Purposeful Utilization of Carbonate Anions in AEM-Based Devices

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History of CO$_2$ in Low T Electrochemical Cells

- Alkaline Fuel Cells
  - KOH Electrolyte

- Ambient CO$_2$
  - O$_2$ + 2H$_2$O + 4e$^-$ \(\rightarrow\) 4OH$^-$
  - 4OH$^-$ + CO$_2$ \(\rightarrow\) HCO$_3^-$
  - HCO$_3^-$ + OH$^-$ \(\rightarrow\) H$_2$O + CO$_3^{2-}$
  - 2K$^+$ + CO$_3^{2-}$ \(\rightarrow\) K$_2$CO$_3$ (s)

- CO$_2$ considered a poison
New Life for Carbonates at Room T

- **Potential Advantages over PEMFC**
  - Non-noble metal catalyst
  - Higher Purity Alcohol fuels

- **Potential Advantages over HEMFC**
  - Improved Electrolyte Stability


Electrochemical CO$_2$ Pumping

- $V = \frac{2.303RT}{nF} \log\left(\frac{P_{CO2,c}}{P_{CO2,a}}\right) = 0.015 \log\left(\frac{P_{CO2,c}}{P_{CO2,a}}\right)$
  - Spontaneous at Room T
  - H$_2$ Compression suggests applying 0.2-0.3 V
  - ~7 kJ/mol CO$_2$ - Competitive with PSA

Important Parameters for AEM Fuel Cells

- Stability of Commercial Membranes in CO$_3^{2-}$ vs. OH$^-$
- Ionic Conductivity
- Impact of CO$_2$/CO$_3^{2-}$ on ORR Activity
- H$_2$ oxidation with CO$_3^{2-}$
Decreases range from 27% to 6% over a 30 day period

Chemical Stability

- ATR-FTIR

Soaked in Water

Soaked in 1M KOH

![Chemical Structures and Wavenumber Table]

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\lambda$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>1640</td>
</tr>
<tr>
<td>$\text{C}=$</td>
<td>1615</td>
</tr>
<tr>
<td>$\text{R-}$-$\text{C-OH}$</td>
<td>1760</td>
</tr>
</tbody>
</table>

No adverse effect of carbonate or bicarbonate

Conductivity of Carbonate & Bicarbonate are lower than OH\(^{-}\).


Hydration radius:
- OH\(^{-}\): 3 Å
- HCO\(_3\)^{-}: 5.6 Å
- CO\(_3\)^{2-}: 3.94 Å

By optimizing several factors in MEA construction, AMFC performances were evaluated. Using Tokuyama’s newly developed nanobane and ionomer of higher conductivity, also with the optimized catalyst-ionomer ratio, maximum power density of 340 mW/cm\(^2\) with clean air and 450 mW/cm\(^2\) with oxygen were achieved, suggesting high potential of AMFCs.

Study of operating conditions and cell design on the performance of alkaline anion exchange membrane based direct methanol fuel cells.

G.K. Surya Prakash, Frederick C. Krause, Federico A. Viva, S.R. Narayanan, George A. Olah

Direct methanol fuel cells using an alkaline anion exchange membrane (AEM) were prepared, studied, and optimized. The effects of fuel composition and electrode materials were investigated. Membrane electrode assemblies fabricated with Tokuyama\(^®\) AEM and commercial noble metal catalysts achieved peak power densities between 25 and 168 mW cm\(^{-2}\) depending on the operating temperature, fuel composition, and electrode materials used. Good electrode stability at the anode was found to be very important for achieving high power densities. The performance of the best AEM cells was comparable to Nafion\(^®\)-based cells under similar conditions. Factors limiting the performance of AEM MEAs were found to be different from those of Nafion\(^®\) MEAs. Improved electrode kinetics for methanol oxidation in alkaline electrolyte at Pt-Ru are apparent at low current densities. At high current densities, rapid CO\(_2\) production converts the hydroxide anions, necessary for methanol oxidation, to bicarbonate.
Direct vs. Indirect Formation of CO$_3$$^{2-}$ in AEM Devices

- **Direct:**
  - $O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$

- **Indirect:**
  - $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
  - $OH^- + CO_2 \rightarrow HCO_3^-$
  - $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

- Pt favors the indirect pathway
  - Local Stability Issues

OH$^-$/CO$_3$$^{2-}$ Balance is dictated by the effective pKa of the AEM headgroups
Design of a Carbonate Selective ORR catalyst

**Desired Characteristics**

- **Surface adsorption**
  - $\text{CO}_2 > \text{H}_2\text{O}$
  - No competition between $\text{O}_2$ and $\text{CO}_2$

- **Electrochemical Activity**
  - Activate $\text{O}=\text{O}$ bond

- **Chemical stability**
  - Alkaline environments

- **High electrical conductivity**
  - Facilitate electron transfer process

$$\text{O}_2 + 2\text{CO}_2 + 4\text{e}^- \rightleftharpoons 2\text{CO}_3^{2-}$$

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$$

1st Generation: $\text{Ca}_2\text{Ru}_2\text{O}_7$

Low Compared to HEMFCs

WHY???

