
IOWA STATE UNIVERSITY
Department of Materials Science and Engineering

# Coal-derived graphene materials for industrial applications

DE-FEO-0032274

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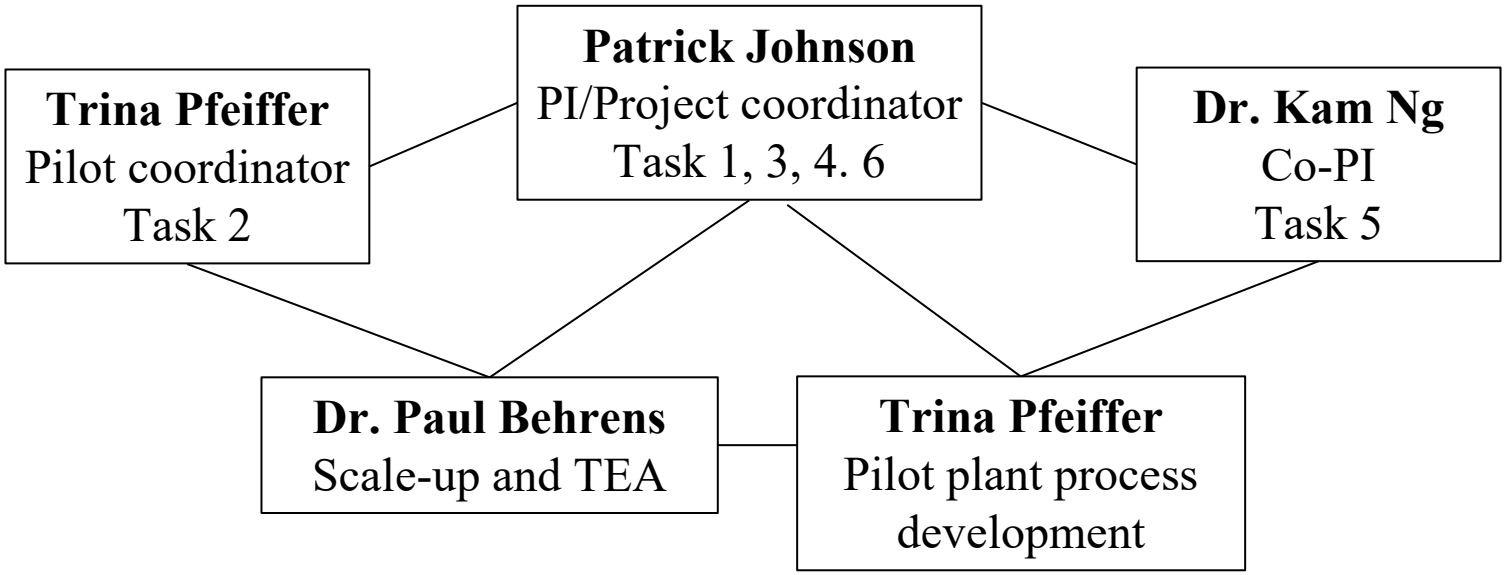
Iowa State University

Material Science & Engineering

U.S. Department of Energy

National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
April 2-4, 2024

- **Funding (DOE and Cost Share)**
- ✓ Federal Share: $ 1,000,000
- ✓ Cost Share: $ 250,000
- ✓ Total Estimated Project Cost: $ 1,250,000




| | | |
|---|---|---|
| Task 1. Project management and planning tasks | Task 2. Flash Pyrolysis Pilot plant process development | Task 3. GO process optimization |
| Task 4. Synthesis of rGO and graphene nanosheets | Task 5. Testing of graphene products concrete additive | Task 6. Sodium-ion battery fabrication/testing |

– The major goal of the project is to seek applications for technologies that use domestic coal and/or carbonaceous coal wastes to produce high-value graphitic products:

1. Flash Pyrolysis of coal to coal char
2. Graphene oxide (GO) process optimization
3. Syntheses of reduced graphene oxide (rGO) and graphene nano sheets
4. Testing GO and rGO as concrete additives/cement replacement
5. Hard carbon anodes in sodium-ion battery (SIBs) fabrication/testing

