Polymer-based fuel cells that operate from 80–220 °C

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Los Alamos National Laboratory
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Overview

Timeline
- Project start date: 5/1/2017
- Project end date: 10/30/2018
- Percent complete: 70%

Budget
- Total project funding: $300K
  - DOE share: 100%
- Funding received in FY18: $270K
- Total DOE Funds Spent*: $200K
  *As of 4/17/2018

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

Project lead
- Los Alamos National Laboratory
  - Yu Seung Kim (PI), EunJoo Park, Albert Lee, Dongguo Li, Gerie Purdy

Collaborators (No cost)
- Sandia National Laboratory
  - Cy Fujimoto
- Rensselaer Polytechnic Institute
  - Chul Sung Bae, Junyoung Han
- National Institute of Advanced Industrial Science and Technology
  - Yoong-Kee Choe
- University of Stuttgart
  - Vladimir Atanasov
- Nanosonic, Inc.
  - William Harrison
- Toyota Motor North America, Inc.
  - Hongfei Jia
Objective

- Development of a feasible ion-pair coordinated polymers to demonstrate a fuel cell that is operational from 80–220°C without humidification.

Cost Reduction of a Fuel Cell Car

- Current fuel cell car retail price: $60,000.
- Projected fuel cell system cost: $45/kW for 500,000 vehicles
- Target cost: $40/kW (2020) $30/kW (ultimate)
- Further cost reduction strategy is necessary

Further cost reduction of fuel cells

Balance of Plant
- Humidifiers
- Large radiators
- Reactant quality control

Simple Balance of Plant

High temperature and low RH fuel cell operation could enable fixed cost savings of $7.5/kW_{net} by eliminating or reducing the size of BOP components such as humidifier and radiator.

N. Dale, Nissan Motors
Approach: Ion-Pair Coordinated Fuel Cells

Previous High-Temperature Membrane Fuel Cell

**Acid-base Interaction**

- Benzimidazole
- Phosphoric acid

\[ E_{\text{INT}} = 17.4 \text{ kcal/mol} \]

**Ion Pair Interaction**

- Benzyl ammonium
- Biphosphate

\[ E_{\text{INT}} = 152 \text{ kcal/mol} \]

LANL Technical Concept High-Temperature Membrane Fuel Cell

* Nature Energy, 1, 16120 (2016)
Approach: Project Phases and Milestones

**DFT Calculation**
- Determine the interaction energy between quaternary ammonium and phosphate (100%)

**Small Molecule Study**
- Determine the best quaternary ammonium and phosphate phase (100%)

**MEA verification**
- Demonstrate the membrane *in-situ* and *ex-situ* performance (conductivity, water tolerance) (60% See below)

### Milestone (4/30/18)

<table>
<thead>
<tr>
<th>Metric</th>
<th>Units</th>
<th>Baseline* (2016)</th>
<th>Target</th>
<th>Current Status (as of April 15 2018)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASR (160 °C)</td>
<td>Ω cm²</td>
<td>0.24</td>
<td>&lt; 0.10</td>
<td>0.09</td>
</tr>
<tr>
<td>Peak Power Density (H₂/O₂)</td>
<td>mW cm⁻²</td>
<td>800</td>
<td>1000</td>
<td>1134</td>
</tr>
<tr>
<td>Water Tolerance (Go-No-Go, April 30, 2018)</td>
<td>kPa</td>
<td>21.3</td>
<td>38.5</td>
<td>42.6</td>
</tr>
<tr>
<td>Durability during 80-180 °C AST</td>
<td>V loss at 160 °C</td>
<td>30%</td>
<td>&lt;10%</td>
<td>Not evaluated yet</td>
</tr>
</tbody>
</table>

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* *Nature Energy, 1, 16120 (2016)*
Accomplishment: DFT Calculation

- Ion pair coordinated system has higher interaction energy with PA than acid-base coordinated system at a given number of PA.
- Better water retention can be achieved with stronger interaction energy.
Accomplishment: Interaction Measurement ($^{31}$P NMR)

- $^{31}$P NMR shows a single peak, indicating exchanging electrons in the phosphate phase.
- Ion pair coordinated system has higher interaction energy – consistent with DFT study.
- Interaction energy HMG > TBA > TMA >> guanidine > benzimidazole > pyridine
Accomplishment: Proton Conductivity

- Ion pair coordinated system has stronger interaction at a given conductivity.
- Hexamethyl guanidinium (HMG\(^+\)) exhibits the strongest interaction at a given conductivity.

