pressures and provide a medium for electrolysis to useful compounds**

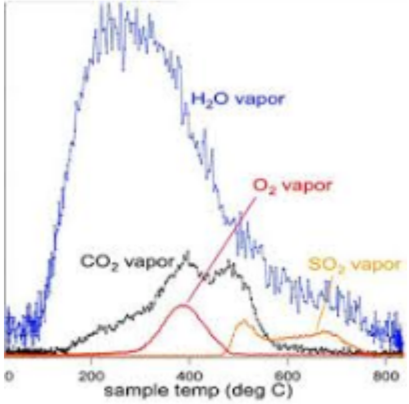


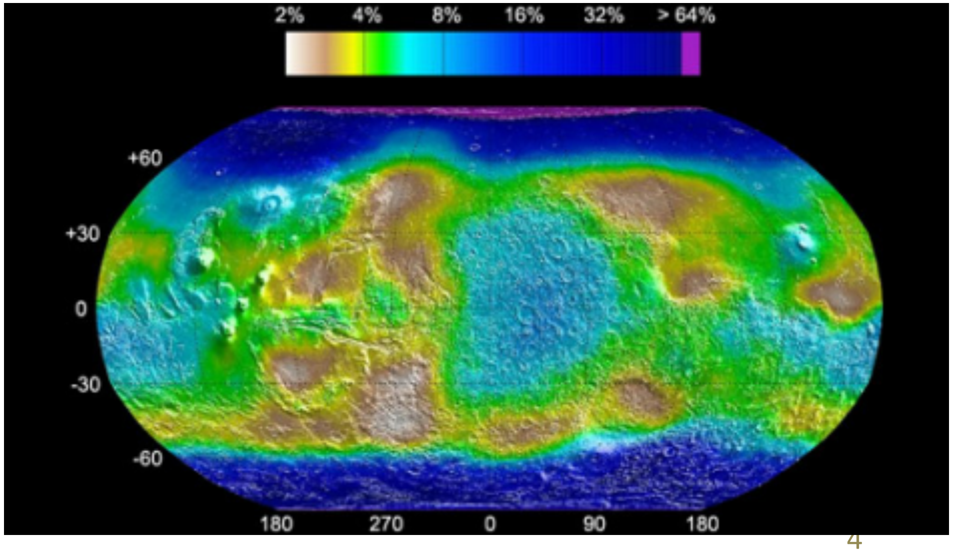
Typical Ionic Liquid Cations and Anions

Resources on Mars

- **Atmosphere of Mars**
  - 95.9% CO_2
  - 2% Ar, 1.9% N_2
  - <1% pressure of Earth's atmosphere (~7 mbar)
- **Significant Amounts of Water in the Top 1-Meter of Regolith**
  - Water ice caps at the poles
  - ~2% at least everywhere else
  - ~10% even at equatorial regions