# Technology Background

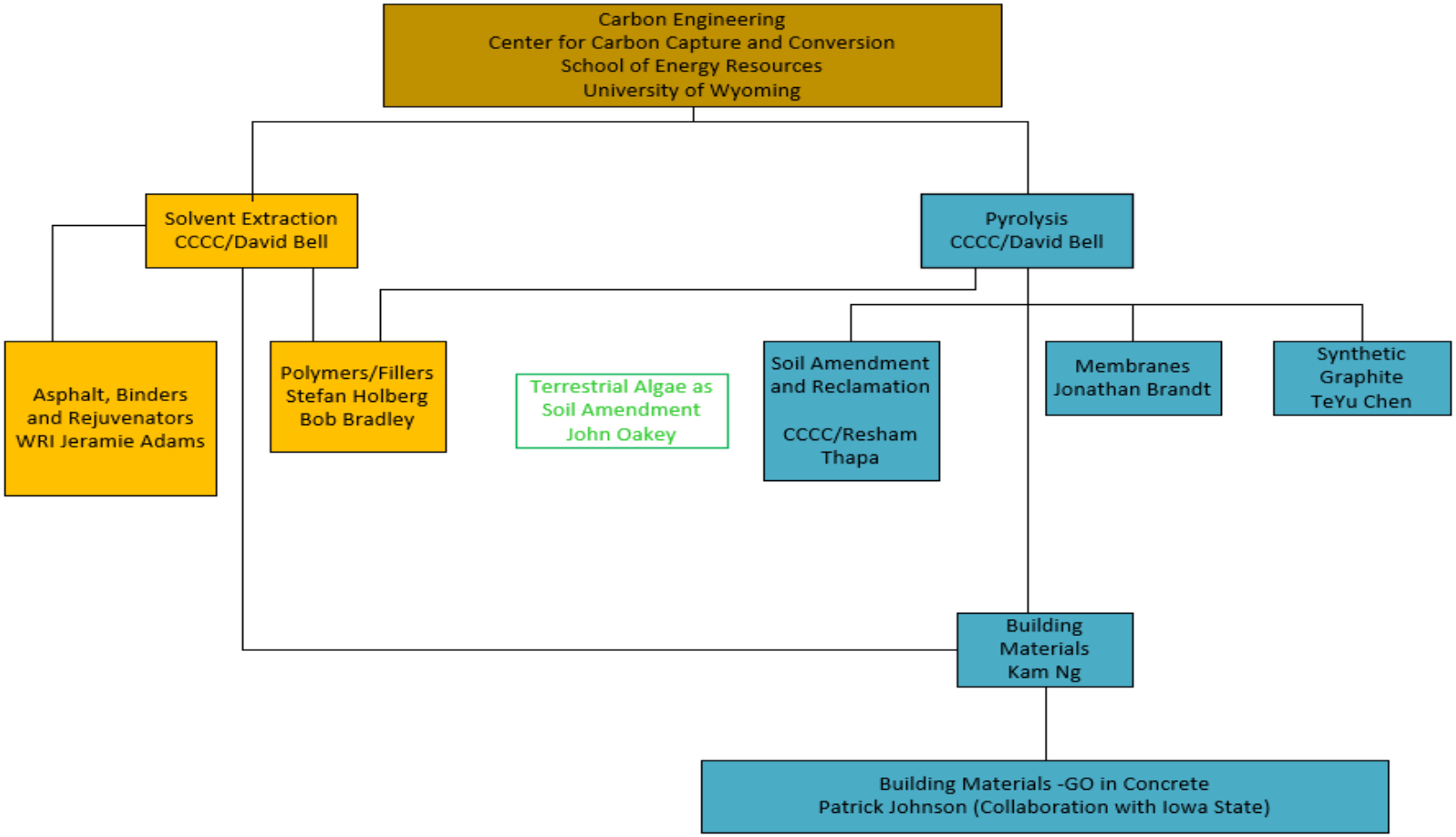
Economic advantages of your technology

Estimated cost (GO) and (rGO) - $/kg

| Precursor and Products | Price [$/kg] |
|---|---|
| Wyoming subbituminous PRB coal | 0.016 |
| Industrial Graphene Oxide Bulk Powder products | 32 |
| Hard Carbon Powder for Sodium Ion Battery Anodes | 1,190 |
| High Quality Monolayer Graphene Oxide | 5,000 |
| 99% Purity Industry Graphene Powder for batteries | 2,500 |
| Graphene, Monolayer graphene film | 100,000 |
| Reduced Graphene Oxide Powder | 3,000 |
| Nano Reduced Graphene Oxide Dispersion Nanoparticles Colloid and Slurry | 50,000 |
| Few Layer Reduced Graphene Oxide | 13,000 |

# Technology Background

Economic advantages of your technology

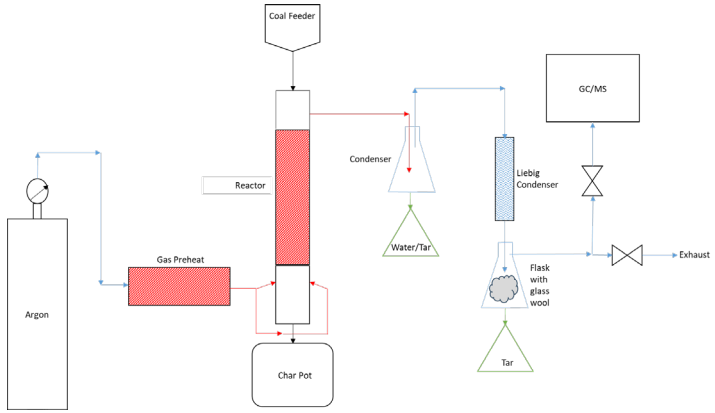


# Technology Background

Economic advantages of your technology

## Flash Pyrolysis - Progress

- Two different reactor configurations have been tested to evaluate temperatures and flowrates and various carrier gas flow rates and directions for optimal product production
- An additional lower temperature pretreatment step before flash pyrolysis has been evaluated (Two-Step Flash Pyrolysis)
- Scaled up Pyrolysis pilot plant to begin June 2024 to provide much needed feedstock for downstream product research. This plant will benefit from the data gathered in the smaller unit show on this slide.