Measured the proton conductivity of the ion-pairs by the AC impedance using a liquid cell.

\[ \text{Ionic Conductivity (mS/cm)} \]

\[ \Delta \text{ ppm} \]

\(25^\circ\text{C}\)

\(~0.5\text{ ppm }^{31}\text{P NMR peak shift difference at } 10-50\text{ mS cm}^{-1}\)
Accomplishment: Water Tolerance

Highlight: Met the water tolerance go-no-go decision criteria (max. conductivity at $P_{H2O} > 38.5$ kPa) with two newly designed ion-pair coordinated systems.

- Cy Fujimoto

**Chemical structure of ion-pair coordinated membrane**

- QAP cation/anion: TMAOH/PA
- New ion pair 1, 2 cation/anion: proprietary info.

**Graphs**

- Proton conductivity vs. RH at 80 °C
- Proton conductivity vs. time at 80 °C, 60% RH

PA doping process: see Back-up Slide #1.
Membrane Synthesis

**Membrane:** Ammonium-phosphate ion-pair coordinated cross-linked poly(biphenylene) (PA-XL-BPN, Technical Back-up Slide #2)*

IEC = 2.6 meq/g  
Mₙ = 70,000 Daltons  
PDI = 1.8

**Ionomer:** Ion-pair coordinated polystyrene (PA-QAPS, Technical Back-up Slide #3)

High IEC ion-pair coordinated crosslinked poly(biphenylene) is developed.

**Highlight:** Fuel cell peak power density (> 1 W cm⁻²) milestones.

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*H₂/O₂, 285 kPa abs backpressure; membrane: PA-XL-BPN; ionomer: PA-QAPS, Pt 0.6 mg/cm² for both electrodes*
Accomplishment: Ionomer development

**Membrane:** Ion-pair coordinated poly(phenylene) (PA-DAPP)

**Ionomer:** Phosphonated poly(pentafluorostyrene) (PPFS, Technical Slide 4)*

Developed phosphonated ionomer (non-acid leachable) for ion-par system.

**Highlight:** Obtained ASR of 0.09 Ω cm² at 160°C Exceed the ASR (< 0.1 Ω cm²) milestone

Measured in H₂/O₂, 147 kPa abs backpressure; membrane: PA-DAPP; Pt-Ru 0.5 mgPt/cm² for anode and Pt 0.6 mg/cm² for cathode
Responses to Previous Year Reviewers’ Comments

