Advanced Materials for Fully-Integrated MEAs in AEMFCs

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Los Alamos National Laboratory
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Overview

Timeline
- Project start date: 11/2/2015
- Project end date: 11/2/2018
- Percent complete: 60%

Budget
- Total project funding: $3,060K
  - DOE share: 98%
  - Contractor share: 2%
- Funding received in FY17: $1,020K
- Total DOE Funds Spent*: $1,040K
  *As of 4/26/2017

Barriers
- B. Cost
- C. Electrode performance
- A. Durability

Project lead
- Los Alamos National Laboratory
  - Yu Seung Kim

Partners
- Sandia National Laboratory
  - Cy Fujimoto
  - Michael Hibbs
- Rensselaer Polytechnic Institute
  - Chul Sung Bae
- Argonne National Laboratory
  - Vojislav Stamenkovic
Relevance

Objective
- Development of improved AEMs, ionomeric binders and integration of catalysts and AEMs into high-performance MEAs.

Technical Target

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>ASR</td>
<td>(\Omega/\text{cm}^2)</td>
<td>0.2</td>
<td>(\leq 0.1)</td>
<td>0.05</td>
</tr>
<tr>
<td>AEMFC Performance</td>
<td>mA/cm(^2) at 0.6 V</td>
<td>980 (3.0 atm)(^1)</td>
<td>600 ((\leq 1.5) atm)</td>
<td>1,610 (3.0 atm)</td>
</tr>
<tr>
<td>AEM Durability</td>
<td>ASR after 500 h run at 600 mA/cm(^2)</td>
<td>0.8 after 300 h run at 0.3 V</td>
<td>0.1</td>
<td>0.05 after 300 h run at 0.3 V</td>
</tr>
<tr>
<td>AEMFC Durability</td>
<td>% voltage loss after 2000 h run at 600 mA/cm(^2) at (\geq 60^\circ)C</td>
<td>60% after 300 h run at 0.3 V at (60^\circ)C(^3)</td>
<td>&lt; 10% (2Q, 2019)</td>
<td>Not evaluated yet</td>
</tr>
</tbody>
</table>

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AEM Stability (2015-2016)
- Polymer backbone stability: Aryl-ether free polymer backbone.
- Cationic group stability: Alkyl ammonium or resonance stabilized cationic group.

AEMFC Performance (2016-2017)
- Benzene adsorption at HOR potential:
  (i) Synthesis of ionomers with less-benzene.
  (ii) Implementation of Pt-Ru alloy catalyst.

AEMFC Durability (2017-2018)
- Time-dependent cation-hydroxide-water co-adsorption
- Investigating other performance degradation mechanism
### Approach: Milestone & Go-No-Go Decision

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone &amp; Go-No-Go</th>
<th>Status# (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mar. 2016</td>
<td>Down-select AEM</td>
<td>100 (Feb. 2016)</td>
<td>Selected poly(phenyl alkylene) &amp; Diels-Alder poly(phenylene)s</td>
</tr>
<tr>
<td>Sep. 2016</td>
<td>Assess baseline AMFC performance</td>
<td>100 (Nov. 2016)</td>
<td>Accomplished with testing 20+ MEAs</td>
</tr>
<tr>
<td>Dec. 2016</td>
<td>Down-select ionomeric binder</td>
<td>80</td>
<td><strong>Delayed due to the delayed HOR study</strong></td>
</tr>
<tr>
<td>Mar. 2017</td>
<td>In-situ AEM ASR measurement; ( \leq 0.1 , \Omega , \text{cm}^2 ) for 500 h at 600 mA/cm(^2) (G-NG)</td>
<td>80</td>
<td>Obtained 0.05 ( \Omega , \text{cm}^2 ) for 300 h (stopped test due to the gradual fuel cell performance loss)</td>
</tr>
<tr>
<td>SEP. 2017</td>
<td>Integrate MEAs using down-selected AEM and ionomer; <strong>Peak power density</strong> &gt; 0.6 W/cm(^2) in H(_2)/O(_2) (Milestone)</td>
<td>100 (Apr. 2017)</td>
<td>Obtained 1 W/cm(^2) peak power density (used commercial Pt-Ru alloy catalyst)</td>
</tr>
<tr>
<td>Dec. 2017</td>
<td>Down-select HOR catalyst</td>
<td>30</td>
<td>Selected PtRu alloy catalyst</td>
</tr>
<tr>
<td>Mar. 2018</td>
<td>AMFC performance with down-selected HOR catalyst; <strong>Peak power density</strong>: 1 W/cm(^2) (Milestone)</td>
<td>90</td>
<td>Obtained 1 W/cm(^2) peak power density (used commercial Pt-Ru alloy catalyst)</td>
</tr>
</tbody>
</table>