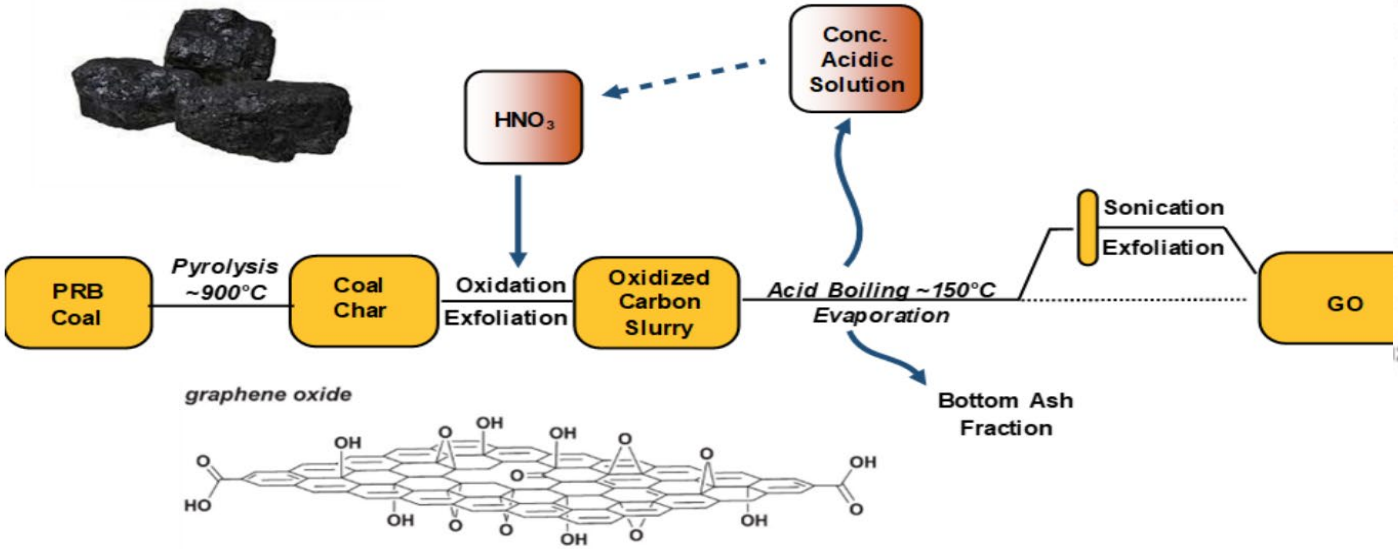
# Flash Pyrolysis – Current Status

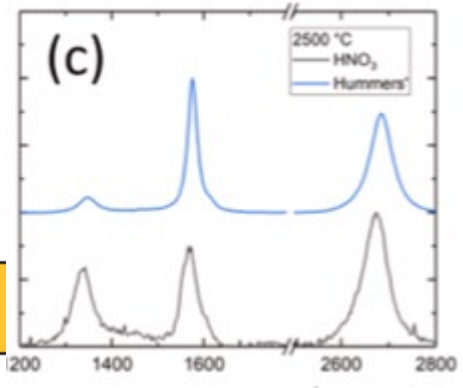
- Significant increase in char production (60 g/day a year ago)
  - Single-Step: 1 kg/week
  - Two-Step: 0.7 kg/week
- Supply GO group with 0.6 kg of char per month
- Evaluating effect of other environments (methane and steam) and their effects on product yield and composition
- 2 undergraduate students hired to work on project – Kalin Hicswa (Fr. ME) during school year and Riley Milburn (Jr. ME) during summer.

# Flash Pyrolysis – Future Development/Commercialization

- Design of new, higher throughput flash pyrolysis system on University of Wyoming campus in progress
  - 5 kg of char per day (~10 kg of raw coal per day)
  - Startup in Summer 2024
- Construction of flash pyrolysis Semi Works plant in Gillette, WY with Wood Engineering underway
  - 6 TPD of raw coal feed
  - Startup in Spring/Summer 2025

# Technology Background




Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

## Evolution of structural and electrical properties in coal-derived graphene oxide nanomaterials during high-temperature annealing

Ana Paula Martins Leandro, Michael A. Seas, Kaitlyn Vap, Alexander Scott Tyrrell, Vivek Jain, Hud Wahab *, Patrick A. Johnson *

*Department of Chemical Engineering, University of Wyoming, 1000 E University Avenue, 82071 Laramie, WY, United States of America*

**Table 3**
Comparison of powder electrical conductivity with literature.

| Material | Annealed temperature [°C] | Conductivity [$10^3$ S $m^{-1}$] | Ref. |
|---|---|---|---|
| Ordered mesoporous carbon | 1500 | 2.82 | [39] |
| Graphite | – | 2.12 | [38] |
| Graphene | | 0.26 | |
| Graphite | – | 2.50 | [66] |
| Reduced GO | | 2.42 | |
| Reduced GO | – | 1.50 | [67] |
| Anthracite | 950 | 1.00 | [34] |
| Flake graphite | – | 10.6 | [42] |
| Natural graphite | | 19.7 | |
| Graphene microflower | 2000 | 4.5 | [60] |
| | 3000 | 21.2 | |
| Catalytic-microwave exfoliated graphite oxide | – | 53.1 | [63] |
| Graphite | 2500 | 8.98 | This work |
| $HNO_3$ rGO nanocrystals | 2000 | 2.38 (2.63) | |
| (Hummers' rGO nanocrystals) | 2500 | 4.81 (4.34) | |

# Technology Background

PRB Coal

Pyrolys
~900°

graph


ELSEVIER

US 20210214231A1

(19) **United States**

(12) **Patent Application Publication**

**JOHNSON et al.**

(10) **Pub. No.: US 2021/0214231 A1**

(43) **Pub. Date: Jul. 15, 2021**

(54) **METHODS FOR PRODUCTION OF GRAPHENE OXIDE**


(71) Applicant: **UNIVERSITY OF WYOMING**, Laramie, WY (US)

(72) Inventors: **Patrick JOHNSON**, Laramie, WY (US); **Ana Paula MARTINS LEANDRO**, Laramie, WY (US)

(73) Assignee: **UNIVERSITY OF WYOMING**, Laramie, WY (US)



(21) Appl. No.: **17/149,242**

(22) Filed: **Jan. 14, 2021**

**Related U.S. Application Data**

(60) Provisional application No. 62/961,550, filed on Jan. 15, 2020.

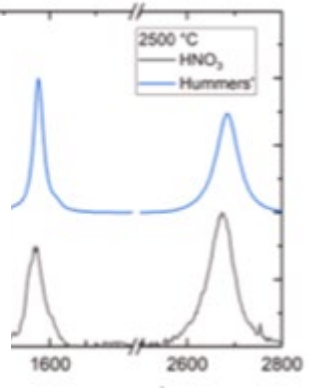
**Publication Classification**

(51) **Int. Cl.**
***C01B 32/198*** (2006.01)

(52) **U.S. Cl.**
CPC ..... ***C01B 32/198*** (2017.08)


(57) **ABSTRACT**


Methods for producing graphene oxide products are disclosed. In one embodiment, a method of producing a graphene oxide product includes contacting a carbon-containing feedstock with an oxidizing composition comprising aqueous nitric acid, wherein the concentration of nitric acid is 50 to 63 wt %, to from a reactant slurry, in response to the contacting step, oxidizing the carbon-containing feedstock of the reactant slurry to form a graphite oxide slurry; and processing the graphite oxide slurry into a graphene oxide product.


Evolution of structural and electrical properties in coal-derived graphene oxide nanomaterials during high-temperature annealing


Ana Paula Martins Leandro, Michael A. Seas, Kaitlyn Vap, Alexander Scott Tyrrell, Vivek Jain, Hud Wahab *, Patrick A. Johnson *

