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Electrochemical Conversion of Carbon Dioxide to Oxygen in Ionic Liquid Media

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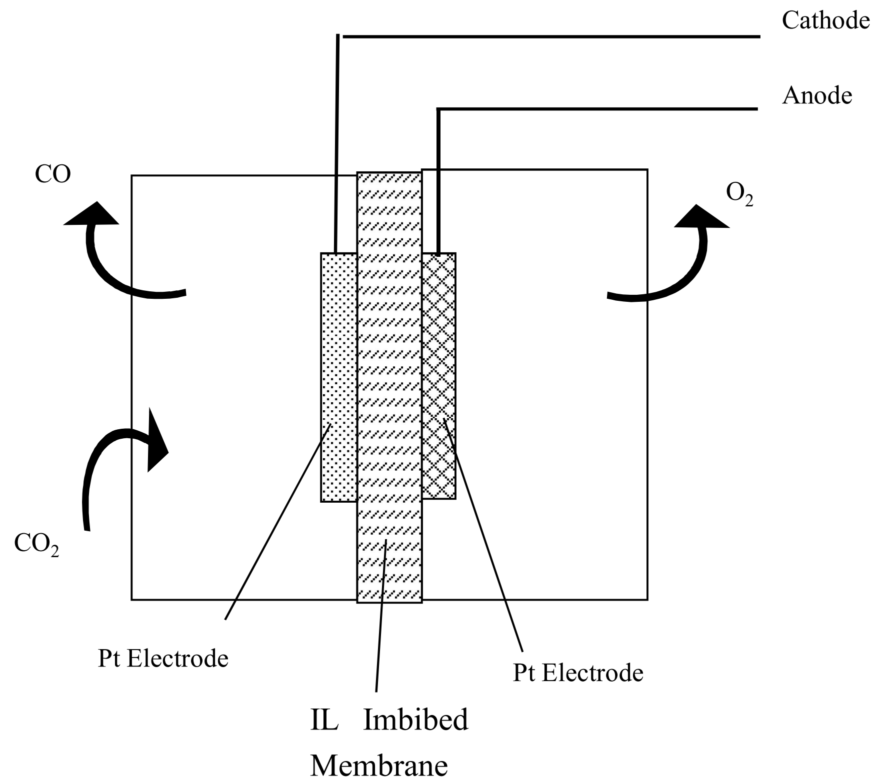
Problem Background

- NASA missions need to extract oxygen from carbon dioxide for advanced life support and human exploration missions
- Martian In-Situ Resource Utilization (ISRU) aims to process carbon dioxide (95% in atmosphere) to oxygen
  - Sabatier: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ and then $H_2O \rightarrow H_2 + 1/2O_2$
  - Electrolysis: $2CO_2 \rightarrow 2CO + O_2$
- Ionic liquid based carbon dioxide reduction can enable low temperature operation less than 100 °C
- Goal is to electrochemically reduce CO_2 in an electrochemical reactor based on an immobilized ionic liquid in the separator
  - Cathode: $CO_2 + 2e^- \rightarrow CO + O^{-2}$
  - Anode: $O^{-2} \rightarrow 1/2O_2 + 2e^-$
- Major challenges are in finding the right ionic liquid to conduct an oxide ion and optimizing the electrochemical reactions