# as of April 26, 2017, *result shown in Reviewers Only Slide R1.
Anion Exchange Membranes Developed from This Project

- Styrene-Ethylene-Butylene-Styrene Triblock Copolymer (SEBS series)
  - Developed at RPI (Mohanty & Bae)
  - Flexible Elastomeric AEMs

- Poly Bi-(or Ter-)Phenyl Alkylene (PBPA series)
  - Developed at RPI (Lee, Park & Bae)
  - High M_w Engineering Plastics

- Hexamethyl Ammonium Poly(Phenylene) (TMAC6PP series)
  - Developed at SNL (Hibbs & Fujimoto)
  - Whole Phenylene Backbone by Diels-Alder reaction

- Phenyl Guanidinium Poly(Phenylene) (PGP series)
  - Developed at SNL & LANL (Fujimoto & Kim)
  - Extended-resonance Stabilization

- Down-selected PBPA for AEM applications.
- Down-selected TMAC6PP for MEA study.
- Developing PGP for a potential ionomer candidate.

Provided the synthesis and alkaline stability of SEBS, PBPA PGP series in the Technical Back-up Slide T1-T3.
**Ex-situ Alkaline Stability of TMAC6PP AEM**

- **Highlight**: No conductivity & structural changes for TMAC6PP after 0.5 M NaOH treatment at 80°C for 3600 h.
**Ex-situ Alkaline Stability of Phenyl Guanidinium Ionomer**

**Graph:**
- **Y-axis:** Hydroxide conductivity (mS/cm)
- **X-axis:** Time (h)
- **Legend:**
  - PGP (0.5 M NaOH, 80°C)
  - Ketone-PP (0.5 M NaOH, 80°C)

**Graph Details:**
- The conductivity of PGP remains stable over time, indicating good stability.
- Ketone-PP shows a significant decrease in conductivity over time.

**FTIR:**
- **CN3 C=O peak change during stability test**
- **Pristine**
- **1000 h**
- **10,000 h**

**Extended-resonance Stabilization Concept**

- **Unstable**
- **Stable**

**Key Points:**
- No chemical structural change after 10,000 h 0.5 M NaOH or 100 h at 80°C, 4 M NaOH* conditions.
- **Highlight:** Developed alkaline-stable ionomer by extended-resonance stabilization.
**In-situ Areal Specific Resistance Improvement**

**F-PAE (2010)**
- Membrane thickness: 80 µm
- Degradation mechanism:
  \[
  \text{H}_2/\text{O}_2 \text{ at } 0.3 \text{ V, } 60^\circ\text{C}
  \]

**ATM-PP (2013)**
- Membrane thickness: 80 µm
- Degradation mechanism:
  \[
  \text{CO}_2 + 2(-\text{R}_4\text{N}^+) \text{ (OH)} \rightarrow (-\text{R}_4\text{N})_2 \text{ (CO}_3)^{-2} + \text{H}_2\text{O}
  \]

**TMAC6PP (2017)**
- Membrane thickness: 50 µm
- Degradation mechanism:
  \[
  \text{H}_2/\text{O}_2 \text{ at } 0.3 \text{ V, } 60^\circ\text{C}
  \]