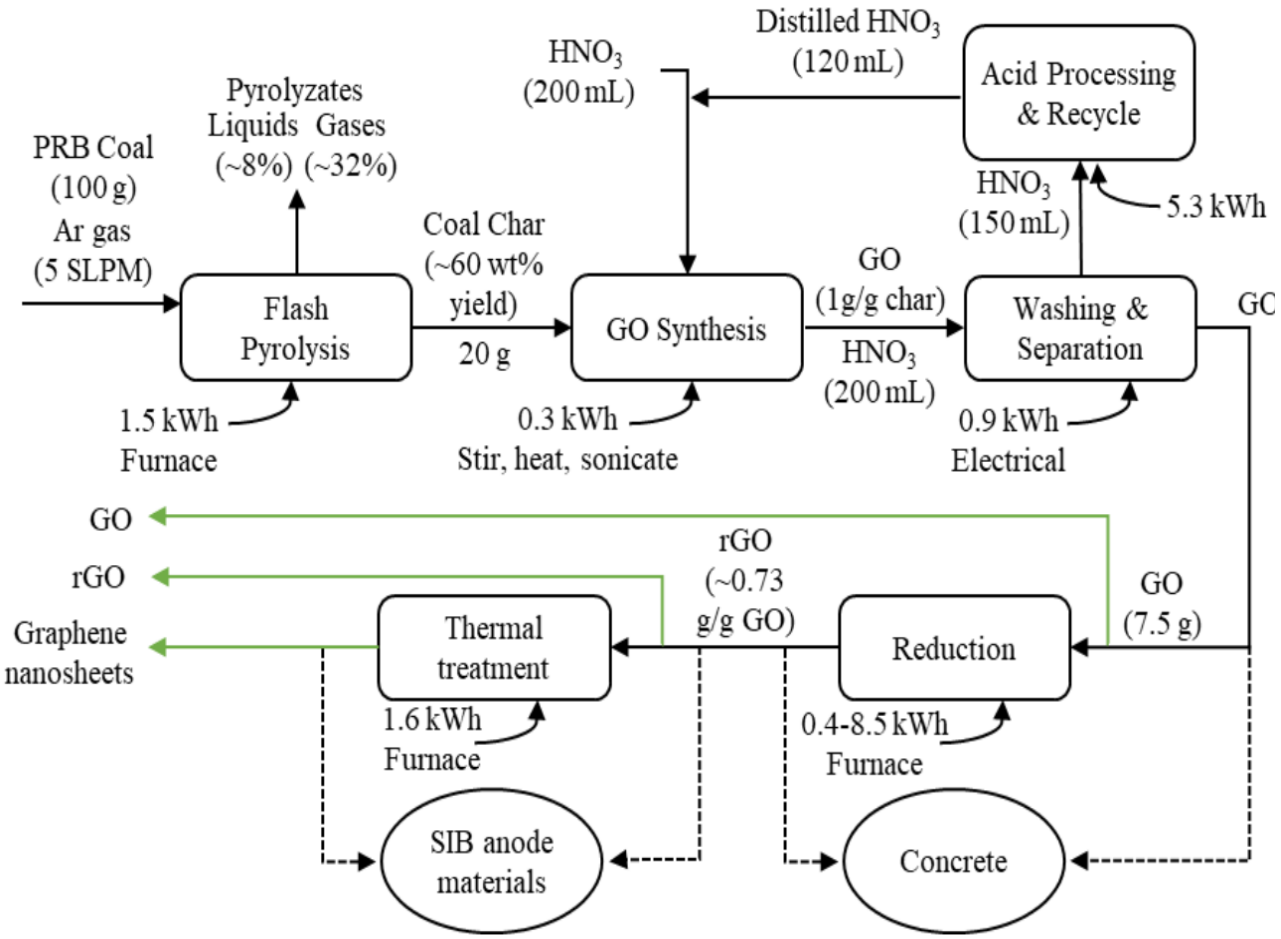
*Department of Chemical Engineering, University of Wyoming, 1000 E University Avenue, 82071 Laramie, WY, United States of America*


y with literature.

| | | Conductivity [$10^3$ S m$^{-1}$] | Ref. |
|---|---|---|---|
| Natural graphite | | 2.82 | [39] |
| Graphene microflower | 2000 | 2.12 | [38] |
| | 3000 | 0.26 | |
| Catalytic-microwave exfoliated graphite oxide | – | 2.50 | [66] |
| Graphite | 2500 | 2.42 | |
| $HNO_3$ rGO nanocrystals (Hummers' rGO nanocrystals) | 2000 | 1.50 | [67] |
| | 2500 | 1.00 | [34] |
| | | 10.6 | [42] |
| | | 19.7 | |
| | | 4.5 | [60] |
| | | 21.2 | |
| | | 53.1 | [63] |
| | | 8.98 | This work |
| | | 2.38 (2.63) | |
| | | 4.81 (4.34) | |

# Technology Background

**Production process/application**



# Technical Approach/Project Scope

## Experimental design or project steps and work plan

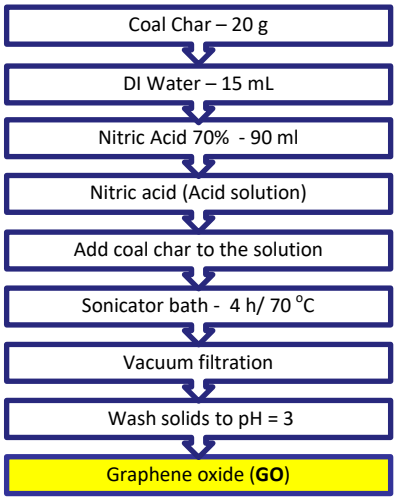
| | | |
|---|---|---|
| Task 2<br>Flash Pyrolysis | Flash Pyrolysis | Temperature range 700-1000 °C, range of carrier gas flow rates, oxidative agent use (O2, CO2, and/or steam) |
| | Gas Pyrolysis | Gas Chromatography Testing / Mass Spectrometry Testing |
| | Liquid pyrolysis | High-performance liquid chromatography (HPLC) / Inductively coupled plasma mass spectrometry (ICP-MS) |
| | Coal char | Raman, TGA, FT-IR, XRD, UV-vis, BET surface area, ICP-MS* and Elemental Analysis*. |
| Task 3<br>GO Process Optimization | GO synthesis | HNO3 in an ice bath, followed by sonication at 70 °C. Washing with DI water to pH = 6~6.9. Filtration and freeze-drying. |
| | GO | Raman, XPS, TGA, FT-IR, XRD, NMR, UV-vis, SEM, TEM, Conductivity, BET surface area, ICP-MS* and Elemental Analysis*. |
| | Process nitric acid | HNO3 recycling via vacuum distillation at 120 °C. ICP-MS* validation for impurities. |
| Task 4<br>rGO<br>graphene nanosheets | Reduction to rGO | Tube furnace reduction under flowing inert gas at 1100 °C. |
| | rGO | Raman, XPS, TGA, FT-IR, XRD, NMR, UV-vis, SEM, TEM, Conductivity, BET surface area, ICP-MS* and Elemental Analysis*. |
| | Annealing Induction | Induction furnace treatment under inert gas up to 2500 °C. |
| | Graphene nanosheets | Raman, XPS, TGA, FT-IR, XRD, NMR, UV-vis, SEM, TEM, Conductivity, BET surface area, ICP-MS* and Elemental Analysis*. |
| Task 5<br>Testing as a concrete additive | Concrete mix | Slump test |
| | Cylinders, beams, slabs | Triaxial testing, three-point flexural test, rate of absorption. |
| Task 6<br>Sodium ion battery fabrication/testing | Hard Carbon | Raman, XPS, TGA, FT-IR, XRD, NMR, UV-vis, SEM, TEM, Conductivity, BET surface area, ICP-MS* and Elemental Analysis* |
| | Swagelok half-cell assembly | Galvanostatic charge-discharge test, Coulombic efficiency test, Cyclic voltammetry (CV) test, Current rate test cycled at different densities, Cycle life test. |
| | Parallel electrochem. testing | Galvanostatic charge-discharge test (GCD), Cyclic voltammetry (CV) test, Cycle life test. |