Electrochemical CO_2 Reactor Approach

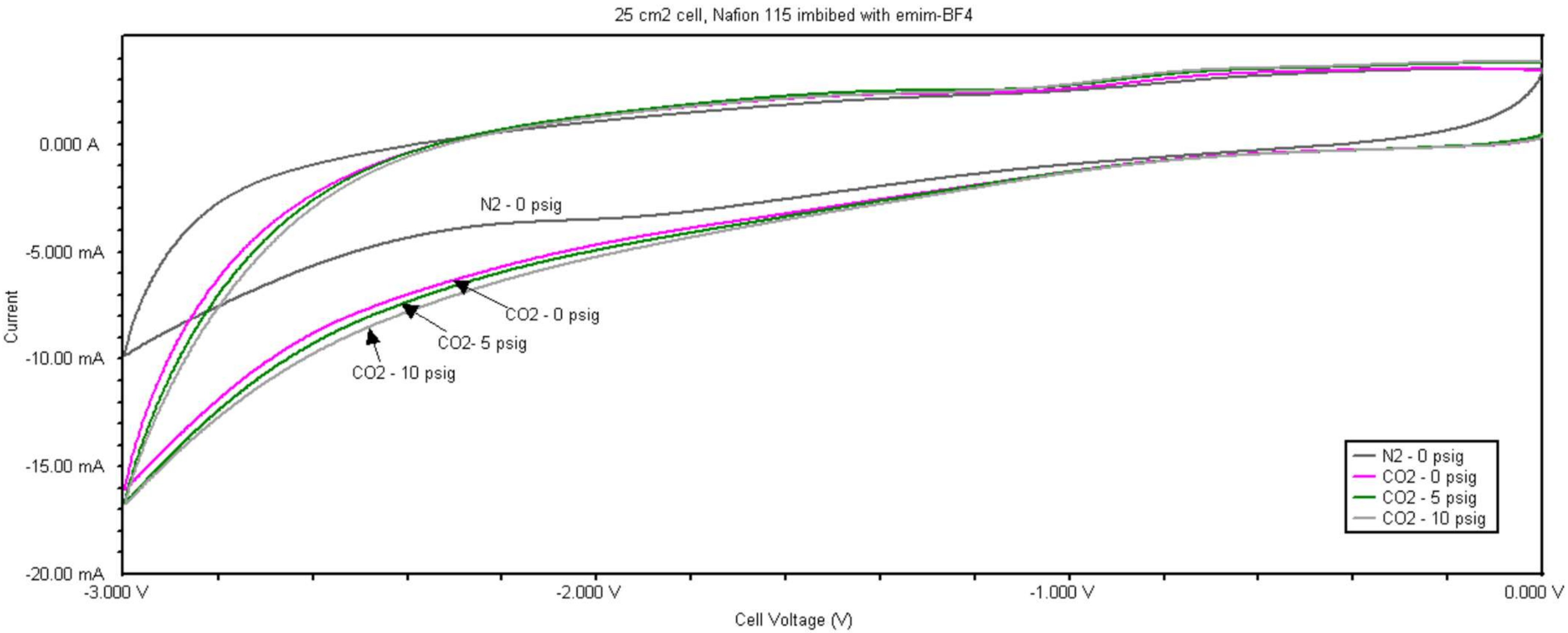
- R&D activities focused on
  - Membrane separator
    - Ion-exchange: Nafion
    - Micro-Porous: Polypropylene
  - Ionic liquid electrolyte
    - Separator Imbibement
    - Absorb CO_2, release CO, O_2
    - Oxide ion conduction
  - Anode and cathode catalysts
    - Pt, Pt/Ru, Ag, Cu, Pt/C
  - Electrode Design
    - Catalyst deposition methods
    - Electrical conductivity vs chemical activity
  - Operational
    - Applied voltage range