**Major Degradation Mode**
Polymer backbone degradation due to aryl-ether cleavage reaction.


**Major Degradation Mode**
Neucloephilic substitution of benzyltrimethyl ammonium group.

**Chem. Mater. 26, 5675 (2014)**

**Major Degradation Mode**
(bi)-carbonation exchange reaction (reversible).
Removing Carbonate Ions by Replenishing Cell

**AEM:** TMAC6PP (thickness: 40 µm), **Ionomer:** TMAC6PP, **Catalyst:** Pt/C 0.2 mgPt/cm² for both anode and cathode

**Graph 1:**
- Time (h) 0 50 100 150 200 250 300 350
- ASR (Ω cm²) 0.00 0.05 0.10 0.15 0.20
- i (A/cm²) 0.0 0.1 0.2 0.3 0.4

Tested in H₂/O₂ at 80°C at 0.3 V

**Graph 2:**
- Time (h) 0 50 100 150 200 250 300 350
- ASR (Ω cm²) 0.00 0.05 0.10 0.15 0.20

**FT-IR of TMAC6PP AEM after 100 h Test**

- Absorbance vs Wavenumber, cm⁻¹
- Pristine vs 100 h in Fuel cell

- Maintained low ASR after replenishing cell with 0.5 M NaOH.
- No indication of AEM chemical degradation.
- **Highlight:** Achieved 0.05 Ω cm² ASR for 300 h.
- **Next step:** Improving AEMFC performance

Other stable ASR examples are shown in Technical-Backup Slide T4
Benzene Adsorption on Pt (New Performance Inhibition Mechanism)

Adsorption Position (side view) of BTMA on Pt(111) at U = 0 V

Effect of Applied Potential on the Interaction

\[\Delta E_{ad,field} = E_{surface + ad, field} - E_{surface, field} - E_{ad}\]

Conformational change

\[U = 3\AA \times E_{field}\]

DFT calculation, Ivana Gonzales (UNM, LANL)
Impact of Benzene Ring Containing Ionomer on HOR of Pt

HOR voltammogram of ionomer-coated Pt (after preconditioning at 1.4 V for 20 sec.)

* For synthesis, see Macromolecules 46, 7826 (2013)

** Highlight:** First identified benzene adsorption driven HOR inhibition

* Film thickness normalized

** Highlight:** First identified benzene adsorption driven HOR inhibition
Effect of Alloying Pt with Mo, Ni, and Ru on BTMA Adsorption

Pt alloy HOR Voltammogram in BTMAOH

Adsorption energies of BTMA on Pt, Pt$_3$Mo, PtNi and PtRu

<table>
<thead>
<tr>
<th>$\Delta E$ (eV)</th>
<th>conf1</th>
<th>conf2</th>
<th>conf3</th>
<th>conf4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>-2.30</td>
<td>-2.15</td>
<td>-1.51</td>
<td>-2.15</td>
</tr>
<tr>
<td>Pt$_3$Mo(111)</td>
<td>-1.61</td>
<td>-1.67</td>
<td>-0.99</td>
<td>-1.71</td>
</tr>
<tr>
<td>PtNi(111)</td>
<td>-1.45</td>
<td>-1.56</td>
<td>-0.47</td>
<td>-1.52</td>
</tr>
<tr>
<td>PtRu(111)</td>
<td>-1.32</td>
<td>-1.42</td>
<td>-0.37</td>
<td>-1.39</td>
</tr>
</tbody>
</table>

Alloying Pt with Ru decreases the benzene adsorption on Pt surface.

New direction: Benzene adsorption mitigating strategy: 1. Use Pt/Ru alloying catalyst (ANL); 2. Use phenyl free or less phenyl containing ionomer (LANL, RPI).
Synthesis and Characterization of Pt$_1$Ru$_8$ Nanoparticles

- **Before annealing**
  - 0.1 g scale synthesis
  - 20% (Pt+Ru)
  - TEM images

- **After 185°C in air**
  - Current (mA) vs. Potential (V vs. RHE)
  - CV 0.1 M KOH
  - HOR/HER
  - Double layer corrected

- **0.6 g scale synthesis**
  - (15% Pt+Ru)
  - TEM images
  - (~3 nm)
  - Achieved 6X scale up synthesis.
  - Demonstrated higher HOR/HER activity than Pt/C.
  - Observed particle sintering after annealing.
Achievement: AEMFC Performance

- **Highlight:** Achieved 1 W/cm² peak power density with commercial Pt/Ru catalyst and hydrocarbon AEM/ionomer.
- **Next step:** Use ANL catalysts with lower PGM loading.