| Milestone Title/Description | Planned Completion | Actual Completion | Comments |
|---|---|---|---|
| 2. Flash Pyrolysis of coal to coal char | Feb 2024 | Feb 2024 | This step has been carried out successfully. |
| 3. GO quality – Raman D/G-ratio higher than coal char, and >1 | Jun 2024 | N/A | This step has been carried out successfully. In the next Q3 report, more data will be added as arguments attesting to the success of this step. |
| 4. Synthesis of rGO | Nov 2024 | N/A | This step has been carried out successfully. In the next Q3 report, more data will be added as arguments attesting to the success of this step. |
| 5.Testing as concrete additive/cement replacement | Mar 2025 | N/A | This step has been carried out successfully. In the next Q3 report, more data will be added as arguments attesting to the success of this step. |
| 6.Sodium-ion battery fabrication /test | Jun 2025 | N/A | Initial tests have been conducted |

| Milestone Title/Description | Planned Completion |
|---|---|
| 3. GO quality – Raman D/G-ratio higher than coal char, and >1 | Jun 2024 |

**Johnson's Laboratory - Iowa State University**
Process coal char - 120g / week
GO production – 110 g/ week

**GO - HNO3 Method**



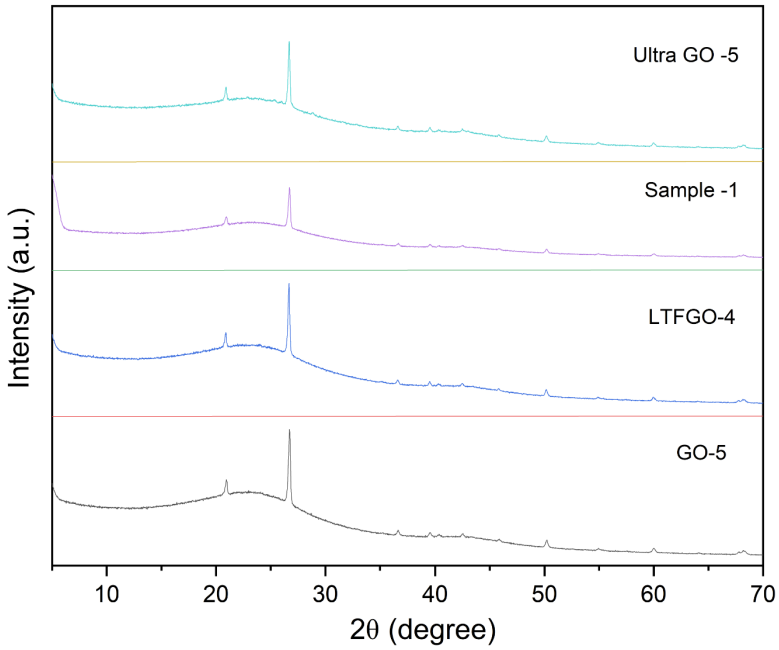




**Figure 3: XRD spectra of coal rGO -1100 oC/2h.**

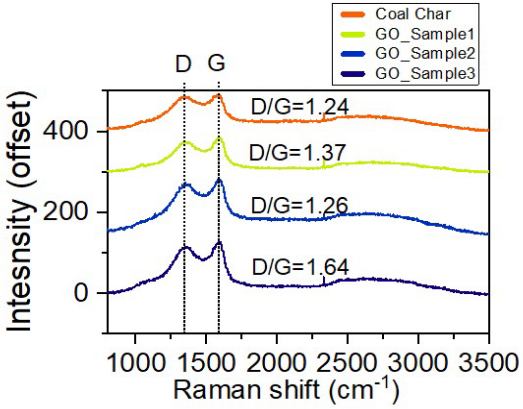



**Figure 4: Raman spectrum to coal char and Graphene Oxide.**

| Milestone Title/Description | Planned Completion |
|---|---|
| 4. Synthesis of rGO | Nov 2024 |