* In collaboration with Prof. John Varcoe at Univ. of Surrey
Impact of CO$_2$/Carbonate on ORR in AEM Fuel Cells

- There is minimal impact on intrinsic kinetics
- The primary impact of carbonate is mass transport of O$_2$ at the electrode/electrolyte interface
HOR - Experimental

- Aqueous solution of:
  - (A) 1M KOH
  - (B) 0.3M Na$_2$CO$_3$ & 0.55M NaClO$_4$
  - (C) 0.5M Na$_2$CO$_3$ & 0.25M NaClO$_4$

- Rotation rates (@10mV/s)
  - 400, 900, 1600 & 2500 rpm

- $T = 25^\circ C$

### Table

<table>
<thead>
<tr>
<th>Solution</th>
<th>A</th>
<th>B</th>
<th>C</th>
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</thead>
<tbody>
<tr>
<td>$n$</td>
<td>2.0</td>
<td>1.9</td>
<td>1.9</td>
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<tr>
<td>$j_0$ (mA/cm$^2$)</td>
<td>0.14</td>
<td>0.24</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Mechanism for oxidation reactions with $\text{CO}_3^{2-}$ are fundamentally different from $\text{OH}^-$

Can this facilitate new chemistries?

Room Temperature Carbonate Electrochemical Conversion Reactor running on (a) pure methane and (b) biogas feedstocks for direct methanol conversion.
Syngas Formation
- Steam reforming
  - $\Delta H \approx 200 \text{ kJ/mol}$
  - $\text{C-H bond has high dissociation energy}$
  - $105 \text{ kcal/mol}$
- Energetically circuitous
  - Emits significant $\text{CO}_2$
  - $0.43 \text{ mol CO}_2/\text{mol CH}_4$
Electrocatalyst Needs

- Methane-active surface sites
- Adsorb $\text{CO}_3^{-2}$ anions
- High electronic conductivity
- Stable in alkaline media
- Low cost

First Electrocatalyst Choice: Nickel(II) Oxide (NiO)
NiO Activity

CVs:
- 0.1M Na$_2$CO$_3$, 20mV/s, EIS at 0.7V vs. SCE
  - Ni$^{+2}$/Ni$^{+3}$ redox
  - $\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^-$
  - Oxygen Evolution Rxn
  - No anodic activity
  - ~20mV shift positive

EIS:
- 37% resistance increase
- CH$_4$ likely adsorbed, but not oxidized
- Oxygen donor (CO$_3^{2-}$) not adsorbed
- 0.1M Na$_2$CO$_3$, 20mV/s, EIS at 0.7V vs. SCE
Anode Electrocatalyst Selection

CH₄ adsorption, electrocatalytic activity

NiO

CO₃⁻² Adsorption

t-ZrO₂

Synthesis Procedure
NiO-t-ZrO$_2$ Synthesis and Characterization

- **Aqueous solution of** $0.4\text{M Ni(NO}_3\text{)}_2 + 0.1\text{M ZrOCl}_2$ (80:20) mole ratio, similar 0.5M total concentration
- **10M NaOH** added quickly, capped 24 hours
- **Rinsed** until Cl$^-$ free, AgNO$_3$ tested
- **Dried, calcined 500°C for 3hrs**
- Denoted (80:20)NiO:t-ZrO$_2$

- **SEM:** Blade-like t-ZrO$_2$, ~100 nm
- **Uniform distribution**
- **BET:** 97.6 m$^2$/g

- **XRD:** Primarily tetragonal phase ZrO$_2$
- **Slight peak shifts** indicate stacking faults
CVs:
- Additional anodic activity after Ni^{2+}/Ni^{3+} redox with CH\(_4\) present.

EIS:
- 87% resistance decrease.
- CH\(_4\) adsorbed by NiO, and oxidized.
- Oxygen donator (CO\(_3^{2-}\)) adsorbed by t-ZrO\(_2\).

Question: What product(s) formed?