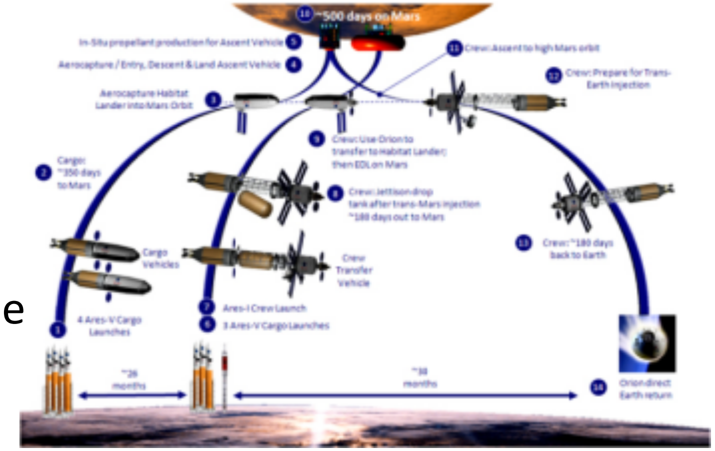






Utilizing Martian Water and CO_2/Advantages of ISRU

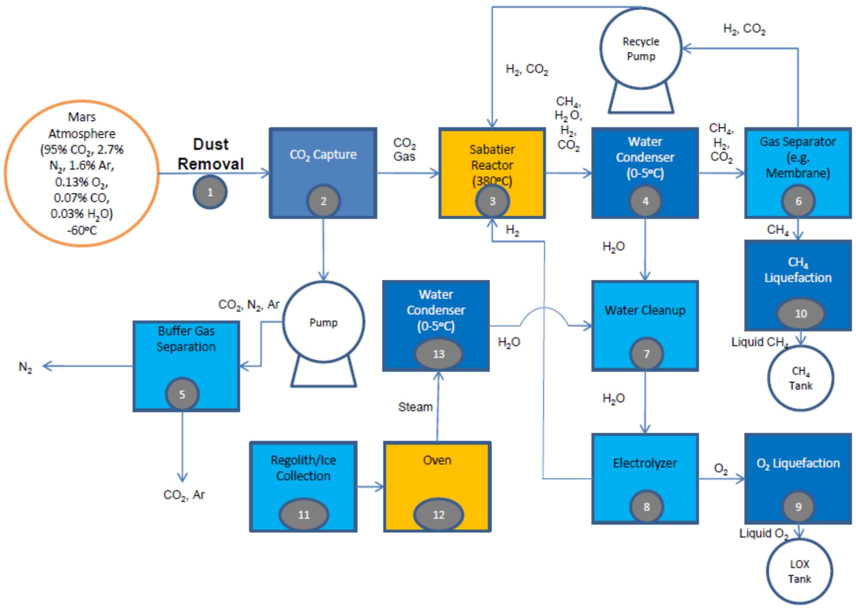
- **ISPP: In Situ Propellant Production**
  - Electrolysis: $4\ H_2O \rightarrow 4\ H_2 + 2\ O_2$
  - Sabatier Reaction: $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$ (Ni or Ru catalyst, 300-600^{o}C)
  - Net Reaction: $CO_2 + 2\ H_2O \rightarrow CH_4 + 2\ O_2$ = Rocket Propellant! I_{sp} = 369 s
- **Human Mars Mission Outline (DRA 5.0)**
  - Launch Surface Hab/Lander and Mars Ascent Vehicle in Year 1
  - MAV lands on Mars after 9 months
  - MAV produces ascent fuel for 11 months
  - Launch Transfer Vehicle and Crew (6) in Year 2
  - Crew lands on Mars after 6-9 months
  - Crew explores Mars for 1.5 years
  - Crew launches MAV to return to Transfer Vehicle
  - Crew returns to Earth in 6 months
  - Total Crew time away from Earth is ~2.5 years



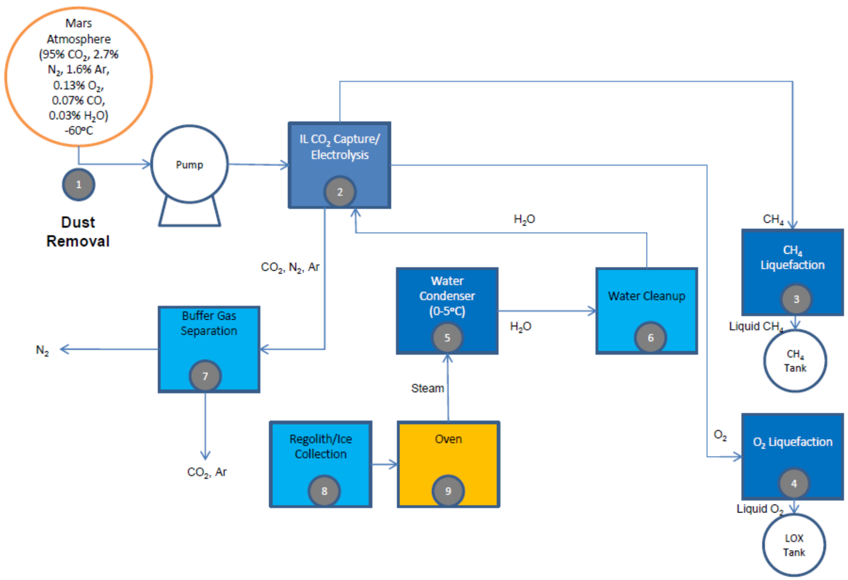
- **ISPP saves ~30 metric tons of landed mass**
- **Also provides breathing oxygen for life support**
- **Eliminates two super heavy lift launches!**