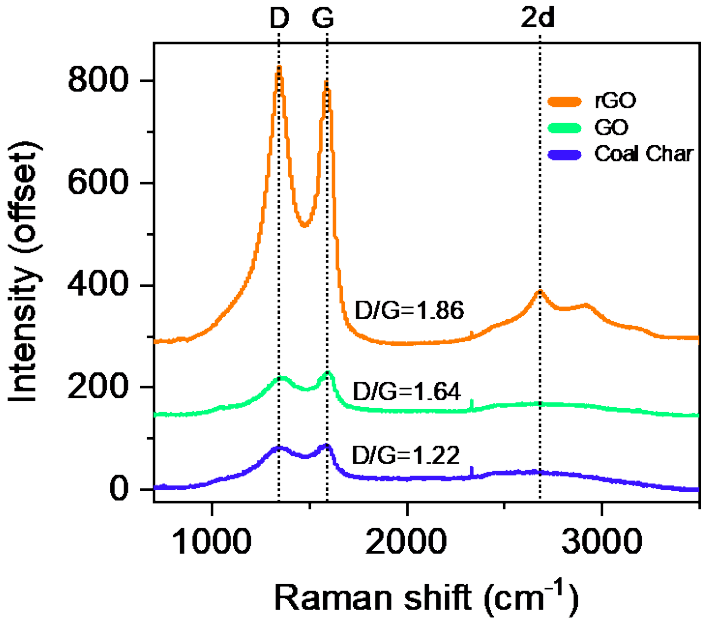



**Figure 5: Raman spectrum to coal char, graphene oxide and reduced Graphene Oxide**

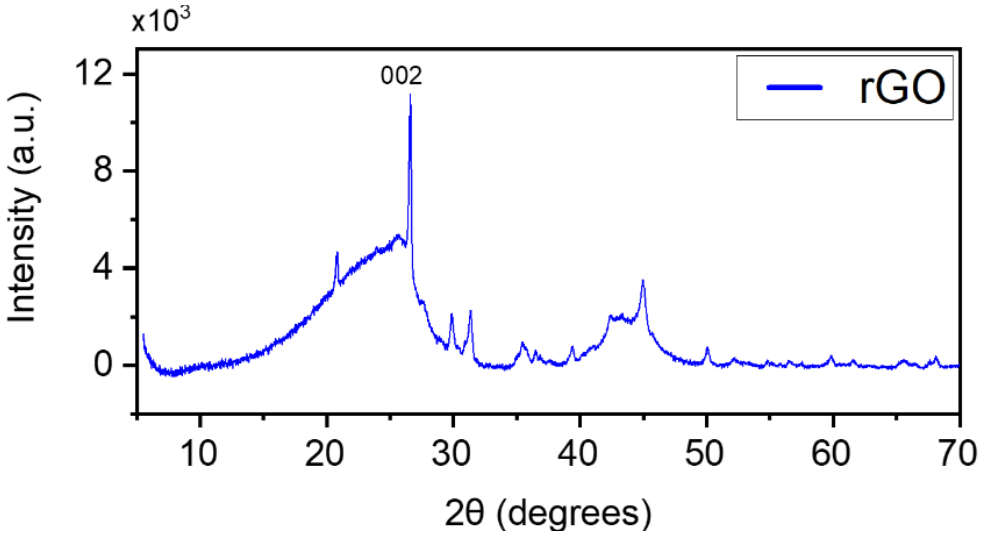



**Figure 6: XRD spectra of coal rGO -1100 oC/2h.**

| Milestone Title/Description | Planned Completion |
|---|---|
| 4. Synthesis of rGO | Nov 2024 |

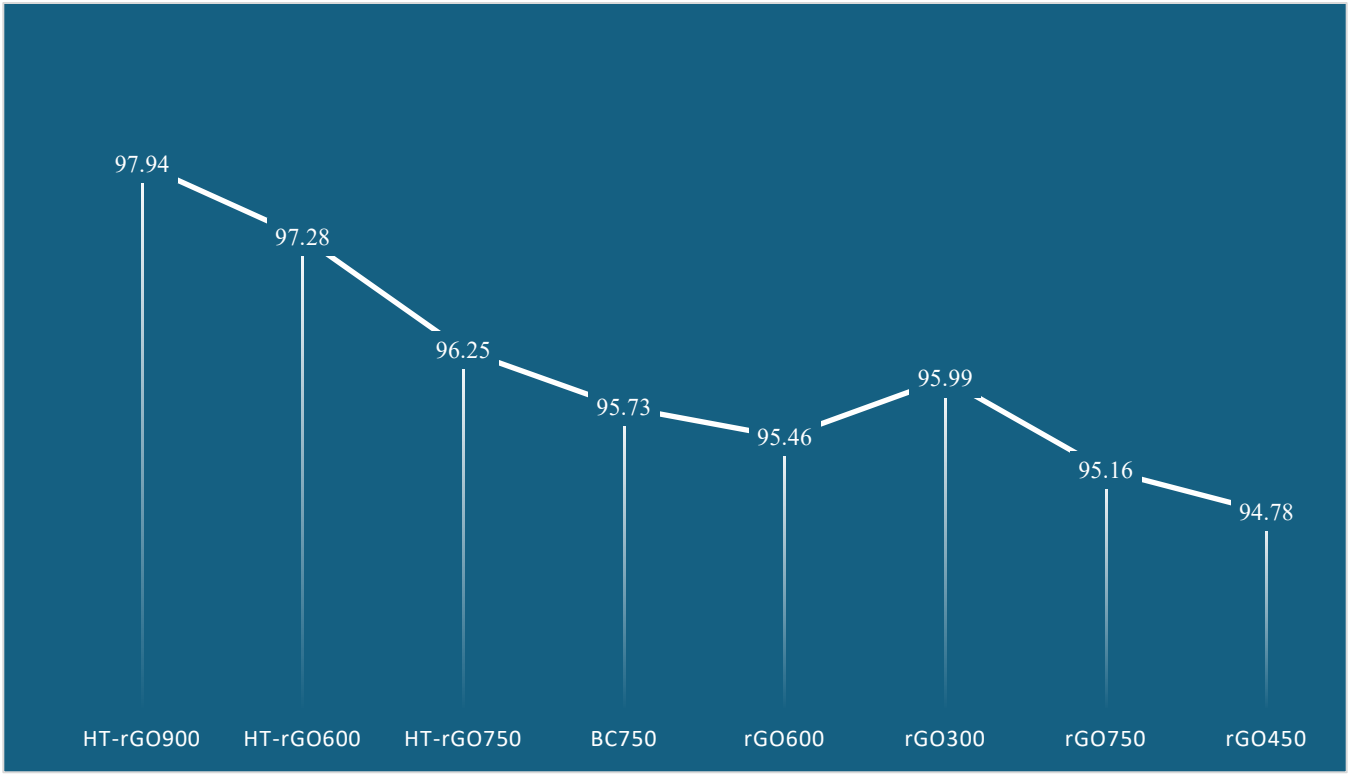



**Figure 7: XPS results, sp2 (%) for C1s.**

| Milestone Title/Description | Planned Completion |
|---|---|
| 5.Testing as concrete additive/cement replacement | Mar 2025 |