**December 2013**

- AEM: ATM-PP
- Ionomer: ATM-PP
- Catalyst: Pt black 3 mg Pt/cm² for both anode and cathode

**January 2017**

- AEM: Poly(terphenyl alkylene) (down-selected)#
- Ionomer: AS4 (Tokuyama)
- Catalyst: Pt/C 0.6 mg Pt/cm² for both anode and cathode

**April 2017**

- AEM: Ter(Phenyl) Alkylene (down-selected)
- Ionomer: FLN2-55* (candidate)
- Catalyst: Pt₂–Ru₁/C 0.5 mg Pt/cm² (anode), Pt/C 0.6 mg Pt/cm² (cathode)

* See Reviewer-only Slide R2 for synthetic procedure

# See Technical Backup Slide T2 for synthetic procedure
HOR activity of Pt/C in TMAOH decreases with time as the cationic group adsorption occurs.

HOR Degradation Mechanism

Impedance of Pt/C in 0.1 M TMAOH at OCV

Diffusion related arc (see Technical Backup Slide T5)

H₂ Permeability in H₂SO₄ and KOH at 30°C#

H₂SO₄

KOH

Concentration (M)

0 2 4 6 8 10 12 14 16

0.1 1 10 100

Surface IR Spectra change during Chronoamperometry of Pt at 0.1 V vs. RHE

νₐₛₛ (OH<sub>water</sub>)  Pt surface
νₐₛₛ (OH<sub>hydroxide</sub>)

55 min

15 min

Initial

Solution

Absorbance

Wavenumber / cm⁻¹

3600 3400 3200 3000 2800 2600 2400

• HOR activity loss of Pt is due to the cation-hydroxide-water co-adsorption which blocks the H₂ access through OH⁻ rich adsorbed layer.

Next step: Mitigating strategy for the co-adsorption: Use bulky cations*

• See Reviewers Only Slide R4 for the impact of cationic group structure on the co-adsorption.

# J. Electrochem. Soc. 113, 301-305, 1966
Responses to Previous Year Reviewers’ Comments

- **It is unclear for what applications AEMFCs will be used.**
  AEMFC approaches are at a much earlier stage and much is still unknown about the ultimate limits of AEMFCs. For this year, we have demonstrated 1 W/cm² peak power density with the materials we developed. While we agree that we still have long way to go for a competitive system with PEMFCs, the performance gap between AEMFCs and PEMFCs is getting smaller than the time project started.

- **The project should eliminate the perfluorinated ionomer work or at least ensure that it does not overlap with NREL’s work.**
  We included the perfluorinated ionomer work because i) the perfluorinated work was originally proposed ii) our early work back in 2012 indicated an excellent AEMFC performance with perfluorinated ionomer. However, our recent results suggested that hydrocarbon materials could perform well. So we decided to eliminate the perfluorinated ionomer work from this project.

- **The approaches to low-PGM loading or non-PGM were not addressed.**
  Although the use of non-PGM catalysts is the ultimate goal for AEMFCs, this project focuses on critical issues related to the AEMs and ionomers. DOE is supporting AEMFC catalyst development through other projects. The role of our catalyst partners is to provide high-performing catalysts rather than develop new catalysts.
Collaboration and Partners

Yu Seung Kim (Project Lead), Sandipkumar Maurya, Kwan-Soo Lee, Hoon Chung, Ivana Matanovic

AEM & Ionomer Synthesis
Cy Fujimoto (PI), Michael Hibbs

HOR Catalyst Preparation
Vojislav Stamenkovic (PI), Rongyue Wang, Dongguo, Li

AEM & Ionomer Synthesis
Chulsung Bae (PI), Sangtak Noh, Jongyeob Jeon, Junyoung Han, Eun Joo “Sarah” Park

SNL AEMs sent to a large chemical manufacture to test for commercialization.

