Developing A New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber

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Overview

**Timeline**
- Project start date: 9/1/2017
- Project end date: 8/31/2020
- % complete: 30%

**Budget**
- Total project funding: $930,888
  - DOE share: $804,462
  - Penn State share: $127,181
- Funding for FY2017-18: $306,363
- Go/no-Go decision: August 2018

**Barriers**
- System weight & volume
- System cost, efficiency, durability
- Charging/discharging rates
- Suitable H$_2$ binding energy
- High polymer surface area

**Partners**
- LightMat consortium
- Oak Ridge National Lab.
Relevance

Research Objectives

- Developing a new polyolefin precursor that is melt-processible and high thermal conversion yield to form carbon fiber (CF).
- Co-carbonization with B-containing precursor to prepare B-doped CF with reduced temperature, high yield, smaller d-spacing.
- Cost savings can be realized through the combination of low cost precursor, melt-spinning fiber process, low carbonization temperature, high mass yield, and high tensile strength in the B-doped CF.

Potential Benefits and the Impact on Technology

- If successful, this new technology can offer a cost-effective CF for fabricating onboard storage vessel with compressed hydrogen (700 bars) in FCEVs. The main objective is to achieve the DOE cost target of $10/kWh (about $1,900 per vehicle with 5.6 Kg of usable hydrogen). It also can impact other energy-relative applications, such as wind blades, flywheels, transportation, etc.
**Relevance: DOE cost targets**

Composite overwrapped pressure vessel for 5.6 Kg usable hydrogen

<table>
<thead>
<tr>
<th></th>
<th>Energy cost ($/kWh)</th>
<th>System cost ($/vehicle)</th>
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<td>2013 system</td>
<td>$17</td>
<td>$3,200</td>
</tr>
<tr>
<td>2015 system</td>
<td>$15</td>
<td>$2,800</td>
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<tr>
<td>DOE Target</td>
<td>$10</td>
<td>$1,900</td>
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Type IV COPV system with polymer liner and annual production rate of 500,000 systems

DOE 2015 cost analysis indicated that 62% of the system cost would come from the cost of carbon fiber (CF)

5 gallon tank with 700 bars pressure
5 kg H₂ storage for 300 miles driving range (45-60 miles/kg H₂)
High Cost (~ $3,000 per vehicle)
Relevance: Current CF precursors

**Polyacrylonitrile (PAN)**

![Polyacrylonitrile (PAN) molecular structure]

**Pitch (petroleum)**
Oligomeric mixture of polycyclic aromatic hydrocarbons (PAH) with molecular weight 200-800

**Pitch (coal tar)**
PAH and Phenols make up two large classes of chemicals.

![Chemical structures of PAH and Phenols](image)
Advantages of Pitch precursor:
Low cost, melt-processible, and high C yield (up to 70%)
Relevance: Current thermal production process

PAN Polymer Precursor → PAN Fiber
- wet spinning + stretching

Surface Treatment & Sizing

Carbonization
(1000-2000 °C in N₂ atmosphere) + Stretching

Stabilization
(200-300 °C in air for 30-120 minutes) + Stretching

N₂

air
Relevance: PAN thermal conversion

Stabilization  
(200-300 °C)

Carbonization  
(1000-2000 °C)

Overall thermal conversion yield ~50%
## Milestone Summary Table

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### 1st Go/No-Go Decision

A new low-cost polyolefin precursor that can be prepared and transformed to C with mass yield (>80%), more than 60% higher than that of current PAN. Send 10 slides to LightMat /DOE.

| 4           | Scaling Up the Selected Polyolefin Precursors | Milestone                  | M4.0            | Selected precursors with Kg quantity         | $^1$H NMR, GPC, DSC and TGA spectra.               | 13-15                     | 5                             |
| 5.1         | Melt-Spinning of Polyolefin Precursors       | Milestone                  | M5.1            | Fiber-spinning to polyolefin fibers          | Pictures and Strain-stress curves.                 | 16-21                     | 6-7                           |
| 5.2         | Carbonization of Polyolefin Fibers           | Milestone                  | M5.2            | New polyolefin based CF products             | TEM, SEM, XRD,Instron, and elemental analysis.     | 19-24                     | 7-8                           |

### 2nd Go/No-Go Decision

A new low-cost and high-quality carbon fiber obtained from a new polyolefin precursor and melt-spinning process. Send 10 slides to LightMat /DOE.