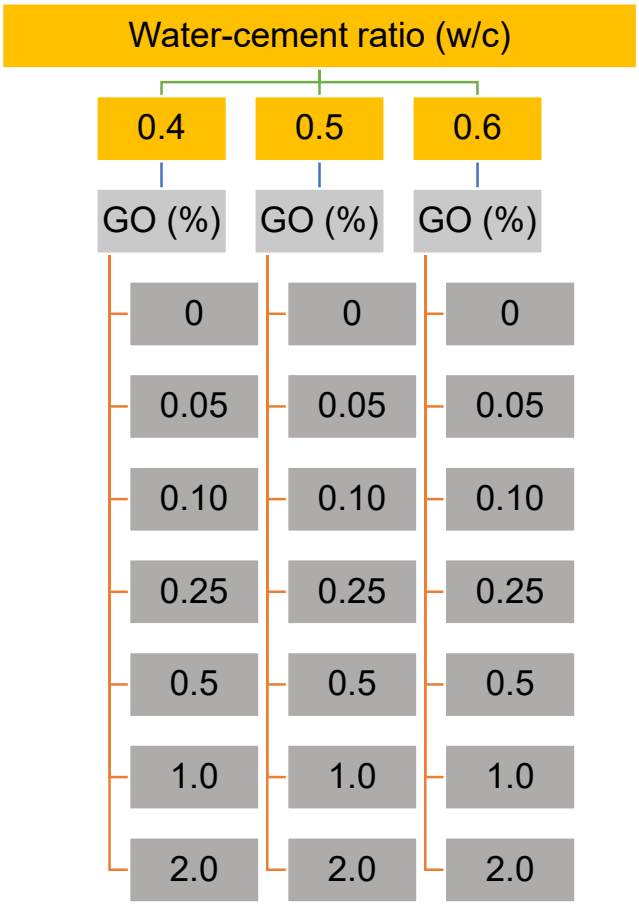







| Milestone Title/Description | Planned Completion |
|---|---|
| 5.Testing as concrete additive/cement replacement | Mar 2025 |

GO as a replacement




GO as an additive

| Milestone Title/Description | Planned Completion |
|---|---|
| 6.Sodium-ion battery fabrication /test | Jun 2025 |

- **Initial charge discharge testing was performed using 22 $mAg^{-1}$.**

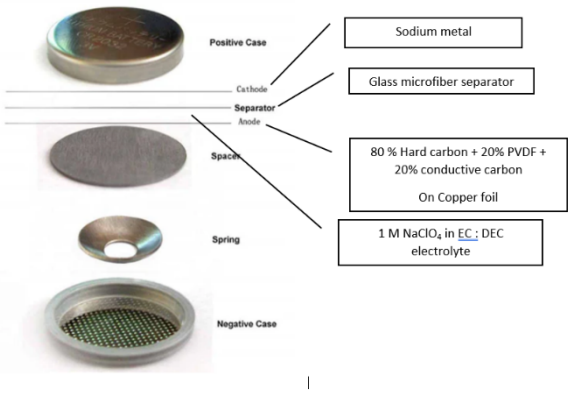
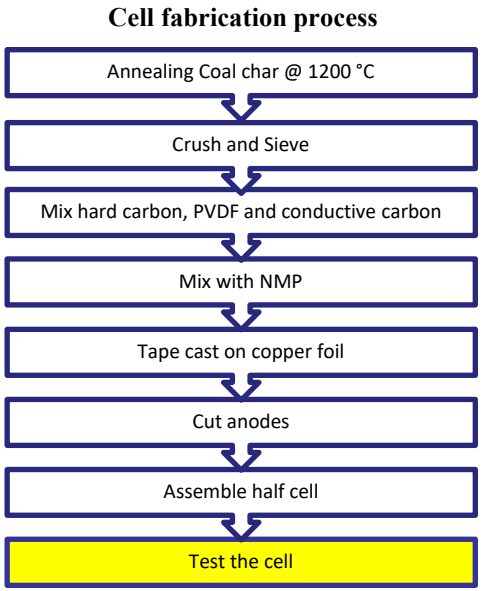



**Figure 8: Sodium ion half cells have been fabricated as shown in the following diagram.**

**Figure 9: Tape cast anode from coal char hard carbon.**



# Plans for future testing/development/ commercialization (1-2 Slides)

Plans for future testing/development/commercialization (one or two slides)

a. In this project
b. After this project (i.e., next project)
c. Scale-up potential, if applicable

a. Successful scale of coal char production achieved for project

b. Successful scale of graphene oxide production achieved.