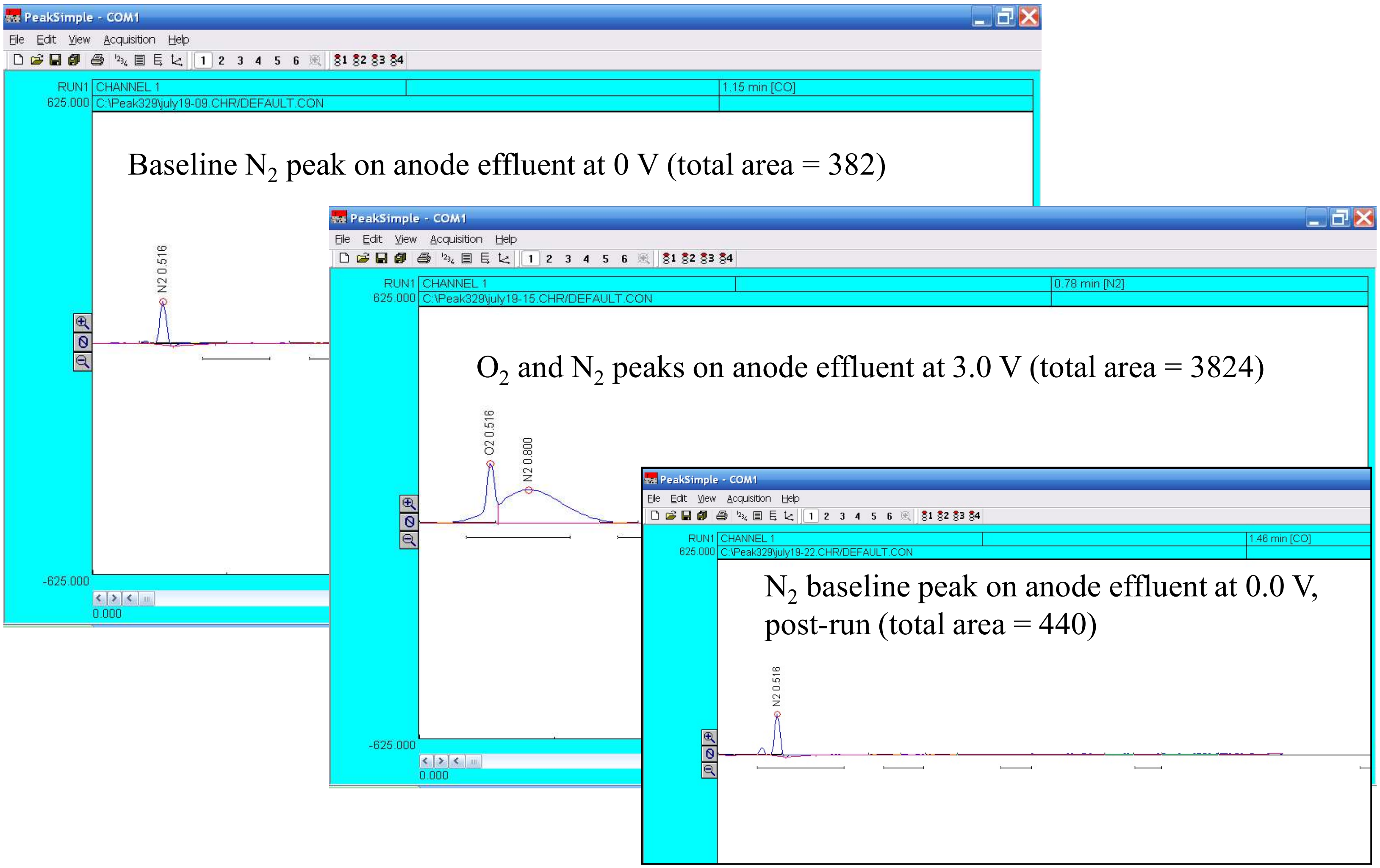
Methodology for Screening Ionic Liquid Imbibed Membranes

- Developed a list of ionic liquid anion/cation combinations considering
  - aprotic, protic, zwitterion type ILs, ionic association, size
- Utilize a chemical catalyzation technique to electrolessly deposit platinum catalyst onto Nafion 115 ion-exchange membranes
- Imbibe ionic liquids into platinized Nafion films
- Ionic liquid cation groups
  - Emim: 1-*ethyl,3-methylimidazolium*
  - Bmim: *1-butyl,3-methylimidazolium*
  - BFP: *butylmethylpyrrolidinium*
- Ionic liquid anion groups
  - BF4: *tetrafluoroborate*
  - PF6: *hexafluorophosphate*
  - FMS: *trifluoromethanesulfonate*
  - TFSI: *bis-trifluoromethylsulfonylimide*
  - CH3CO2: *Acetate*
- Evaluate samples using cyclic voltammetry and chronoamperometry

Representative Cyclic Voltammogram for CO_2 Reduction – Slight Increase in Reactivity with Increasing Pressure



GC Analysis Shows Oxygen Production on Anode Effluent



Comparison of CO_2 Reduction Over N_2 Baseline Emim-BF4 Gives Highest CO_2 Reduction Rate

