# Electrochemical Production of Highly Valuable Carbon Nanotubes from Flue-Gas Sourced $CO_2$

## DE-FE-0031913

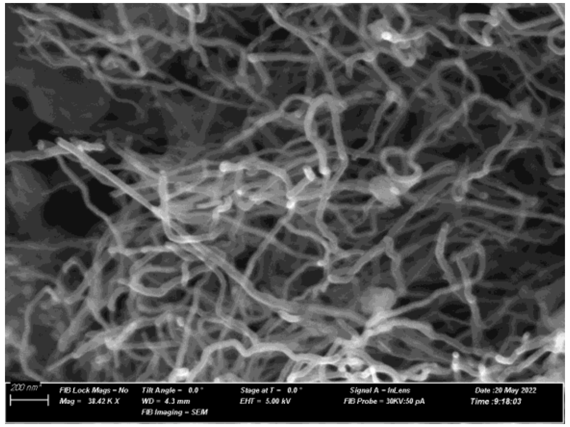
**Dr. Anna Douglas | SkyNano**

U.S. Department of Energy

National Energy Technology Laboratory
Carbon Management Project Review Meeting
August 15-19. 2022

# PROJECT GOALS

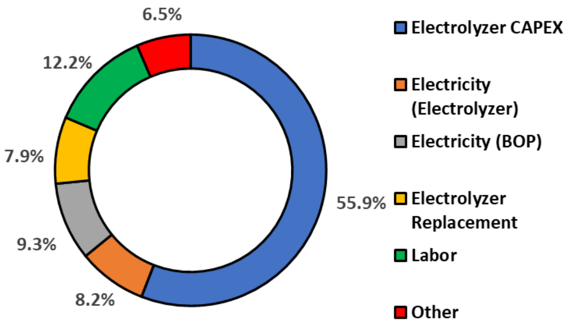
$CO_2$ capture from NGCC flue gas



Market-ready production of MWCNTs from TVA flue gas-derived $CO_2$

End of project scale: $0.2 kg_{CNT}/hr$

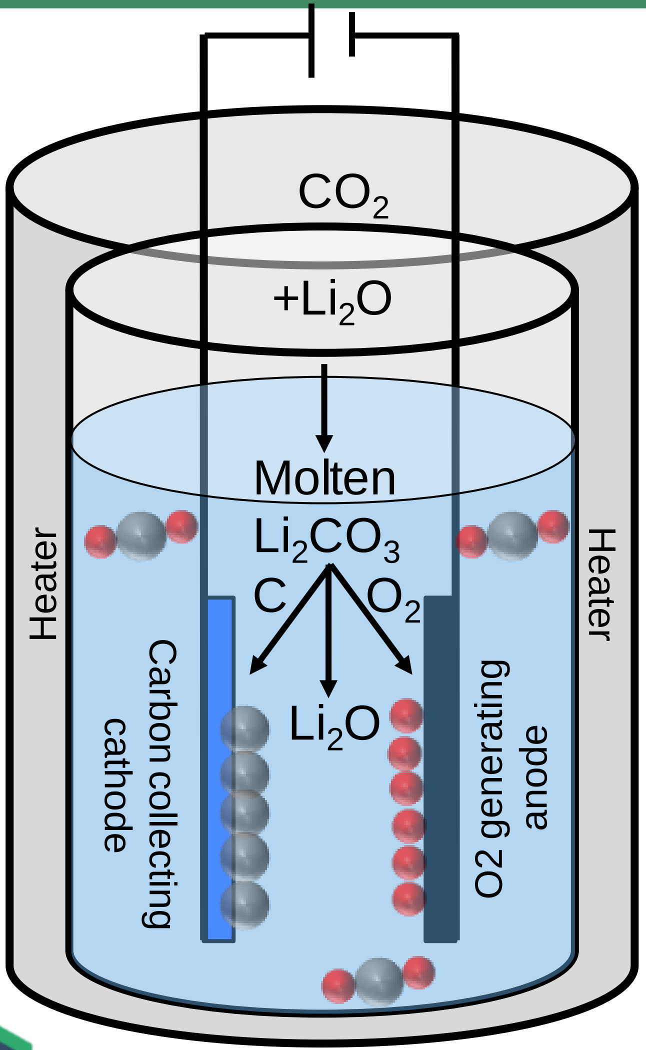
80% $CO_2$ capture; 80% CE; <30nm diameter; ID/IG<1




TEA + LCA in collaboration with NREL – MWCNT MSP goal 80-90% less than today's market

**Total project budget**
*$2.5M*
**Timeline**
*10/01/2020-09/30/2023*
**NETL PM**
*Natalie Iannacchione*

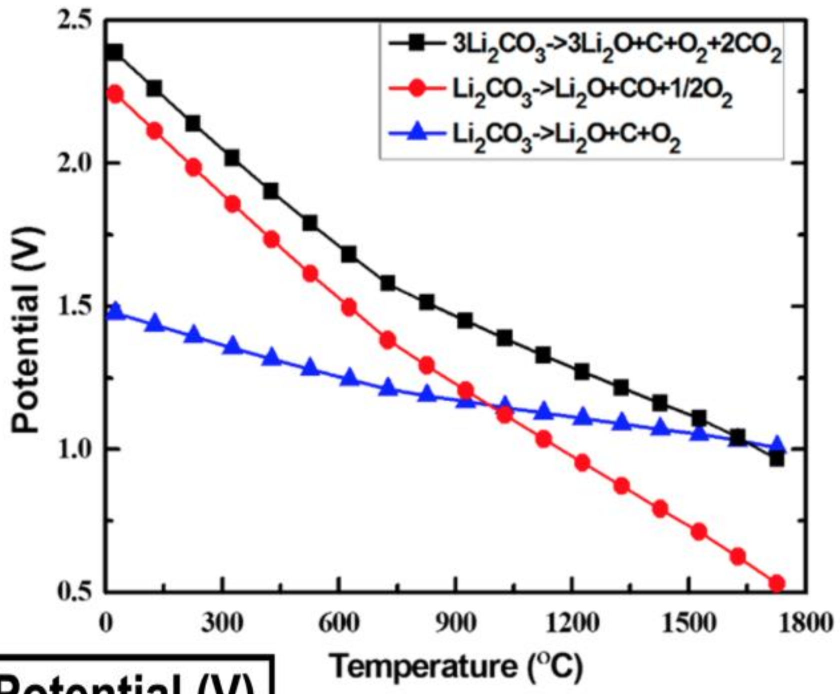
# ELECTROLYTIC $CO_2$ REDUCTION CHEMISTRY