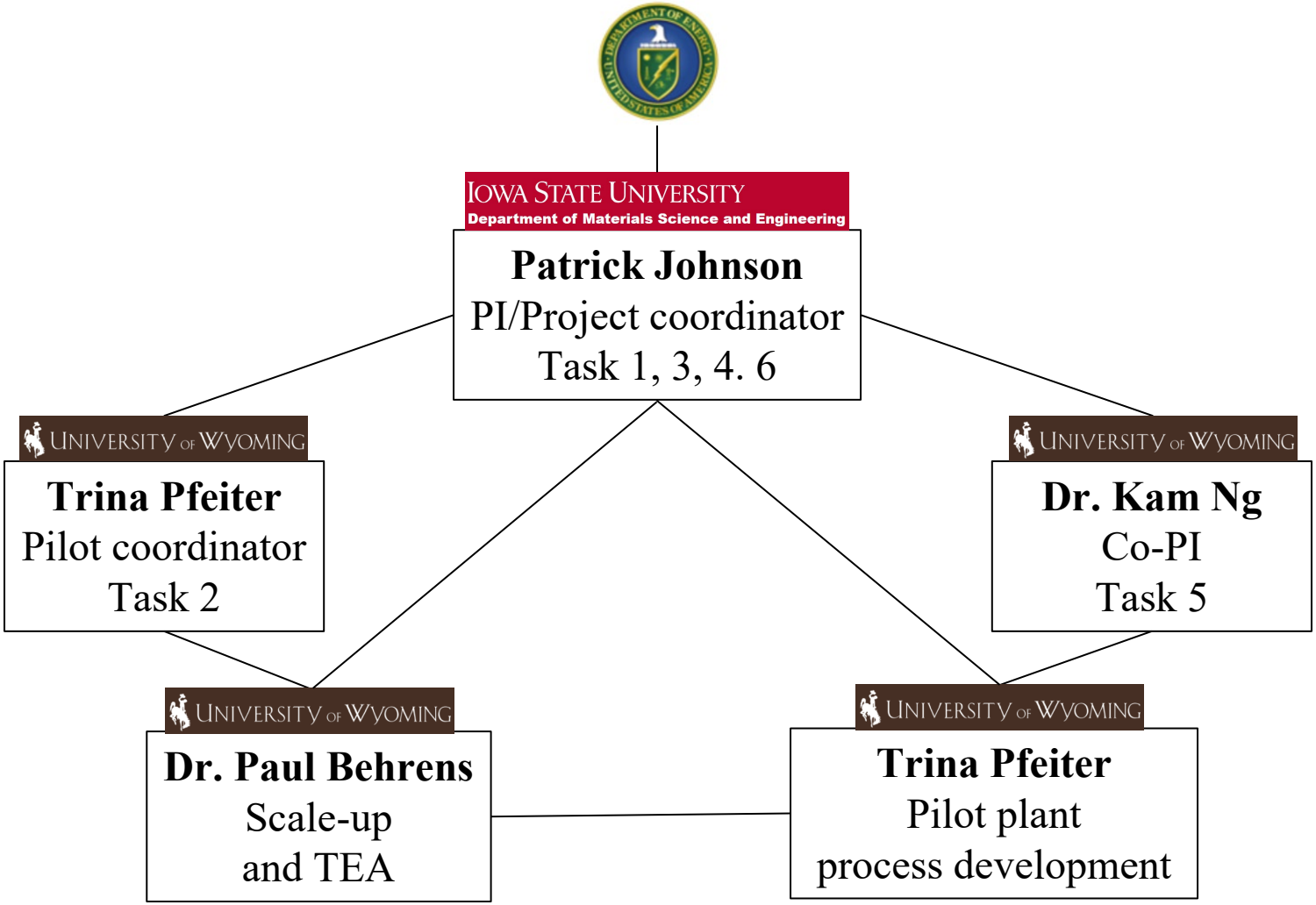
c. Cement testing underway

d. Battery fabrication and testing underway with hard carbons

# Appendix

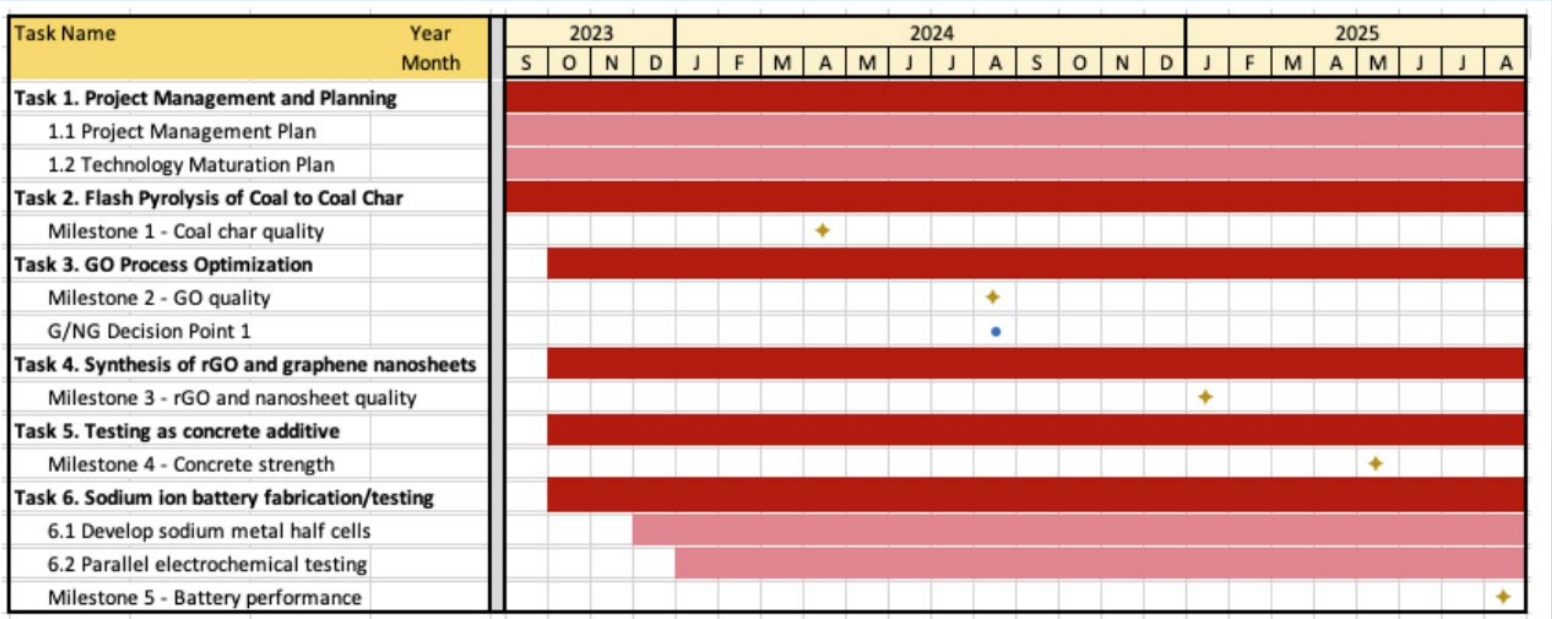
- These slides will not be discussed during the presentation but are mandatory.

# Organization Chart



# Gantt Chart

- Provide a simple Gantt chart showing project lifetime in years on the horizontal axis and major tasks along the vertical axis. Use symbols to indicate major and minor milestones. Use shaded lines or the like to indicate duration of each task and the amount of work completed to date.



| | FY 2024 | | FY 2025 | |
|---|---|---|---|---|
| | DOE Funds | Cost Share | DOE Funds | Cost Share |
| **Applicant ISU** | $297,533 | $71,381 | $289,998 | $75,519 |
| **Subaward to UW** | $194,473 | $51,550 | $217,912 | $51,550 |
| **Total ($)** | $492,006 | $122,931 | $507,910 | $127,069 |
| **Total Cost Share %** | | 20% | | 20% |

| Precursor and Products | Price [$/kg] |
|---|---|
| Wyoming subbituminous PRB coal | 0.016 |
| Industrial Graphene Oxide Bulk Powder products | 32 |
| Hard Carbon Powder for Sodium Ion Battery Anode | 1,190 |
| High Quality Monolayer Graphene Oxide | 5,000 |
| 99% Purity Industry Graphene Powder for battery | 2,500 |
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| Few Layer Reduced Graphene Oxide | 13,000 |