Imbibing Ionic liquid		**membrane**	**Test number**	**Current @ 2.9V (mA)**		
cation	anion			N_2	CO_2	Delta
EMIM	TFMS (Control)	Ptcatalyzed Nafion H^+	1	3.64	4.96	1.32
EMIM	TFSI	Pt-catalyzed Nafion H^+	2	5.4	4.8	-0.6
EMIM	CH3CO2 acetate	Pt-catalyzed Nafion H^+	3	2.2	2.98	0.78
EMIM	BF_4	Pt-catalyzed Nafion H^+	4	1.62	3.08	1.46
BMIM	BF_4	Pt-catalyzed Nafion H^+	5	1.6	2.44	0.84
BMP	TFSI	Pt-catalyzed Nafion H^+	6	0.85	0.85	0
EMIM	TFMS	Pt-catalyzed Nafion pretreated with Emim-Br salt	7	3.56	4.58	1.02
EMIM	TFSI	Pt-catalyzed Nafion pretreated with Emim Br salt	8	0.96	1.19	0.23
none	none	Pt-catalyzed Nafion pretreated with Emim Br salt	9	4.14	4.48	0.25
EMIM	BF_4	Pt-catalyzed Nafion H+ Pt electroplated	10	1.22	3.47	2.25
EMIM	BF_4	Pt-catalyzed Nafion H^+ Pt electroplated	11	1.34	2.53	1.19

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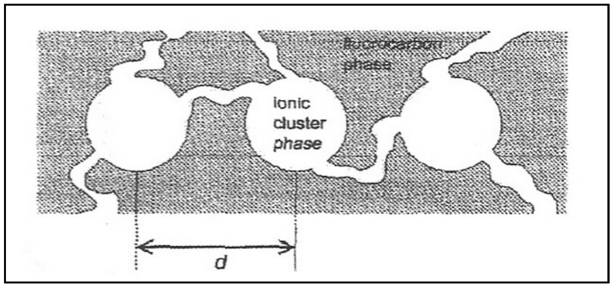
Summary of CO_2 Reduction in IL Imbibed MEAs

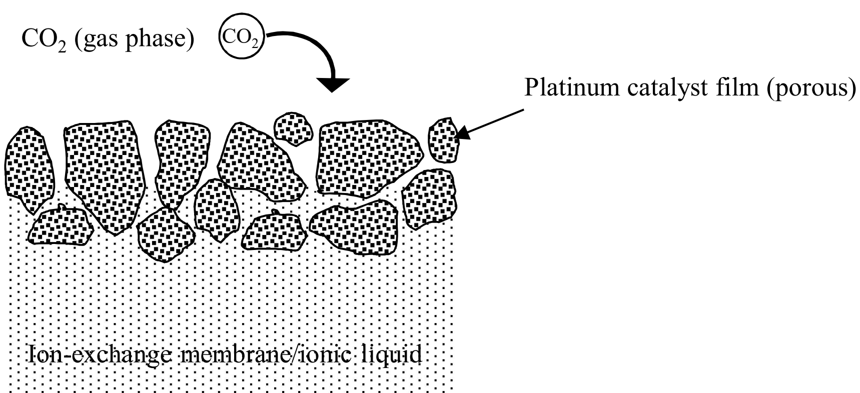
- High CO_2 reduction rates were observed with MEAs imbibed with ionic liquids having the BF_4 anion, TFMS also gives high performance
- Low CO_2 reduction rates were observed with MEAs imbibed with TFSI
- MEAs having the ionic liquids with the EMIM cation performed better than those with the BMIM cation
- Results indicate decreasing reactivity with increasing anion size
  - CO_2 reactivity trend: BF_4> TFMS> TFSI
  - Consistent with a cluster network model of the Ionic liquid/Nafion Composite Structure
  - Primary charge transfer from counter ions: imidazolium cations
  - Large anions hinder access and decrease IL packing density in pores

