Composite PEMs from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s

2019 DOE Hydrogen and Fuel Cells Program Review Presentation

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Overview

Timeline
- Project Start Date: 1/9/19
- Project End Date: 12/31/20
- Percent Complete: 8%

Budget
- Total Project Budget: $752,049
  - Total Recipient Share: $152,049
  - Total Federal Share: $600,000
  - Total DOE Funds Spent: $14,331 (as of 3/01/19)

Barriers
- High cost of PFSA membranes
- Low proton conductivity at reduced humidity (water partial pressure)
- Performance drop above 80°C

Targets
- Cost < $20/m²
- ASR at 80°C and water partial pressure from 25-45 kPa - 0.02 Ohm⋅cm²
- Operating temperature up to 120°C

Funded Partners
- Prof. Peter N. Pintauro (Co-PI) - Vanderbilt University
- Prof. Morton Litt (Consultant) - Case Western Reserve University
This project’s objective is to fabricate a novel electrospun, non-PFSA fuel cell membrane that can meet all 2020 FCTO MYRDD technical targets.

2020 DOE FCTO TARGETS:
- Max H₂ and O₂ crossover ≤ 2 mA/cm²,
- ASR at 30°C and H₂O partial pressures up to 4 kPa - 0.3 Ohm·cm²,
- ASR at 80°C and H₂O partial pressure 25-45 kPa - 0.02 Ohm·cm²,
- Mechanical durability - 20,000 cycles,
- Chemical durability > 500 hours,
- Cost - $20/m².

TARGETS FOR THE CURRENT PROJECT YEAR:
- **Expected results**: Synthesized poly(phenylene sulfonic acid)s (cPPSA), identified working carrier and electrospinning conditions for well-formed fibers, prepared dual fiber cPPSA/PPSU membranes and performed basic ex-situ characterization (water uptake, conductivity and tensile strength).
- **Go/No-Go Decision point**: Demonstrate composite membrane with in-plane conductivity > 0.05 S/cm at 30-80°C and 30-90%RH, and tensile strength >20 MPa in wet state at room temperature.

Low RH conductive, robust, nanofiber composite all-hydrocarbon PEM
Robust, low-cost composite all-hydrocarbon membrane will be fabricated via dual fiber co-electrospinning of a crosslinkable poly(phenylene sulfonic acid) (cPPSA) and poly(phenyl sulfone) (PPSU) mixture mat, followed by mat densification via solvent vapor induced softening of PPSU fibers and thermal crosslinking.

THREE STEP APPROACH:
1. Synthesize, optimize and test crosslinkable, highly proton conductive poly(phenylene sulfonic acid) (cPPSA) ionomers (IEC > 5 mmol/g).
2. Fabricate, employing dual fiber electrospinning, mixed cPPSA/PPSU nanofiber mats and compact them into dense films. Thermally crosslink the ionomer.
3. Characterize and test fuel cell performance of the resultant membranes.
The project builds on two earlier, DOE-funded studies demonstrating:

1. **Exceptionally high proton conductivity**, even at very low RH, of cPPSA solution cast films (Litt’s group), and

2. **Excellent durability** of electrospun perfluorosulfonic acid (PFSA) ionomers/PPSU composite membranes, exceeding that of the pristine PFSA (Pintauro’s group).

- An order higher conductivity compared to Nafion (0.07 S/cm vs. 0.007 S/cm at 20%RH, 80°C)
- Very low crossover
- Stable above 80°C
## Approach

### PROJECT MILESTONES AND DELIVERABLES

| Year 1 | • Demonstrate stable composite membrane with conductivity > 0.05 S/cm at 30-80°C and 30-90%RH, and tensile strength >20 MPa in wet state at room temperature. |
| Year 2 | • Demonstrate meeting 2020 technical targets of the FCTO MYRDD Plan: H₂ crossover ≤ 2 mA/cm², ASR at 80°C and water partial pressures from 25-45 kPa - 0.02 Ohm·cm², at 80°C, mechanical durability - 20,000 cycles, chemical durability > 500 hours, cost - $20/m².  
• Deliver samples to LANL for fuel cell testing |

### Q1 MILESTONE

<table>
<thead>
<tr>
<th>Task No</th>
<th>Task or Subtask Title</th>
<th>Milestone Type</th>
<th>Milestone Number</th>
<th>Milestone Description (Go/No-Go Decision Criteria)</th>
<th>Milestone Verification (What, How, Who, Where)</th>
<th>Date (Months)</th>
<th>Date (Quarters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Synthesis of lithium dibromodisulfonate monomers</td>
<td>Milestone</td>
<td>1</td>
<td>Demonstrate 60 g of DBBDSA-Li, 50g of DBBPDSA-Li and 10 g of DBFDSA-Li, and confirm their purity &gt;99% with ¹H NMR spectra.</td>
<td>NMR spectra available</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>
Accomplishments and Progress

• All of the necessary Q1 supplies have been ordered and most of them have been received:
  – Rotary evaporator, overhead stirrer and glassware
  – Fuming sulfuric acid, dibromobenzene, dibromobiphenyl and dibromofluorene
  – Cation-exchange resin and the column
  – Sodium and lithium hydroxides
  – Other necessary labware

