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Los Alamos, NM, 87545

Project ID: fc043
**Overview**

**Timeline**
- Project start – September 2009
- Project end – September 2011
- Percent complete – 35%
  - Polymer synthesis (50%)
  - Catalyst synthesis (20%)
  - MEA processing (10%)

**Budget**
- Total Project Funding: $1,320k
- Funding Received in FY 09: $462k
- Funding for FY 10: $528k
  No cost shared

**Barriers**
- A. Durability
- B. Cost
- C. Electrode Performance

**Partners**

**Project Lead:**
- Yu Seung Kim
- Dae Sik Kim
- Andrea Labouriau

**Collaborators:**
- Cy Fujimoto
- Michael Hipps
- Sri Narayan
- Chuck Hays

**Interactions:**
- Cellera Technologies (S. Gottesfeld)
- Ovonic Fuel Cell Company (R. Privette)
- Virginia Tech. (J. McGrath)
- Univ. New Mexico (P. Atanassov)
- NREL (B. Pivovar)
- Canada NRC (M. Guiver)
Relevance

Objectives

- Develop anion exchange polymer electrolytes that have **high hydroxyl conductivity** and **stability** in high pH conditions.

- Demonstrate an improved single cell performance of solid-state alkaline fuel cells using the polymer electrolytes and non-precious metal catalyst.

Impact on Technical Barriers

<table>
<thead>
<tr>
<th>ISSUES</th>
<th>Technical Barriers</th>
<th>Recent Reported Value</th>
<th>Technical Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td>Significantly low due to low mobility of OH(^-), carbonate formation etc.</td>
<td>27 mS/cm (20(^\circ)C) [1]</td>
<td>&gt; 50 mS/cm at 80(^\circ)C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34 mS/cm (50(^\circ)C) [2]</td>
<td></td>
</tr>
<tr>
<td>Stability</td>
<td>Fast degradation of AEM at high PH conditions</td>
<td>&gt; 48 h 1M KOH at 60(^\circ)C [1]</td>
<td>&gt; 500 h at 80(^\circ)C in 1 M NaOH solution</td>
</tr>
<tr>
<td>Electrode Processing</td>
<td>Poor solubility of AEM and lack of understand electrode structure</td>
<td>196 mW/cm(^2) H(_2)/O(_2), 80(^\circ)C [1]</td>
<td>&gt; 200 mW/cm(^2) H(_2)/air at 80(^\circ)C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>130 mW/cm(^2) H(_2)/O(_2), 50(^\circ)C [3]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>94 mW/cm(^2), H(_2)/O(_2), 50(^\circ)C [2]</td>
<td></td>
</tr>
</tbody>
</table>

Approach - Stability

- **Major degradation route** of anion exchange polymer electrolytes is **nucleophilic substitution ($S_N^2$)**. The reaction rate usually **inverse to the basicity** of the tertiary amine.

- Guanidine base is **10,000 times more basic*** than tri-alkyl amine (TAA) base.

- **Resonance structure** of guanidine base possibly further enhances the cation stability and hydroxyl conductivity.

- Guanidine bases are **commercially available and cheap**. ($300/kg, Aldrich)

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*Nucleophilic Substitution ($S_N^2$)*

**Basicity**

1: Triethylamine: H$_2$O (1:1 v/v)
2: Tetramethylguanidine: H$_2$O (1:1 v/v)
3: 1 M NaOH

* http://www.cem.msu.edu/~reusch/VirtualText/amine1.htm
Approach – Electrode Performance

Hydrocarbon (HC) based polymer electrolytes have lower gas permeability (and chain mobility) than perfluorinated (PF) based polymer electrolytes.

Low gas permeability is desirable to membrane but undesirable to electrode binder since it gives a detrimental effect on electrode performance.

Ideal combination

HC membrane (SNL, LANL) + Perfluorinated ionomer (LANL) + Non-precious metal catalyst (JPL)

Non-aqueous Quaternization

Traditional aqueous quaternization*

Traditional aqueous quaternization produces large discrepancy between theoretical IEC and actual IEC while non-aqueous quaternization provides precise control of amination.