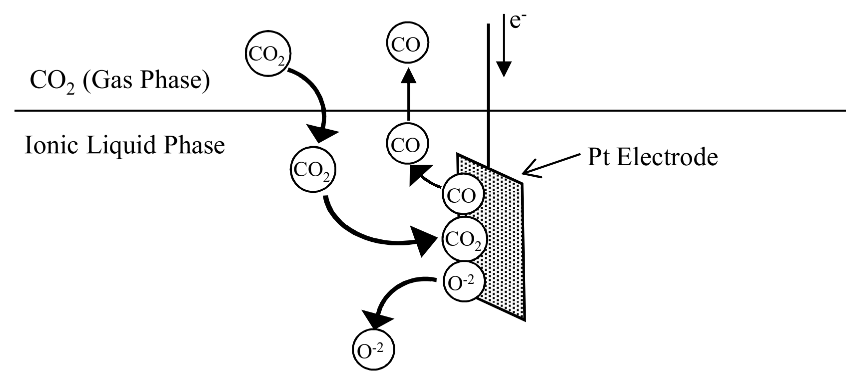


- Electrode surface area is also playing an important role in this process. High surface area platinum electrolytically deposited onto the catalyzed MEA gave the highest activity

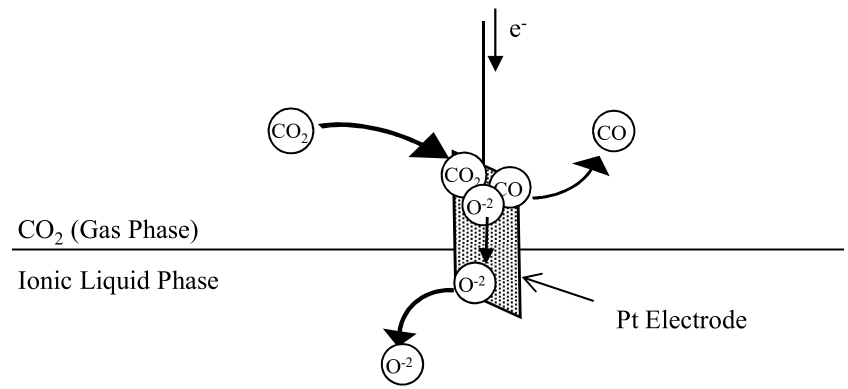
CO_2 Reactivity in Ionic Liquids/Platinum Electrodes

- Want to understand what governs the reaction behavior of CO_2 in the ionic liquid system
  - Is it the dissolution of CO_2 in the ionic liquid, followed by its diffusion to a reaction site, or
  - Is the charge-transfer kinetics at the electrode surface, or
  - Is it the gas-solid phase reduction of CO_2 on the electrode?





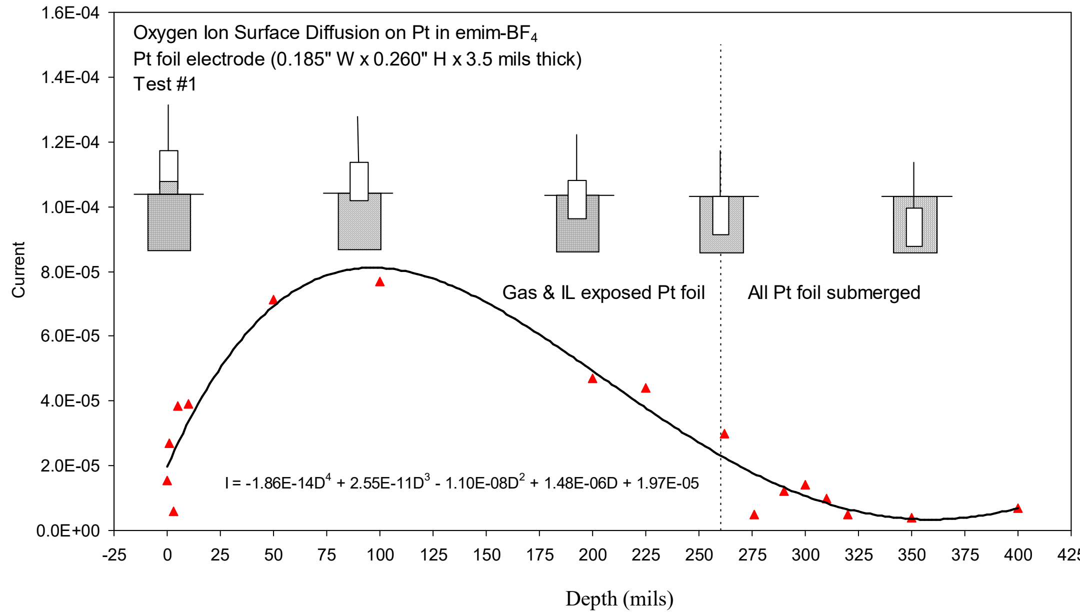
Dissolution/Diffusion Controlled Reaction