This project was not reviewed last year.
### Project Coordination

**Material Design**
- Cationic group
- Phosphate group
- Structure-property relationship

**Material Preparation**
- Down selection

**Material Preparation**
- Conductivity
- Water tolerance

**Fuel Cell Test**
- Initial performance
- Durability

**Polymer Synthesis**
- Poly(biphenylene)s

**Polymer Precursor**
- Diels-Alder PPs

**Ionomer Preparation**
- Phosphonated polymers

**Scaled-up Synthesis**
- Poly(arylene ether)s

**DFT Modelling**
- Ion-pair interaction

**Tech Validation**

**Los Alamos National Lab**
- Yu Seung Kim
- Albert Lee
- Eun Joo Park
- Dongguo Li
- Gerie Purdy

**RPI**
- Chulsung Bae
- Junyoung Han

**Sandia National Laboratories**
- Cy Fujimoto

**U of Stuttgart**
- Vladimir Atanasov

**Nanosonic Inc.**
- William Harrison

**Toyota Motors**
- Hongfei Jia

**AIST (Japan)**
- Yoong-Kee Choe
Collaboration

- **Material Exchange:** Critical component to achieve the project objective
  - Sandia National Laboratory (Cy Fujimoto) – **Federal Lab., within DOE program**
    - Hexamethyl ammonium functionalized poly(phenylene)s 6 pieces (5” × 5”)
    - Benzyl ammonium functionalized poly(phenylene)s 3 pieces (5” × 5”)
  - Rensselaer Polytechnic Institute (Chulsung Bae) – **University, within DOE program**
    - Crosslinked biphenylene membranes: 6 pieces (4” × 4”)
    - Crosslinked terphenylene membranes: 6 pieces (4” × 4”)
  - University of Stuttgart (Vladimir Atanassov) – **University (foreign), outside DOE program**
    - Phosphonated polystyrenes with different IECs: 10 pieces (2” × 2”)
  - Nanosonic Inc. (William Harrison) – **Industry, inside DOE program (SBIR)**
    - Quaterary ammonium functionalized poly(arylene)s: 9 pieces (4” × 4”)
  - Toyota Motor North America, Inc. (Hongfei Jia) – **Industry, outside DOE program**
    - Ion liquid electrolyte: few grams

- **DFT Modeling:** Useful information provided to design materials
  - National Institute of Advanced Industrial Science and Technology (Yoong-Kee Choe, LANL visit) – **National Lab (Foreign), outside DOE program**
    - Ion-pair interaction calculation
Remaining Challenges and Barriers

- **Within the project (ending October 30/2018)**
  No substantial technical challenges remained.

- **After the project**
  - Electrode development
    - Ionomer design
    - Understanding catalyst-ionomer interfacial reaction
    - Low Pt loading and non-PGM catalysts
  - Membrane development
    - Increasing molecular weight & IEC
    - Mechanically stable thin film construction
    - Incorporating super-base cations into polymeric materials
    - Understanding proton conduction in the ion pair networks
  - Tech validation
    - Correlation of fuel cell AST and field test performance
    - Fuel cell start-up stability
    - Techno-economic analysis
Current and Proposed Future Work - Technical

With this project
Membrane development
- Complete synthesis of guanidinium poly(phenylene)s (Technical Backup Slide #5).

Ionomer development
- Synthesis of phosphonated ionomers.

Fuel cell testing
- Initial performance with Pt-based catalysts under $\text{H}_2/\text{O}_2$ and $\text{H}_2/\text{air}$ conditions.
- *In-situ* water tolerance test (humidity-temperature cycling 80 – 160 °C).

- Currently no alternative development pathways is planned; however we may add some additional work based on AMR comments.

Beyond this project
Investigation of interface between catalyst and ion-paired ionomer
- Hydrogen oxidation reaction
- Oxygen reduction reaction
- Funding (LANL-Toyota CRADA)

Any proposed future work is subject to change based on funding levels.
Current and Proposed Future Work - Technology Transfer Activities

**SBIR Phase II**

- Technology transfer effort to Nanosonic Inc. (SBIR Phase II) to produce scale-up synthesis of ion-pair coordinated membranes.

**Patent application**

- Sarah Park, Sandip Maurya, Yu Seung Kim, “Polymer electrolytes for alkaline membrane fuel cells” S133606 (March, 2, 2018)
- Albert Lee and Yu Seung Kim, “Polymer electrolytes for fuel cells” (Feb. 9, 2018).

The performance of Nanosonic membrane tested by LANL
Summary

Objective: Development of feasible ion-pair coordinated polymers to demonstrate a fuel cell that operates at 80–220°C without humidification.

Relevance: Aiming to make ion-pair coordinated membranes having comparable proton conductivity and durability without humidification. Successful development of such ion-pair coordinated membranes enable to operate fuel cells at the wide-range of temperature without humidification.

Approach: DFT modeling and small molecule study (\(^{31}\)P NMR) determine the best candidate materials that have strong ionic interactions. The selected ion pairs are incorporated in membranes and demonstrate good water tolerance and low cell resistance in membrane electrode assemblies.