Potential Benefits for ISRU

Current Mars Propellant Production Process Diagram

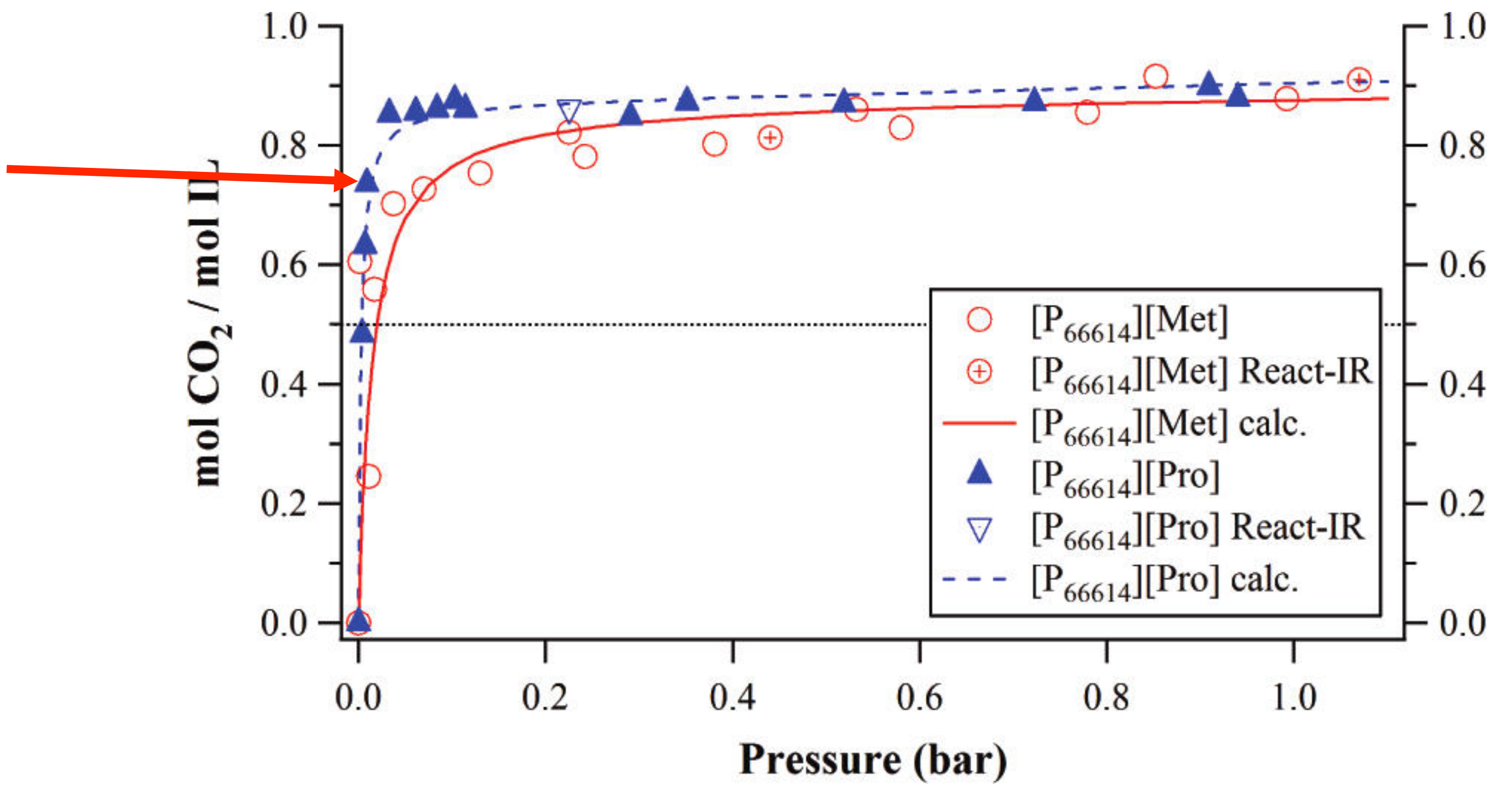


Mars Propellant Production Process Diagram with IL Electrolysis



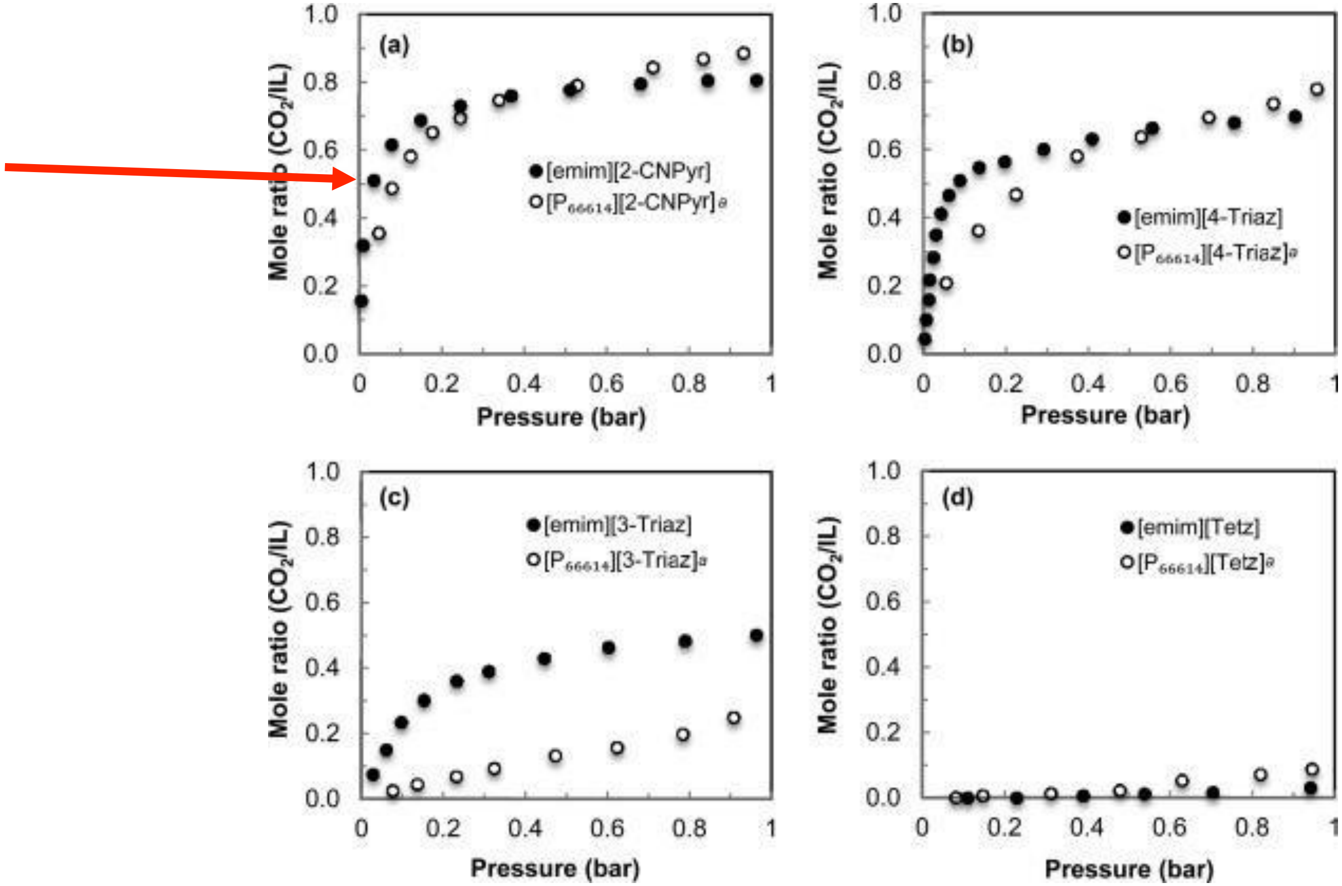
- **Advantages of IL capture/electrolysis:**
  - — No high temperature processing of CO_2
  - — One less pump and no cryocoolers
  - — Four fewer major process steps
  - — Estimated ~50% less mass and ~25% less power