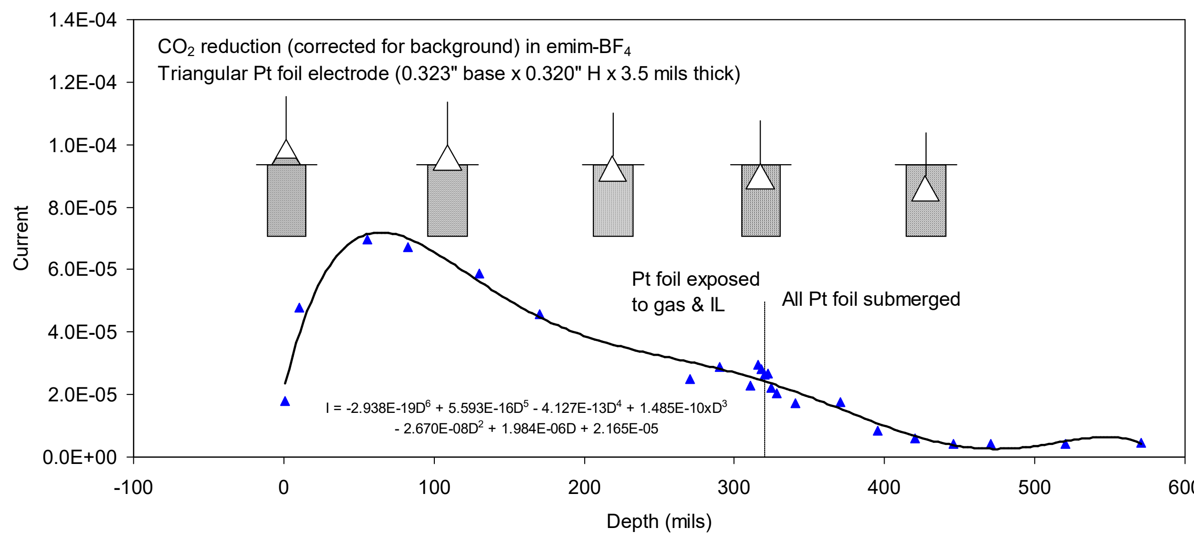


Direct Gas-Solid Controlled Reaction

Experimental Measurements Show Significant Direct CO_2 Gas Phase Reduction on Platinum

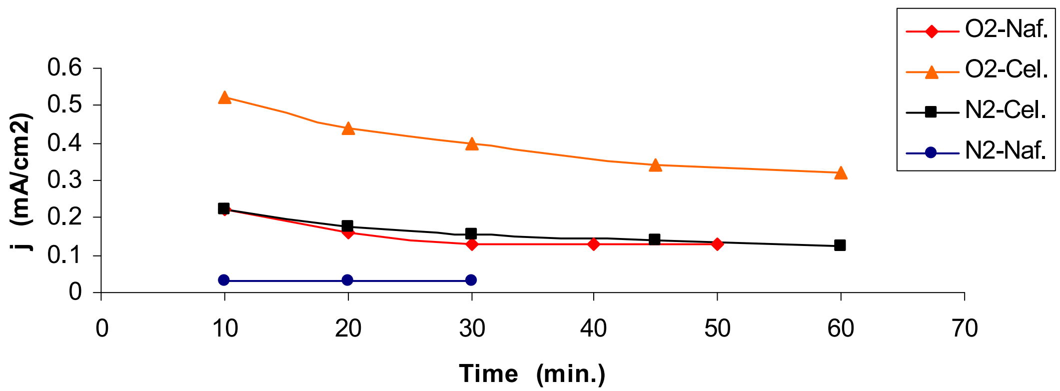
- Higher CO_2 Reduction Currents Measured When More Platinum Electrode is Exposed to Gaseous CO_2
- Implications that Higher Surface Area Platinum Electrodes be Developed on the Outer Surface of the Ionic Liquid-Membrane