Aqueous Batch Cell
- In-situ electrochemical FTIR
- Collect effluent for NMR

Collaboration with John Flake – LSU

- Anode effluent at 2V
- Condensed over dry ice
- Analyzed using $^1$H NMR

Continuous Flow Reactor
- Polarization (Performance)
- Chronoamperometry

Cell V: 2V Applied
- 40°C, 90% RH
- 2 Cases:
  - No Ionomer
  - 30 wt% Fumion FAA

Product Analysis: no ionomer

- Anode effluent collected at 2.0V applied

Graph showing mass spectrometry data with peaks labeled CO and HCHO.

Product Analysis: with ionomer

- Anode effluent collected at 2.0V applied

How are our Observations Affected by Temperature, Voltage, etc.?

- Product Analysis: Case 2 Steady-State Current vs. Voltage
MS Results vs. V (with ionomer)

- w/increasing Voltage:
  - Peaks at 29, 31 increase
  - 28 peak becomes visible at -1.75 V
  - CO$_2$ peak @ 44 decreases
New Pathways for Oxygenate Production from CH₄ at Room Temperature

- At low Applied Voltages:
  - Not enough energy to further oxidize the intermediates
- As $V_{\text{applied}} > 1.5$ V
  - What does this mean?
    - We should be able to optimize conditions for oxygenate production
  - Promise: Even in an unoptimized laboratory scale reactor, CO₂ emissions are very low.
    - 0.18 mol CO₂/mol CH₄
    - 60% Reduction in CO₂ compared to MSR
Summary

- **Carbonate has key advantages over hydroxide**
  - Weak nucleophile – membrane stability no longer an issue!
  - Unique Chemistries are possible

- **Carbonate Systems have Potential for High Impact**
  - Fuel Cells
  - CO$_2$ Pumping/Purification
  - Electrochemical Synthesis

- **Opportunities for Significant Progress Remain**
  - High efficiency carbonate selective electrocatalysts
  - Membranes designed for carbonate balance
We have demonstrated room temperature activation and conversion of CH$_4$ to oxygenates

- NiO:t-ZrO$_2$ bifunctional electrocatalyst
  - MeOH, HCHO, CO, CO$_2$
  - O$_2$ and CO$_2$ (through CO$_3^{2-}$ electrolysis, OER)

Limitations & Future: Quantification of products, precise tailoring of cell (geometry+operating conditions) to direct particular product formation

- Purchased Custom Agilent 7890B GC
  - FID + TCD (down to 1 ppm CO, CH$_3$OH; 10 ppm HCHO)
Acknowledgements

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  - Travis Omasta
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**FACILITIES:**

C2E2

Institute of Materials Science
Membranes Tested
- AMI-7001s (Membranes Internat.)
- AMB-SS (ResinTech)
- Ralex AMH-PAD (Mega a.s.)
- Excellion I-200 (SnowPure)
- MA-3475 (Lanxess Sybron)

All Membranes received in Cl⁻ form
- Exchanged to OH⁻ 1M KOH
- Soaked 1-30 days in 1M KOH
- Measured Conductivity

\[ R_{\text{mem}} = R_{\text{total}} - R_{\text{sol}} \]

\[ \sigma = \frac{l}{R_{\text{mem}} A} \]

CVs – Organic Product Oxidation

0.1M Na$_2$CO$_3$, 20mV/s
NiO Synthesis and Characterization

- 10M NaOH + 0.5M Ni(NO$_3$)$_2$
- Filtered and rinsed
- Dried, calcined 500°C 3h

SEM: Spherical 20-30nm particles

XRD: crystalline NiO
NiO-ZrO$_2$ XPS

- BE shifts suggest substantial NiO-ZrO$_2$ electronic interaction

<table>
<thead>
<tr>
<th>Configuration</th>
<th>(80:20)NiO:t-ZrO$_2$ composite</th>
<th>(80:20)NiO:t-ZrO$_2$ physical mixture</th>
<th>NiO</th>
<th>t-ZrO$_2$</th>
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<tbody>
<tr>
<td></td>
<td>Binding Energy (eV)</td>
<td>Binding Energy (eV)</td>
<td>Binding Energy (eV)</td>
<td>Binding Energy (eV)</td>
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<tr>
<td>O 1s</td>
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<td>528.4</td>
<td>530.8</td>
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<td>872.2</td>
<td>871.8</td>
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<td>182.9</td>
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<td>182.9</td>
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<tr>
<td>Zr 3d 3/2</td>
<td>183.7</td>
<td>185.3</td>
<td>--------</td>
<td>185.3</td>
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</table>
Three Electrode Cell Measurements

- Thin-Film Disk Electrodes
  - Cyclic Voltammetry (CV)
  - Electrochemical Impedance Spectroscopy (EIS)
    - Autolab PGSTAT302N

- Adams & Chittenden Scientific Custom Cell
  - Counter electrode: Pt flag
  - Reference electrode: SCE
NiO:ZrO$_2$ as CH$_4$ Electrocatalyst in OH$^-$?