CO_2 Uptake at Low Partial Pressure ~74% Mole Fraction at ~10 mbar



CO_2 absorption by [P_{66614}][Pro] and [P_{66614}][Met] at 22°C. "The lines are Langmuir model fits of the data included to guide the eye." (Gurkan, 2010)

CO_2 Uptake at Low Partial Vacuum ~50% Mole Fraction at ~10 mbar



"CO_2 absorption capacity in (a) [emim][2-CNPyr], (b) [emim][4-Triaz], (c) [emim][3-Triaz], and (d) [emim][Tetz] at 22 °C. The CO_2 solubility in $[P_{66614}]^+$ counterparts from ref 10 are also shown for comparison." (Brennecke, 2014)

Technical Approach

- Select best available candidate COTS ILs and electrocatalysts (KSC)
  - Based on literature review
- Prepare new task-specific ILs (AZ Technology/ MSFC)
- Determine CO_2 capture efficiency and conductivity of ILs (Mercer U. and KSC)
- Measure electrochemical windows (KSC)
- Design/build electrochemical cells (KSC)
- Test electrolysis of $CO_2 + H_2O$ to $CH_4 + O_2$

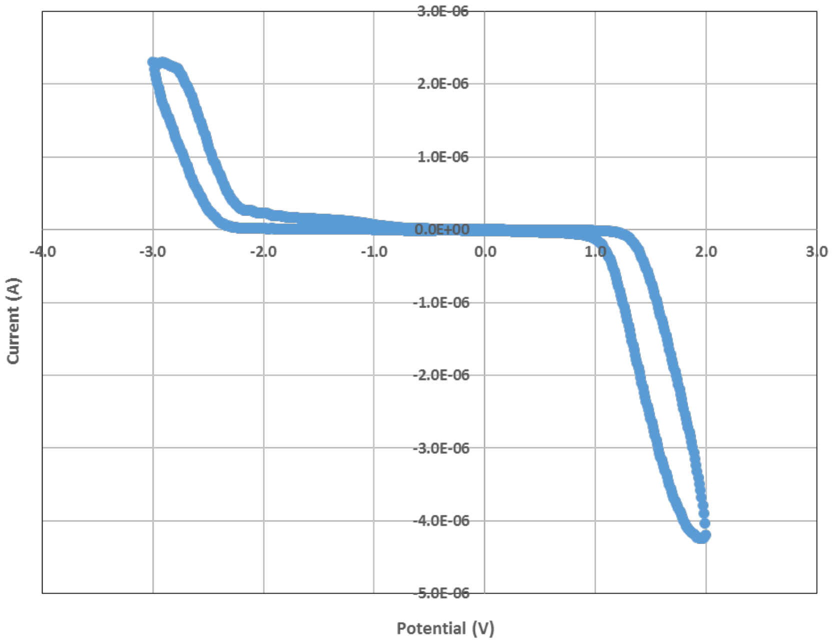
Key Issues/Answers

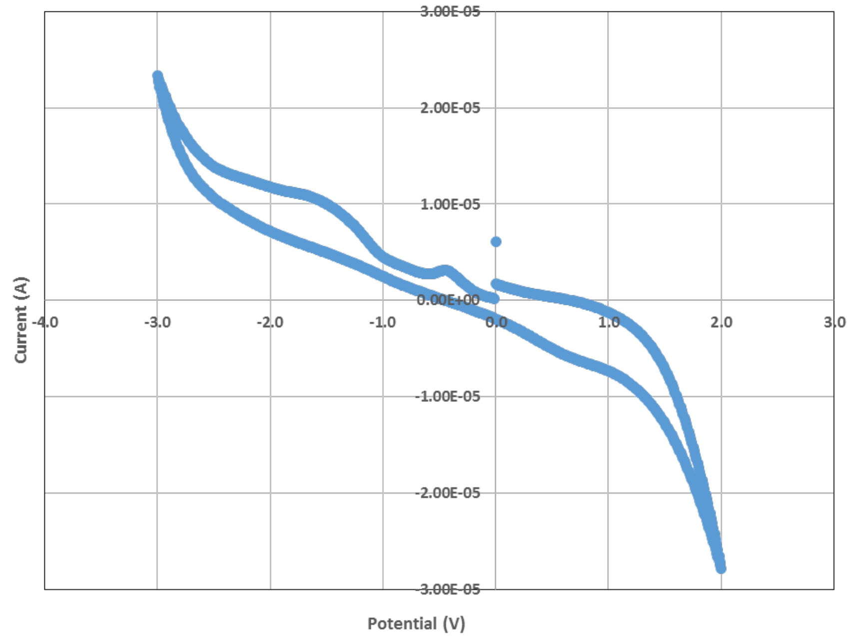
- Conductivity of IL + CO_2 (viscosity)
  - Prepare task specific ILs (TSILs)
- Selectivity of cathode electrocatalysts for CH_4
  - Test best from literature
- Hydrolysis of ILs
  - Two-compartment cell with Nafion separator
- Production rate
  - Evaluate multiple candidates

Current Results

- COTS IL candidates: [EMIM][BF_4], [BMIM][BF_4], [BMIM][TFMSI], [BMIM][PF_6] and [HMIM][$B(CN)_4$]
- Electrocatalysts: Copper cathode/Pt anode, TiO_2 cathode/Pt anode
- Several ILs have good electrochemical windows and conductivity
- Two-compartment cell w/Nafion membrane
  - Polycarbonate not suitable: $CaCO_3$ precipitate, Cu corrosion
  - Testing in glass cell now
- Three TSILs prepared: AZ-1, AZ-2, and AZ-3 (code named to protect IP)
  - High CO_2 sorption and conductivity