Impact of Quaternization on Polymer Properties

Water uptake (Br⁻) vs. IEC (Br⁻)

- Aqueous Quaternization
- Non-aqueous Quaternization
Impact of Quaternization on Polymer Properties

Uniformity of cation distribution can reduce water uptake and enhance the anionic conductivity under fully hydrated conditions!!!
Synthesis of Hydrocarbon Guanidine Base (HCGB) Homopolymer

a) 1) DMAc, Toluene
   2) Formic acid, H₂O₂

b) DMAc, 130°C, tetra methyl guanidine (TMG)

c) Methylation
   NaOH 0.5 M

IECₜ = 1.2 meq./g
Incorporation of Guanidine Base into Nafion® Precursor

Nafion® precursor

\[
\begin{array}{c}
\text{F}_2 \quad \text{C} \quad \text{C} \\
\text{F} \\
\text{O} \quad \text{C} \quad \text{C} \\
\text{F}_2 \quad \text{F} \quad \text{F} \\
\text{S} \quad \text{O} \quad \text{F}_2 \\
\text{C} \quad \text{F}_3
\end{array}
\]

Nafion®-TMG salt form

Converted to proton form after acidification

Cation exchange polymer electrolyte

Converted to hydroxyl form after methylation

Anion exchange polymer electrolyte

PFGB precursor

transmittance

wavenumber (cm\(^{-1}\))

From aqueous soln.

From DMF soln.

From dry DMF
Methylation of PFGB Precursor

PFGB precursor

\[(\text{CH}_3\text{O})_2\text{SO}_4 \rightarrow \text{PFGB (IEC}=0.9 \text{ meq/g})\]

\[\text{PFGB precursor}\]

\[\text{PFGB (IEC}=0.9 \text{ meq/g)}\]

- **Transmittance**
  - 0 hr
  - 3 hr
  - 7 hr
  - 9 hr
  - 1 day

- **Wavenumber (cm}^{-1}\)
  - 1700
  - 1650
  - 1600
  - 1550
  - 1500
  - 1450

- **Resonance structure**
  - 1: 162 ppm
  - 2: 39.5 ppm
  - 1: 156 ppm
  - 2: 41 ppm
  - 3: 52 ppm

- **\[^{13}\text{C}\] solid state NMR**

\[\text{Carbons in Nafion}\^\text{®}\]

- 1: 156 ppm
- 2: 41 ppm
- 3: 52 ppm
Ionic Conductivity of HCGB and PFGB as a Function of Temperature

The conductivity was measured in water after boiling and N₂ purge (without CO₂)
Hydroxyl Conductivity Comparison at RT

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water uptake (wt.%)</th>
<th>IEC (meq./g)</th>
<th>(\sigma) (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1C1(^a)</td>
<td>19</td>
<td>0.5</td>
<td>0.13</td>
</tr>
<tr>
<td>PSQNOH50 (^b)</td>
<td>15</td>
<td>1.9</td>
<td>22</td>
</tr>
<tr>
<td>PSQNOH80 (^b)</td>
<td>86</td>
<td>2.8</td>
<td>65</td>
</tr>
<tr>
<td>A901 (^c)</td>
<td>15</td>
<td>2.6</td>
<td>38</td>
</tr>
<tr>
<td>A201 (^c)</td>
<td>25</td>
<td>1.7</td>
<td>42</td>
</tr>
<tr>
<td>AAEM (^d)</td>
<td>40</td>
<td>-</td>
<td>27</td>
</tr>
<tr>
<td>TMBPA (^e)</td>
<td>51</td>
<td>0.7</td>
<td>38</td>
</tr>
<tr>
<td>PSGOH (^f)</td>
<td>17</td>
<td>1.2</td>
<td>12</td>
</tr>
<tr>
<td>PSGOH (^f)</td>
<td>55</td>
<td>1.9</td>
<td>45</td>
</tr>
<tr>
<td>QAPSF1 (^g)</td>
<td>50</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>QAPSF2 (^g)</td>
<td>100</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>SNL HC TMA</td>
<td>46</td>
<td>1.32</td>
<td>39</td>
</tr>
<tr>
<td>LANL HC GB</td>
<td>8.5</td>
<td>1.2</td>
<td>21</td>
</tr>
<tr>
<td>LANL PFGB</td>
<td>15</td>
<td>0.9</td>
<td>41</td>
</tr>
</tbody>
</table>

a. Poly(CTFE-alt-VE) - Bruno Ameduri
b. Poly(arylene ether sulfone) - Suobo Zhang group
c. Hydrocarbon polymer – Tokuyama Corporation
d. Poly(ethylene-co-tetrafluoroethylene) – John R. Varcoe
e. Poly(arylene ether sulfone) – Michael Hipps
f. Poly(arylene ether sulfone) – Suobo Zhang group
g. poly(arylene ether sulfone) - Paul A.Kohl group
Stability of PFGB