Other Interactions
- Giner Inc. - Hui Xu
- Shanghai Jiao Tong Univ. - Hong Li
- Amsen - Hongxing Hu
- IRD Fuel Cells, LLC - Madeleine Odgaard
- Proton Onsite - Kathy Ayers
- Nanosonic Inc. - William Harrison
- Univ. of New Mexico - Alexey Serov
Remaining Challenges and Barriers

- **Cationic group-hydroxide-water co-adsorption.**
  Design new ionomers which are less adsorbed on catalyst surface.

- **High purity HOR ionomer dispersion.**
  Make a homogeneous dispersion with hydroxide form ionomer which has less phenyl groups.

- **AEMFC MEA integration.**
  Incorporate high-performing HOR and ORR catalysts with preferably low or non-PGM loading.

- **Scale-up AEM and ionomer synthesis.**
  Continues to produce 10-50 g batch membranes by SNL and RPI. We are also looking for industrial partners to produce the AEMs in pilot scale (up to kg).

- **Carbonation issue.**
  Plan to purchase CO₂ degassing equipment for supplying carbonate-free water system.
Proposed Future Work

**Remainder of FY 2017**

AEM synthesis and characterization (SNL, RPI)
- Lab-scale synthesis (10-50g) of AEMs for MEA integration and testing. AEMs include poly(bi(ter)phenyl alkylene)s and Diels-Alder poly(phenylene)s.

Ionomer development (LANL, SNL, RPI)
- Produce small quantity ionomers (1 to 5g) for down-selection to complete 2016 Q4 milestone. Potential candidate ionomers include polyfluorene and polystyrene.

HOR study (LANL, ANL)
- Prepare 200 to 500 mg of PtRu alloy catalyst for HOR reaction.
- Perform RDE, microelectrode, surface FTIR and neutron reflectometry experiments.

**FY 2018**

MEA integration and optimization (LANL, SNL, ANL, RPI)
- Investigate variables that impact fuel cell performance and durability. Variables include GDL, microporous layer, membrane thickness, I/C ratio, catalyst loading, type of catalyst support, and humidification.

AEMFC performance and durability (LANL)
- Evaluate the performance and durability of the integrated AEMFC MEA.

Any proposed future work is subject to change based on funding levels.
Technology Transfer Activities

- **RPI:** Contacted several small business companies to produce large scale AEMs during FY 17.

- **SNL:** Co-PI is participating in DOE’s Lab Corps program, which has included contacting two large manufacturers to produce poly(phenylene) AEMs. One foreign manufacturer completed the AEM evaluation.

- **LANL:** Participated in a SBIR program to license AEM technology. Also participated in several Small Business Voucher (SBV) projects to transfer AMFC MEA technology.

More than 10 patents on AEM and ionomer materials are available.

- **FY 2017 patent and patent applications**
  - **SNL:** “Poly(phenylene alkylene)-based ionomers” US 9,534,097 (2017).
  - **SNL & LANL:** “Poly(phenylene)based anion exchange polymers and method thereof” 62/274,592, (2016).
  - **LANL:** “Polyol-based compositions comprising cationic group functionalized poly(phenylene) polymers” 15/204,523 (2016).
## Summary

### Objective:
Development of improved AEMs, ionomeric binders and integration of catalysts and membranes into high-performance MEAs.

### Relevance:
Aiming to make AEMFC system competitive to PEMFCs in terms of performance and durability. Identifying performance barrier and degradation mechanism of AEMFCs can contribute for further developing advanced materials.

### Approach:
Preparing AEMs without ether or electron-withdrawing groups in the polymer backbone (FY 16). Developing high-performing electrodes through catalyst-ionomer interfacial study (FY 17). Demonstrating good AEMFC durability of fully-integrated MEAs from materials developed from this project (FY 18).