Wide Electrochemical Windows



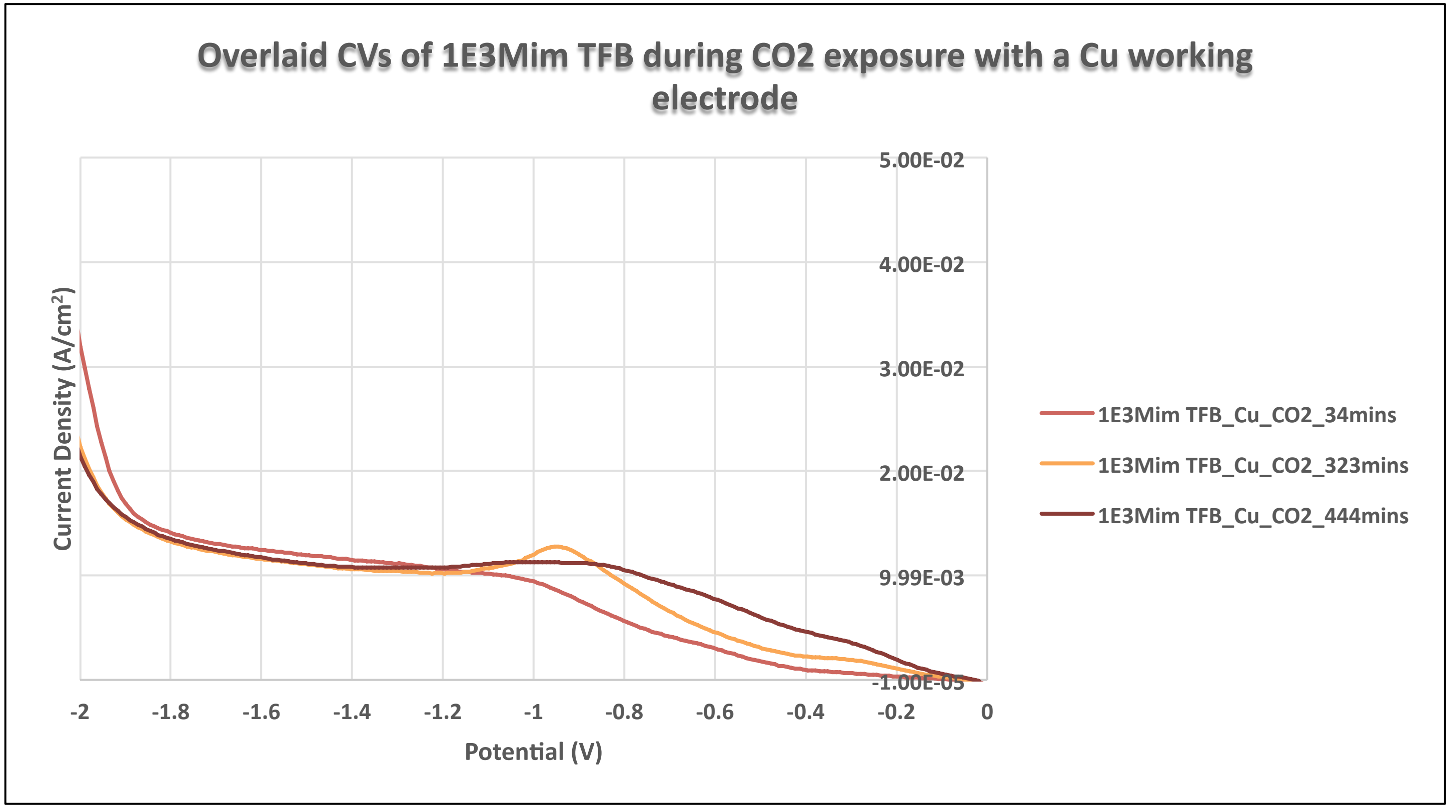


Cyclic voltammograms of AZ-1 with one platinum grid electrode and one platinum wire electrode (left) and one platinum grid electrode and one copper wire electrode (right).

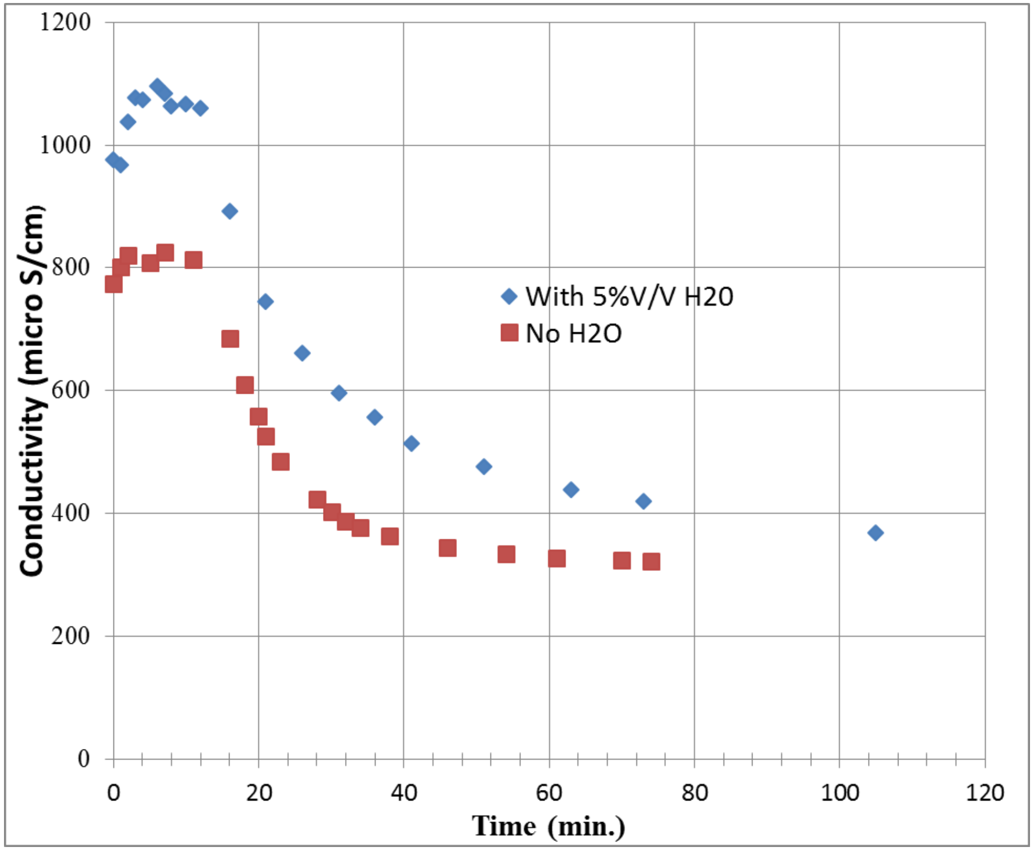
Electrochemical Windows (Ar Purge, Cu Electrode)

Ionic Liquid	Ag reference electrode used	Abbreviation	Potential Limits (V)	Potential Window (V)
AZ-1	No	AZ-1	-2.7 to 1.7	4.4
AZ-2	Yes	AZ-2	-1.6 to 0.8	2.4
1-Butyl-3-methylimidazolium hexafluorophosphate	No	1B3Mim HFP	-1.4 to 0.8	2.4
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	No	1B3Mim TFMSI	-1.6 to -0.5	2.1
1-Butyl-3-methylimidazolium tetrafluoroborate	No	1B3Mim TFB	-2.2 to -0.4	1.8
1-Ethyl-3-methylimidazolium tetrafluoroborate	No	1E3Mim TFB	-1.4 to 0.2	1.6
1-Hexyl-3-methylimidazolium tetracyanoborate	Yes	1H3Mim TCB	-0.8 to -0.2	0.6