• Supplies for Q2 tasks will be ordered in the first week of March:
  – Fuming sulfuric acid
  – Copper bronze powder
  – N-methylpyrrolidone
  – Calcium hydride
Accomplishments and Progress

- Synthesis of 1,4-dibromobenzene 2,5-disulphonic acid lithium salt (DBBDSA-Li) is in progress:
  - 30 g of pure DBBDSA-Na has been prepared
  - Additional 50 g of raw DBBDSA-Na has been synthesized and is currently being purified.
  - Conversion to the Li-form will be performed by mid-March

![1H NMR spectrum of purified DBBDSA-Na in D2O]
Accomplishments and Progress

• Synthesis of 1,4-dibromobiphenylenzene 2,5-disulfonic acid lithium salt (DBBPDSA-Li) is in progress:
  
  2 x 30 g of recrystallized dibromobiphenyl has been sulfonated with fuming sulfuric acid (15% SO$_3$) and is currently being isolated from the reaction mixture, and ion-exchanged.
  
  The Li-form will be ready by mid-March

• Synthesis of 2,7-dibromofluorene-3,5-disulfonic acid (DBFDSA) will start by mid-March.

The monomer synthesis is progressing as planned. The target three batches, (60 g of DBBDSA-Li, 50g of DBBPDSA-Li and 10 g of DBFDSA-Li), should be ready by the end of Q1.
Accomplishments and Progress: Responses to Previous Year Reviewers’ Comments

• This project was not reviewed last year.
Collaboration & Coordination

- Prof. Morton Litt (Case Western Reserve University) serves as a consultant helping in all the polyphenylene ionomer synthesis tasks.

- Prof. Peter N. Pintauro (Vanderbilt University) serves as a Co-PI and will be helping in all the fiber electrospinning tasks.
Remaining Challenges and Barriers

- **Thermal crosslinking of the poly(phenylenesulfonic acid) ionomers:** The reported crosslinking temperature is very close to the ionomer degradation point. Optimization of the ionomer composition, temperature and duration of the crosslinking process will be carried out to overcome the challenge.

- **Electrospinnability of the ionomers:** These polymers have very rigid backbones which may render them poorly electrospinnable. Addition of a second polymer (carrier) will most probably be necessary. A number of carriers are known to the project team and will be investigated when necessary.

- **Poor polymerizability of the disulfonate fluorine derivative:** We may postpone, in case of problems with getting high enough molar mass, working with this co-monomer and focus on the biphenyl and benzene disulfonate monomers only.
Proposed Future Work

This project has just started (Jan 9) and is planned to be executed in two one-year budget periods:

- **Year 1 (2019) - the team will make the membranes and perform their preliminary testing:**
  (i) Three disulfonate monomers will be synthesized, copolymerized and the copolymers will be grafted with biphenyl linker (Q1-Q3)
  (ii) The resultant proton-conducting copolymers will be co-electrospun with poly(phenyl sulfone) into mixed fiber mats which will be compacted and the sulfonate fibers will be thermally crosslinked (Q4)
  (iii) The obtained composite membranes will be characterized ex-situ and in fuel cell (Q4)

- **Year 2 (2020) - optimization of the composite membrane and extensive fuel cell testing will be performed:**
  (i) Composition of the sulfonate graft copolymer will be optimized based on Year 1 results (Q5)
  (ii) Optimization of the (co)electrospinning conditions will be performed in Q6
  (iii) Optimization of the membrane composition/processing will be done in Q7
  (iv) MEA fabrication and testing, including meeting the FCTO 2020 targets will be realized in Q8

The team has prepared alternative development pathways to mitigate risk of not achieving milestones, specifically in Year 1.

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

• The proposed membrane can be used in a number of electrochemical and pressure driven separation processes. Suitable alternative applications will be actively sought after during the project lifetime.

• Upon successful conclusion of Year 1 tasks, the PI will team up with an industrial partner to submit an application for SBIR or STTR funding.

• The team has initiated talks with eSpin Technologies, Inc. (Chattanooga, TN), a commercial manufacturing facility, regarding potential scale-up of the proposed PEM fabrication technology.
Summary

Objective: Fabricate a novel electrospun, non-PFSA fuel cell membrane that can meet all 2020 FCTO MYRDD technical targets.

Relevance: The project could lead to a non-PFSA (environmentally friendly and inexpensive) membrane with excellent mechanical, chemical, and thermal stability, and low fuel crossover, enabling increase in the operating temperature and humidity ranges of fuel cells.

Approach: The composite all-hydrocarbon membrane will be fabricated via dual fiber co-electrospinning of a crosslinkable poly(phenylene sulfonic acid) and poly(phenyl sulfone) (PPSU) mixture mat, followed by mat densification via solvent vapor induced softening of PPSU fibers, and thermal crosslinking.

Accomplishments: The monomer synthesis is progressing as planned: two of the three required monomers are currently being purified, including the major 1,4-dibromobenzene 2,5-disulfonic acid salt.