### Accomplishments (FY 17)
Completed to prepared AEMs with exceptional stability with desired film forming properties. **Achieved ASR ~ 0.05 Ω cm² which is maintained for 300 h without AEM chemical degradation.**
First identified the benzene adsorption that adversely impact the HOR kinetics. **Demonstrated 1 W/cm² peak power density** of AEMFC performance by mitigating the benzene adsorption.

### Collaborations:
Strong team comprised of chemical synthesis, MEA integration, electrochemistry and fuel cell testing. Extensive communications with several industrial partners.
Technical Back-Up Slides
Synthesis and Alkaline Stability of SEBS based AEMs

**Synthetic Scheme of quaternary ammonium functionalized SEBS via C-H borylation and Suzuki coupling reactions**

Alkaline stability of SEBS polymers (IEC change after 1M NaOH, 80°C)

- Alkaline stable cationic functional groups are incorporated into commercial SEBS polymers.
- The AEMs show excellent alkaline stability after 4 week treatment at 1 M NaOH, 80°C.

Photos of films of (A) SEBS-A1, (B) SEBS-A2, (C) SEBS-A3, (D) SEBS-A4, and (E) SEBS-A5 cast from toluene onto Teflon plates.
**Synthesis and Alkaline Stability of Poly(terphenyl alkylene)s**

Chemical structures of para-terphenyl (p-TPN1), meta-terphenyl (m-TPN1) and biphenyl (BPN1) polymers

- **Chemically and mechanically stable terphenyl-based polymers with pendant quaternary ammonium alkyl groups were synthesized.**

IECs (before and after alkaline stability test), water uptake, hydration number and hydroxide conductivity of terphenyl alklyenes.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>IEC&lt;sup&gt;a&lt;/sup&gt;</th>
<th>IEC&lt;sup&gt;b&lt;/sup&gt;</th>
<th>WU (%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>λ (OH&lt;sup&gt;-&lt;/sup&gt;)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>σ (mS/cm)&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-TPN1</td>
<td>2.12</td>
<td>2.15</td>
<td>17(65)</td>
<td>17</td>
<td>43</td>
</tr>
<tr>
<td>m-TPN1</td>
<td>2.15</td>
<td>2.13</td>
<td>25(70)</td>
<td>18</td>
<td>54</td>
</tr>
<tr>
<td>BPN1-65</td>
<td>1.94</td>
<td>1.93&lt;sup&gt;f&lt;/sup&gt;</td>
<td>34(85)</td>
<td>24</td>
<td>41</td>
</tr>
<tr>
<td>BPN1-100</td>
<td>2.70</td>
<td>2.80&lt;sup&gt;f&lt;/sup&gt;</td>
<td>61(124)</td>
<td>26</td>
<td>62</td>
</tr>
</tbody>
</table>

<sup>a</sup>IEC values were determined by 1H NMR analysis (mequiv/g).  
<sup>b</sup>IECs after alkaline test at 1M NaOH at 95°C for 30 days (mequiv/g).  
<sup>c</sup>Water uptake was measured in both Cl<sup>-</sup> and OH<sup>-</sup> form at 80 °C. The values in brackets represent water uptake in OH<sup>-</sup> form.  
<sup>d</sup>Based on water uptake value at 80 °C.  
<sup>e</sup>hydroxide conductivity.  
<sup>f</sup>Lee et al. ACS Macro Lett. 2015, 4, 814.
Synthesis and Stability of Guanidinium Poly(phenylene)s

Extended-resonance stabilized guanidinium poly(phenylene) was synthesized and showed alkaline stability under 4M NaOH conditions.
HFR Changes of Various AEMs During Life Test at 0.3 V

- MEAs prepared with TMAC6PP and SEBS showed stable HFRs after replenishing cell with 0.5 M NaOH.
- Often fuel cell performance decreases even when the cell HFR is stable.
- The MEA with TMAC6PP AEM and AS4 ionomer lost performance after 180h with unknown reason, possibly due to the ionomer failure.
RPM Dependency of Low-Frequency Arc of Impedance

Low-frequency arc is related with a diffusion process not with a kinetic process based on the observation that the HOR impedance changes with rpm.