| 6.1         | Co-carbonization study of Polyolefin Blends with B-Precursors | Milestone                  | M6.1            | New B-doped C (BCx) materials                | $^{13}$C and $^{11}$B NMR spectra and elemental analysis | 25-30                     | 9-10                          |
| 6.2         | Melt-Spinning of Polyolefin Blends with B-Precursors          | Milestone                  | M6.2            | Fibers from B-containing polymer blends      | Pictures and Strain-stress curves.                 | 28-33                     | 10-11                         |
| 6.3         | Carbonization of Polyolefin Blend Fibers                  | Milestone                  | M6.3            | New B-doped CF (B-CF)                        | TEM, SEM, XRD,Instron, and elemental analysis.     | 31-36                     | 10-12                         |
Approach: Design new polyolefin precursors

• Semi-crystalline hydrocarbon polymer (>80% C content)
• Melt-spinning to fibers with good tensile strength
• Reactive side groups for thermal conversion
• Facile stabilization reaction at <300 °C
  ➢ Forming ladder/conjugated chain structure
  ➢ No external reagent required
  ➢ No by-product formed, except H₂ and H₂O
• Effective thermal conversion with a high C yield (>80%)
• Low cost and scalable
Approach: New polyolefin precursors

\[
\begin{align*}
\text{H-C=CH}_2 \\
\text{C}_x
\end{align*}
\]
Accomplishments: Synthesis of Poly(divinylbenzene) 
PDVB precursor

Benefits of Cp*Ti(OCH₃)₃-mediated polymerization:
- Mono-enchainment of DVB monomers
- Processible PDVB polymer (soluble in solvents)
- High polymer conversion
- Syndiotactic polymer backbone structure
- Semi-crystalline morphology
Accomplishments: $^1H$ NMR spectra

DVB monomer

PDVB polymer precursor
Approach: Stabilization mechanism (by heat)

- Low temp. stabilization reactions via styrenyl side groups.
- Both reaction mechanisms require no external reagent.
Accomplishments: TGA curves of PDVB precursors

Carbonization yield is in the range of 65-75%
Accomplishments: TGA curves of PDVB precursors

C yield systematically decreases with the decrease of DVB content.
Accomplishments: Synthesis of Poly(phenylacetylene) derivatives

\[ \text{Pd(pph}_3\text{Cl}_2/Cul} \rightarrow \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{NaOH} \rightarrow \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{WCl}_6/\text{Ph}_4\text{Sn} \rightarrow \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{TBAF} \rightarrow \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

\[ ^1\text{H NMR} \]

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]
Accomplishments: FTIR spectra of Poly(phenylacetylene) derivatives
Accomplishments: DSC and TGA curves of Poly(phenylacetylene) acetylsilane-derivatives

- Relatively weak stabilization reaction
- Stabilization at >250 °C
- Carbonization yield ~55%
Accomplishments: DSC and TGA curves of Poly(phenylacetylene) acetyl-derivatives

- Strong well-defined stabilization mechanism
- Stabilization at 200-220 °C
- Carbonization yield ~85%
Accomplishments: Synthesis of Poly(phenylacetylene) acetylphenyl derivatives

\[ \text{Br} - \text{Si} - \text{C} = \text{C} - \text{H} \xrightarrow{\text{Pd(ppy}_3\text{)}\text{Cl}_2/\text{CuI}} \text{Si} - \text{C} = \text{C} - \text{C} - \text{C} - \text{H} \xrightarrow{\text{TBAF}} \text{H} - \text{C} = \text{C} - \text{C} - \text{H} \xrightarrow{\text{WCl}_6/\text{Ph}_4\text{Sn}} \text{H} - \text{C} = \text{C} - \text{C} - \text{H} \]

\[ ^1H\text{ NMR} \]

\[ \text{ppm} \]

\[ 1.00, 0.80, 0.03 \]
Accomplishments: DSC and TGA curves of Poly(phenylacetylene) acetylphenyl-derivative

- Multiple stabilization mechanisms
- Stabilization happened at >250 °C
- Carbonization yield >75%
Accomplishments: Co-carbonization between Petroleum pitch and B-precursor

- B elements incorporated in pitch in forming mesophase B-pitch precursor
- B enhances carbonization process
- Increase carbonization yield
Summary

- Conducting a systematical study (design, synthesis, and evaluation) to identify the suitable polymers with high carbonization yield.
- Two poly(phenylacetylene) derivatives show carbonization yield higher than 80%.
- Synthesis of B-containing pitch precursor that enhances the carbonization process.
- Collaborating with ORNL in fiber processing, thermal conversion, and carbon fiber evaluation.
### Future Work

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