- No activity for CH$_4$ in OH$^-$ electrolyte
- Expected result – OH$^-$ oxidizes by accepting H$^+$, unlikely at room temp

OH$^-$ oxidation:

CO$_3^{2-}$ oxidation:

Flow Cell Preparation

- Membrane Electrode Assembly (MEA)
  - **Cathode**: $\text{Ca}_2\text{Ru}_2\text{O}_7$ pyrochlore
  - **Anode**: (80:20)NiO:t-$\text{ZrO}_2$
  - **Membrane**: Ralex AM-PAD, exchanged to $\text{CO}_3^{2-}$
  - **Ionomer**: Two cell types
    - Case 1: no ionomer
    - Case 2: 30 wt.% Fumion FAA anion-exchange ionomer

- Equipment and Operating Conditions
  - Scribner 850e Multi-Range Fuel Cell Test System
  - 40°C and 90% relative humidity
  - 0.1 L/min gas flow rates
Polarization Curves

![Graph showing polarization curves with different gases and conditions.]

- **A**: N₂  
  - **C**: N₂
- **A**: CH₄  
  - **C**: N₂
- **A**: CH₄  
  - **C**: O₂ + 10% CO₂

**Current Density (mA/cm²)** vs **Cell Potential (V)**
Anion Composition – Carbonate Selective Catalyst

- Electrolyte equilibrium

\[
\begin{align*}
\text{Anode:} & \quad O_2 + 2CO_2 + 4e^- & \rightarrow & \quad 2CO_3^{2-} \\
\text{Cathode:} & \quad O_2 + 2H_2O + 4e^- & \rightarrow & \quad 4OH^- \\
OH^- + CO_2 & \rightarrow HCO_3^- \\
HCO_3^- + OH^- & \rightarrow CO_3^{2-} + H_2O
\end{align*}
\]
Question: How is the Carbonate Anion Formed?

- Direct vs. Indirect Pathway
  - Cathode (catalyst surface)
    - Direct: \( \text{O}_2 + 2\text{CO}_2 + 4\text{e}^- \rightarrow 2\text{CO}_3^{2-} \) [1]
    - Indirect: \( \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \) [2]
      \( \text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^- \) [3]
      \( \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \) [4]
  - Anode
    \( \text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \) [5]

How can we quantify the carbonate produced in each path?
Theoretical CO$_2$ Yield

$$N_{CO_2} = \int_{t_o}^{t_f} \frac{i(t)}{nF} dt = \frac{i \Delta t}{2F}$$

Measured CO$_2$

$$N_{CO_2} = \frac{M_{CaCO_3}}{MW_{CaCO_3}}$$

Selectivity, $S$

$$S = \frac{N_{meas}/N_{th}}{1 - N_{meas}/N_{th}}$$
Apparent Selectivity of Pt/C and Ca$_2$Ru$_2$O$_7$ for CO$_3^{2-}$ ORR

**Theoretical CO$_2$ Yield**

\[ N_{CO_2} = \int_{t_0}^{t_f} \frac{i(t)}{nF} \, dt = \frac{i \Delta t}{2F} \]

**Measured CO$_2$**

\[ N_{CO_2} = \frac{M_{CaCO_3}}{MW_{CaCO_3}} \]

**Selectivity**

\[ S = \frac{N_{meas}/N_{th}}{1 - N_{meas}/N_{th}} \]

<table>
<thead>
<tr>
<th></th>
<th>Pt/C</th>
<th>Ca$_2$Ru$_2$O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Theoretical</td>
<td>64</td>
<td>92</td>
</tr>
<tr>
<td>Selectivity</td>
<td>1.8</td>
<td>11.5</td>
</tr>
</tbody>
</table>