Proposed Degradation Mechanism
- Nucleophilic *Suicidal* attack

Conductivity of PFGB in boiling water

Hydroxyl conductivity (mS/cm)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Hydroxyl Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>0</td>
</tr>
<tr>
<td>60°C</td>
<td>20</td>
</tr>
<tr>
<td>80°C</td>
<td>40</td>
</tr>
</tbody>
</table>

13C-Solid NMR

Los Alamos National Laboratory
2010 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting
Effect of Electron Density on Stability

Stability increased by higher electron density!!
Future Works – Polymer Chemistry

**Major focus**
- Cation Stability (LANL, SNL)
  
  *Electron donating spacer*

  ![Chemical structure](image)

**Other issue**
- Proton conductivity (LANL, SNL)
  
  *Increasing ion exchange capacity*
  
  *Partial fluorination*
  
  *Copolymer architecture*

- Polymer stability (LANL, SNL)
  
  *Removing sulfone group*

- Continuing investigation of TMA based system (SNL)
Future Works – Electrode and MEA

- Synthesis of Nano-structured thin films (JPL)
  - Prepare sputter-deposited coating on multi-electrode array
  - Electrochemical screening tests and down select catalyst
  - Sputterdeposit catalysts on to NSTF materials

- Electrode optimization and MEA fabrication (JPL, LANL)

- Fuel cell test (JPL, LANL)
Collaborations

Sub Contractors
• Sandia National Laboratory: Polymer Synthesis, extensive collaboration.
• Jet Propulsion Laboratory: Electrode Preparation, extensive collaboration.

Industry
• Cellera Technologies (S. Gottesfeld): Material characterization and licensing issue, moderate interaction.

University
• Virginia Tech. (J. McGrath) and Penn State (M. Hickner): Polymer synthesis, occasional.
• Univ. New Mexico (P. Atanassov): Catalyst synthesis, occasional.

Federal Laboratory
• National Renewable Energy Laboratory (B. Pivovar) through DOE BES Program: cation stability, occasional.
• Los Alamos Neutron Science Center (R. Hjelm) through DOE Applied Science Program: SANS experiments and modeling, moderate interaction.
• Los Alamos National Laboratory (P. Zelenay) through DOE Advanced Catalyst Program: Catalyst issue in alkaline fuel cells, moderate interaction.
• Canada NRC (M. Guiver) through DOE Technical Assistant Program): Polymer synthesis, occasional.
Summary

Synthesis of high MW guanidine base membrane

Milestone 1
March 1, 2010

Highly conductive/stable anion exchange membrane

Milestone 2
September 1, 2010

Optimized electrode formulation and MEA processing Procedure

Milestone 3
June 1, 2011

Current Status (as of April 8, 2010)

<table>
<thead>
<tr>
<th></th>
<th>M2 Criteria</th>
<th>HCGB</th>
<th>PFGB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$ (S/cm)</td>
<td>0.05</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>WU (wt.%)</td>
<td>60</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>$\sigma$ reduction (80°C, 1M NaOH)</td>
<td>10% (500 h)</td>
<td>42 % (380 h)</td>
<td>Not stable</td>
</tr>
</tbody>
</table>

If stable PFGB ionomer is unavailable,

Opt. Milestone 2
September 1, 2010

Development of NSTF Electrode
Supplemental Slides
Stability of Methylated TMG in 0.5 M NaOH Solution

Methylated tetermethyl guanidine is stable in alkali conditions!!!
Conductivity of different Counter ion 1

➢ The conductivity was measured in water after boiling and N₂ purge (without CO₂)

![Conductivity Graph](image-url)

OH⁻ Form : $\sigma_{\text{OH}^-}$

CO₃²⁻ Form : $\sigma_{\text{OH}^-} + \sigma_{\text{CO}_3^{2-}}$

OH⁻ form : $\sigma_{\text{OH}^-}$

CO₃²⁻ form : $\sigma_{\text{OH}^-}$ & $\sigma_{\text{CO}_3^{2-}}$

Conductivity was measured in water after boiling and N₂ purge (without CO₂).
Effect of CO$_2$ on Conductivity

OH$^-$ Form was replaced with HCO$_3^-$ form by the absorption of CO$_2$ from air.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 \\
\text{pH} > 6.5 & \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{pH} > 10.4 & \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]