Micro-Porous Membranes Show Higher Equilibrium Transport Currents

- Applied 3 V across cell
- Measured current over time
- Cathode: N_2 or O_2
- Anode: N_2
- Separator
  - Nafion 115/emim-BF4
  - Celgard/emim-BF4
- Oxide ion transport current higher than nitrogen background current
- Interaction of the Nafion pores/ion-exchange groups and ionic liquid lowers the MEA ionic conductivity



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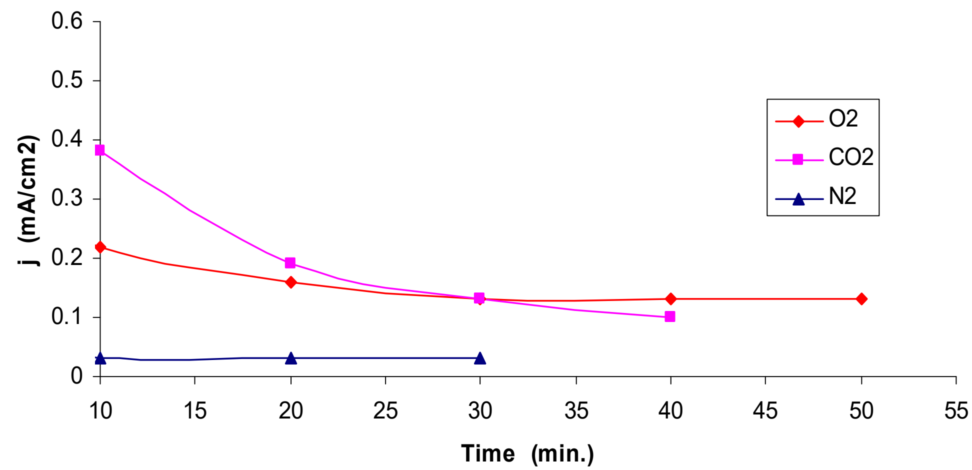
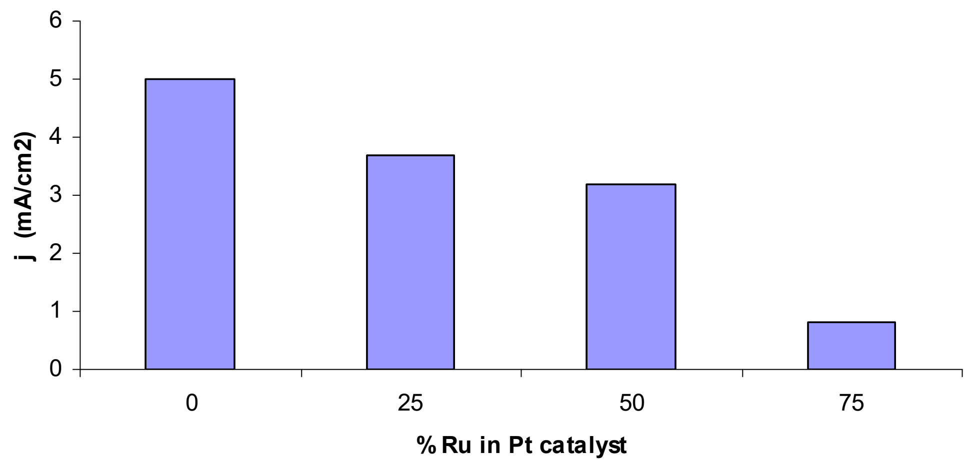
Equilibrium Current Density for CO_2 Reduction

- Applied 3 V across cell
- Measured current over time
- Cathode: N_2 ,O_2 ,or CO_2
- Anode: N_2
- Separator:
  - Nafion 115/emim-BF4
- Oxide ion current (from CO_2 or O_2 reduction) higher than nitrogen background current
- Faster decay rate for CO_2
  - CO poisoning on cathode?