AEM

Anode

Cathode

CO$_3^{2-}$

OH$^-$
Electrochemical Standard Addition of CO₂

Increasing the off time promotes indirect pathway
On-Off AC Polarography

- OFF time allows $\text{CO}_3^{2-}$ to form only by Indirect Pathway
- Varying OFF time similar to standard addition method in chemistry
Experimental Results

\[
\begin{align*}
\text{0.5 Sec ON} & \quad 2\text{OH}^- + \text{CO}_2 & \rightleftharpoons & \text{CO}_3^{2-} + \text{H}_2\text{O} \\
\text{2.0 Sec ON} & \quad \frac{k_f}{k_b} = K = \frac{[\text{CO}_3^{2-}]}{[\text{OH}^-]^2 \cdot P_{\text{CO}_2}}
\end{align*}
\]
Mathematical Model

\[ 2\text{OH}^- + \text{CO}_2 \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O} \]

\[
\frac{d[\text{OH}^-]}{dt} = -2k_fP_{\text{CO}_2}[\text{OH}^-]^2 + k_b[\text{CO}_3^{2-}] \]

\[
\frac{d[\text{CO}_3^{2-}]}{dt} = 2k_fP_{\text{CO}_2}[\text{OH}^-]^2 - k_b[\text{CO}_3^{2-}] \]

\[
\frac{k_f}{k_b} = K = \frac{[\text{CO}_3^{2-}]}{[\text{OH}^-]^2 \cdot P_{\text{CO}_2}} \]

\[
K = \frac{N_{\text{CO}_3^{2-}}}{(N_{\text{OH}^-})^2 \cdot P_{\text{CO}_2}} \cdot V = K' \cdot V \]

\[
\frac{d\varepsilon}{dt} = 2 \frac{k_f}{V} P_{\text{CO}_2}(N_{\text{OH}^-}^0 - 2\varepsilon)^2 - \frac{k_f}{V} \frac{1}{K'} (N_{\text{CO}_3^{2-}}^0 + \varepsilon) \]
Mathematical Model

- **Generalized Solution**

\[
\varepsilon(t) = \frac{1}{16 \cdot K' \cdot P_{CO_2}} \left[ 1 - \frac{1}{K' \sqrt{32K' \cdot N_{CO_3}^0 \cdot P_{CO_2} + 16K' \cdot N_{OH}^0 \cdot P_{CO_2} + 1}} \right] \\
\quad \times \tanh \left( \left( \frac{c}{2} - \frac{k_f t}{2K'} \right) \sqrt{32K' \cdot N_{CO_3}^0 \cdot P_{CO_2} + 16K' \cdot N_{OH}^0 \cdot P_{CO_2} + 1} \right) + \frac{N_{OH}^0}{2}
\]

- **Boundary Conditions**

- \( \varepsilon(t=0) = 0 \)
- \( \varepsilon(t=0.69) = 1 \)
- **Rate of CO₃²⁻ Production**
  \[ \text{Rate of CO}_3^{2-} \text{ Production} = \Sigma \text{[Chemical + Electrochemical rates]} \]

  \[ \frac{N_{CO_3^{2-}}}{N_{OH^-}} = \frac{d[CO_3^{2-}]}{dt} = \frac{\text{ChemRate}_{CO_3^{2-}} + \text{ElectRate}_{CO_3^{2-}}}{\text{ChemRate}_{OH^-} + \text{ElectRate}_{OH^-}} \]

- **Total moles of electrons**
  \[ \frac{i}{F} = 2 \times \text{ElectRate}_{CO_3^{2-}} + \text{ElectRate}_{OH^-} \]

- Combining equations, we can now solve for the electrochemical rate of production of CO₃²⁻!
Electrochemical rate of Carbonate Production

\[ \text{ElectRate}_{CO_3^{2-}} = \frac{i \cdot N_{CO_3^{2-}}}{\left(2 \cdot N_{CO_3^{2-}} + N_{OH^{-}}\right) \cdot F} - \text{ChemRate}_{CO_3^{2-}} \]

- Solution at (t=0) tells us the electrochemical rate of production of carbonate at the surface of the catalyst
Selectivity of Pt/C

- Electrochemical rate of production of carbonate at the surface of the catalyst

- (Pt/C)

\[
\text{ElectRate}_{CO_3^{2-}} = 3.4 \times 10^{-9} \frac{\text{mol}}{\text{sec}}
\]

\[
\text{ElectRate}_{OH^-} = 45.0 \times 10^{-9} \frac{\text{mol}}{\text{sec}}
\]

\[
S = \frac{2 \times \text{ElectRate}_{CO_3^{2-}}}{\text{ElectRate}_{OH^-}} \frac{i}{2*F} = \frac{\text{ElectRate}_{CO_3^{2-}}}{1 - \frac{i}{2*F}} = 0.15
\]
Results using Ca₂Ru₂O₇

- Direct Pathway Dominates for all samples
- Real S ≥ 11.5