Accomplishments (FY 18) Completed the DFT modeling and small molecule study, demonstrating guanidinium-phosphate is the best candidate having strongest interaction. Achieved water tolerance at 80 °C, 80% RH (\(P_{H2O} = 38.5 \text{kPa}\)), met the go-no go decision criteria. Demonstrated > 1 W/cm\(^2\) peak power density of ion-pair coordinated HT-PEMFC.

Collaborations: Collaboration in the area of chemical synthesis, MEA integration, electrochemistry and fuel cell testing. Extensive communications with several industrial partners, including RPI, University of Stuttgart (Germany), Sandia National Laboratories, AIST (Japan) Nanosonic, Inc and Toyota Motors North America.
Technical Back-Up Slides
Determination of Phosphoric Acid Doping Level

Typical doping process

→ Completely submerge membrane in 85 wt% phosphoric acid bath under ambient conditions.
→ Hang dry membrane until excess phosphoric acid drips off.
→ Dry at 80°C under air for 2 hr.
→ 12 h was found to be appropriate to achieve non-excess doping levels.
Synthesis and Properties of Cross-linked BPN

[Chemical structures and reaction equations]

<table>
<thead>
<tr>
<th>Theoretical IEC</th>
<th>IEC_t</th>
<th>WU(%) at 25°C</th>
<th>λ</th>
<th>Swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.61</td>
<td>2.52</td>
<td>109.6</td>
<td>24.1</td>
<td>31.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>50 °C / 50 %RH</th>
<th>25 °C / 50 %RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.2</td>
<td>25.1</td>
</tr>
<tr>
<td>16.5</td>
<td>22.0</td>
</tr>
<tr>
<td>15.3</td>
<td>15.8</td>
</tr>
</tbody>
</table>

Technical Back-up #2
Synthesis and Properties of PA-QAPS*

![Chemical structures and reactions](image)

<table>
<thead>
<tr>
<th>Concentration of base moiety (meq./g)</th>
<th>Number of PA per base moiety</th>
<th>Polymer content(^a) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>2.7 ± 0.0</td>
<td>35</td>
</tr>
</tbody>
</table>

\(^a\) for dry membrane.

<table>
<thead>
<tr>
<th>Number of H(_2)O Per base moiety</th>
<th>Per PA (doped)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-doped</td>
<td>Doped</td>
</tr>
<tr>
<td>23</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
</tr>
</tbody>
</table>

* *Nature Energy, 1, 16120 (2016)*

Los Alamos National Laboratory
Synthesis of Phosphonated Poly(pentafluoro styrene)*

\[
\begin{align*}
\text{PPFS} + \text{TMPS} & \rightarrow \text{Phosphonated PPFS} \\
\text{PPFS} & \rightarrow \text{Phosphonated PPFS}
\end{align*}
\]

19F NMR spectra of PPFS

<table>
<thead>
<tr>
<th>TMPS/PPFS (mol %)</th>
<th>Phosphonation 19F NMR (%)</th>
<th>Phosphonation IEC (%)</th>
<th>IEC-direct/total (mequiv. g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>100</td>
<td>99</td>
<td>7.4/8.0</td>
</tr>
<tr>
<td>90</td>
<td>66</td>
<td>51</td>
<td>1.9/4.1</td>
</tr>
<tr>
<td>80</td>
<td>42</td>
<td>41</td>
<td>1.4/3.5</td>
</tr>
<tr>
<td>70</td>
<td>41</td>
<td>44</td>
<td>1.6/3.8</td>
</tr>
<tr>
<td>60</td>
<td>36</td>
<td>32</td>
<td>1.1/2.9</td>
</tr>
<tr>
<td>40</td>
<td>17</td>
<td>17</td>
<td>0.5/1.6</td>
</tr>
</tbody>
</table>


V. Atanasov & J. Kerres
Synthesis of Phenyl Guanidinium Funct. Poly(phenylene)s


IEC = 1.9 – 2.5 meq/g