Initial Peak Currents for CO_2 Reduction Favor Pt Catalyst Over Pt/Ru alloys

- Applied 3 V across cell
- Measured initial current
- Cathode: CO_2
  - Pt(100%), Pt/Ru(25% molar), Pt/Ru(50%), Pt/Ru(75%)
- Anode: N_2
  - Pt (100%)
- Separator:
  - Nafion 115/emim-BF4
- Highest initial CO_2 reduction for 100% Pt catalyst on cathode
- Lower activity with Ru addition suggests Pt/Ru composition and catalyst loading could be optimized



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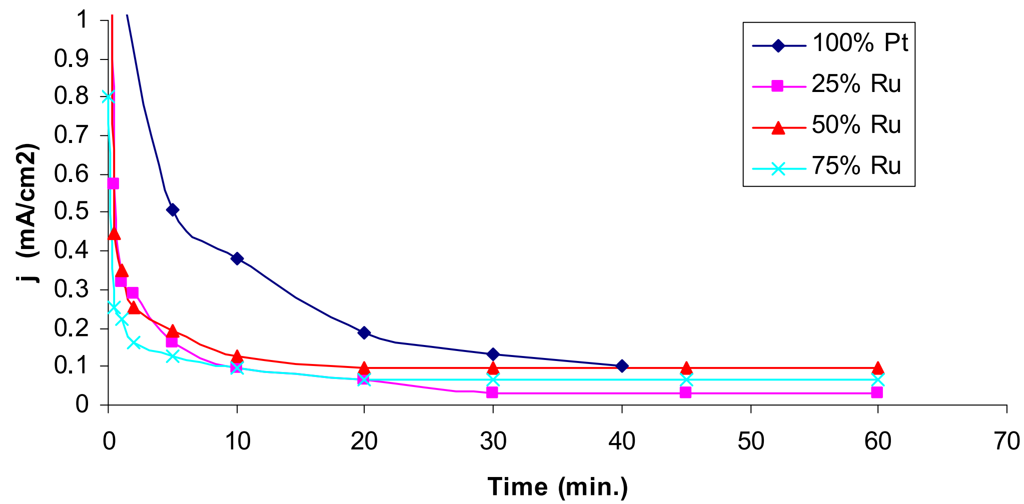
Ruthenium Addition to Platinum Cathode Stabilizes Decay

- Applied 3 V across cell
- Measured current over time
- Cathode:
  - CO_2
  - Pt(100%), Pt/Ru(25% molar), Pt/Ru(50%), Pt/Ru(75%)
- Anode:
  - N_2
  - Pt (100%)
- Separator:
  - Nafion 115/emim-BF4
- Pt/Ru cathode catalysts stabilize performance
- Significant lowering in initial activity suggests Pt/Ru optimization



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Summary - Electrode Development

- Identified platinum as a preferred catalyst choice for CO_2 reduction
  - Stable with ionic liquids and potential windows (0 to 3 volts)
  - Can be deposited on ion-exchange membranes using electroless and electrolytic techniques
  - Some indications that CO is poisoning the Pt, adding Ru stabilizes the performance
- CO_2 reaction process investigated
  - Higher CO_2 reduction rates obtained with the direct gas-solid reaction of CO_2 on platinum outside the ionic liquid phase
  - Overcomes slower CO_2 dissolution and diffusion in the ionic liquid that occurs if the Pt catalyst is coated or submerged in the ionic liquid/membrane phase
  - Optimal electrodes will have a high surface area of platinum outside the ionic liquid environment to maximize the reduction of CO_2

Summary – Electrochemical CO_2 Reduction Reactor

- Ionic Liquid
  – High CO_2 reduction rates observed with MEAs imbibed with ionic liquids having BF_4 anion
  – MEAs having the ionic liquids with the EMIM cation performed better than those with the BMIM cation
  – Anion of the ionic liquid is very important to the reduction process
- Processing metrics
  – At 0.36 mA/cm^2 CO_2 reduction rate, Reactive Innovations' electrochemical reactor module can reduce 0.08 g/hr of CO_2 producing 0.03 g/hr of O_2

Acknowledgment

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