CVs for [EMIM][BF_4] Exposed to Carbon Dioxide

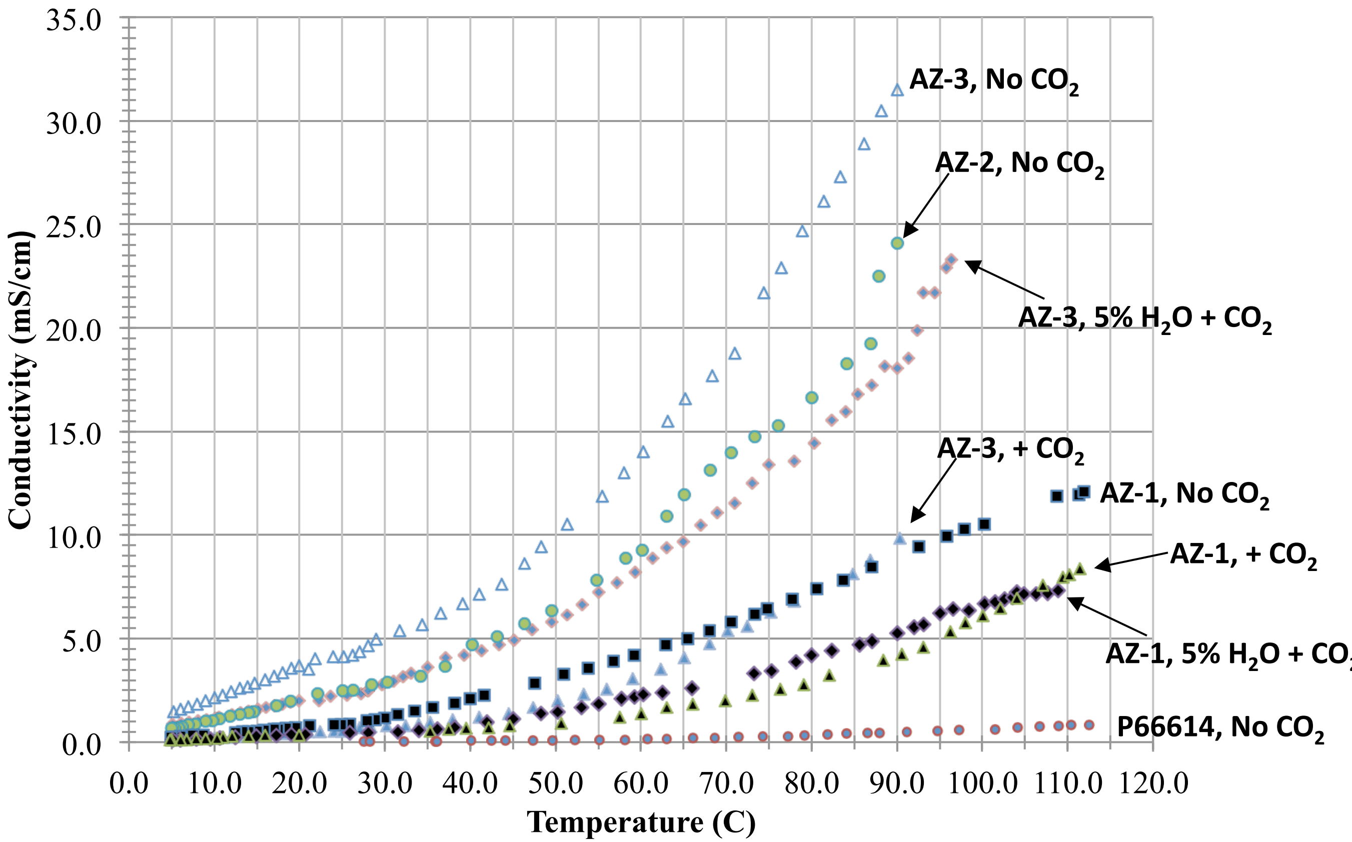


Good IL Conductivity with CO_2 and $CO_2 + H_2O$



Conductivity vs. CO_2 uptake time for AZ-1 with and without 5% dissolved water

AZ-3 Shows High IL Conductivity with CO_2 and $CO_2 + H_2O$



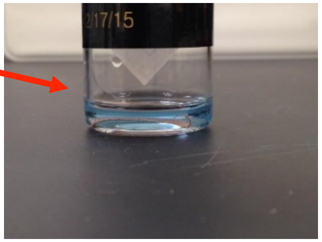
Conductivity of AZ-1, AZ-2, AZ-3 and [P_{66614}] [3-CF_3Pyra] vs. time for CO_2 uptake with and without 5% dissolved water

AZ-3 Shows High CO_2 Uptake (No Water Added)

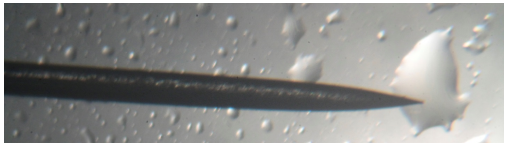
Ionic Liquid	CO_2 Uptake at ~25°C, wt%	CO_2 Uptake at 60°C, mol%
AZ-1	10	
AZ-2	9.6	9.1
AZ-3	15.6	
[BMIM][PF_6]	0.50	
[HMIM][BF_4]	0.70	
[EMIM][BF_4]	2.6	

Current Results (Cont.)

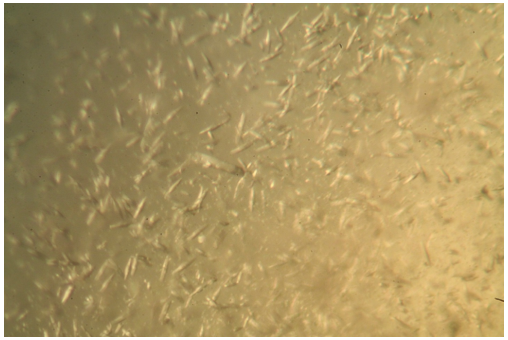
- **Some ILs dissolve copper electrode**



- **AZ-1 has high CO_2 capacity, but higher melting point (~18°C) with CO_2 present**
- **Single pot scouting electrolysis experiments (TiO_2-Pt/AZ-3/CO_2 + H_2O)**
  - **Gas generated, but precipitate formed**

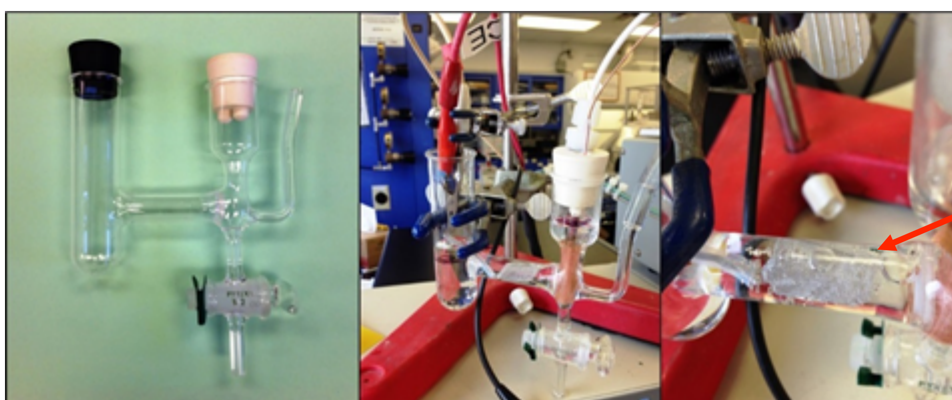


For scale: steel needle at same magnification as photo on right



KSC Electrolysis Results

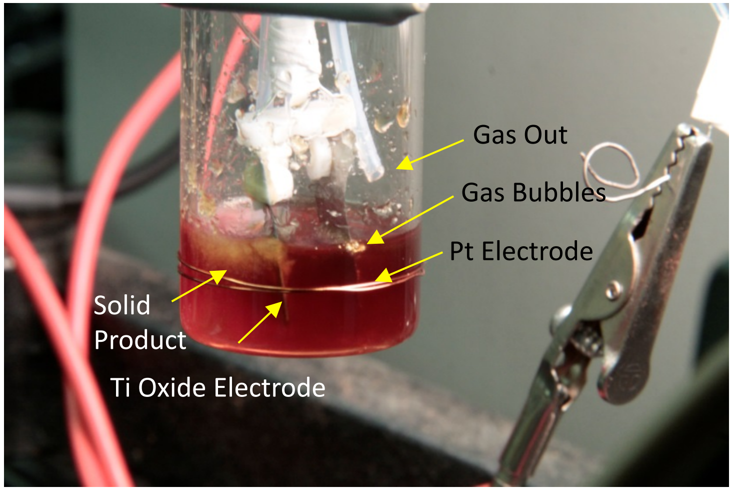
- **Glass H-Cell w/glass frit and Cu and Pt electrodes**
- **1mM H_2SO_4/[BMIM][PF_6]/-3.5 V/1.58 mA/1 hr.**
- **Cu working electrode showed no signs of degradation**
- **Gas bubbles were observed at the Pt and Cu**
- **FTIR with re-circulating reservoir of CO_2 used to monitor CH_4 production**
- **If any methane formed it was below the current detection limit of the system**



Gas Bubbles

Mercer University Electrolysis Results with AZ-3

- Glass vial w/TiO_2 and Pt electrodes/2% H_2O/CO_2/~34°C
- -2.02 V/12.9 mA/recirculating CO_2
- Gas bubbles on Pt and solid on TiO_2 electrodes
- Possible detection of CH_4 and CO w/RGA
- Needs replication and verification



Summary
(Underlined ILs = Candidates)

Ionic Liquid	CO_2 Capacity, wt.% (R.T., 1 atm, dry)	Electro-chemical Window, V	Conduc-tivity with CO_2 (mS/cm, 40°C)	Compatible with Cu	Other Issues	Tested Solubility of Water, v/v%	Methane Production Rate
[BMIM][TFSI]	0.46	2.1		No			TBD
[BMIM][PF_6]	0.50	2.4		Yes			TBD
[BMIM][BF_4]	0.55	1.8		Yes			TBD
[HMIM][$B(CN)_4$]	0.70	0.6		No			TBD
[EMIM][BF_4]	2.6	1.6		No			TBD
AZ-1	9.0	4.4	0.67	No		5	TBD
AZ-2	9.6	2.4		Yes			TBD
AZ-3	15.6		1.2	?	Precip.	5	TBD

Questions?