$Li_2CO_3 \rightarrow Li_2O + C + O_2$

$Li_2O + CO_2 \rightarrow Li_2CO_3$

NET: $CO_2 \rightarrow C + O_2$




| | | Reduction Potential (V) | |
|---|---|---|---|
| Molten Salt | MP (C) | Alkali Metal | Carbon |
| Li2CO3 | 723 | -2.964 | -1.719 |
| Na2CO3 | 851 | -2.546 | -2.551 |
| K2CO3 | 891 | -2.612 | -3.083 |

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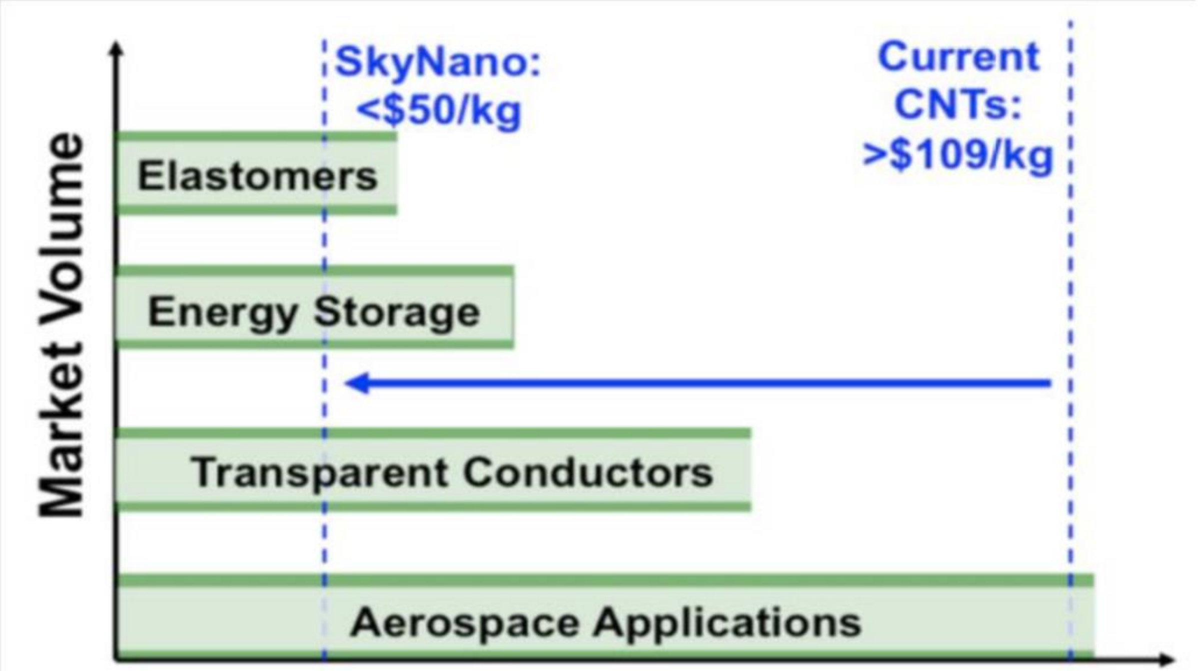
J. Ren, et. al. J. Phys. Chem. C. 2015 (119)

# CNTS: HIGH $CO_2$ VALUE

| Species | #e- | Pathway | US Market Price ($/kg)[a] | $/e- req. (x10[3])[b] | Global Production (MMT/y) | $CO_2ec$ (MMT $CO_2$/y) |
|---|---|---|---|---|---|---|
| Carbon Monoxide | 2 | EC, TC | 0.18 | 2.6 | 150 | 236 |
| Formic Acid | 2 | EC, TC | 0.66[d] | 15.2 | 0.6 | 0.60 |
| **Carbon Nanotubes** | **4** | **EC** | **110.2** | **331.0** | **0.003[e]** | **0.01** |
| Methanol | 6 | EC, TC | 0.35 | 1.9 | 91.8[f] | 126 |
| Methane[g] | 8 | EC, TC, BC | 0.15 | 0.3 | 2336 | 6410 |
| Acetic Acid | 8 | EC, BC | 0.61 | 4.6 | 14.3 | 21 |
| Ethylene Glycol | 10 | EC | 0.93 | 5.8 | 28.3[h] | 40 |
| Acetaldehyde | 10 | EC | 1.42 | 6.3 | 0.9[e] | 1.8 |
| Dimethyl Ether | 12 | TC | 0.65[i] | 2.5 | 3.7 | 7.1 |
| Ethanol | 12 | EC, TC, BC | 0.52 | 2.0 | 89.6 | 171 |
| Ethylene | 12 | EC, TC, BC | 0.71 | 1.7 | 156 | 490 |
| Acetone | 16 | EC | 1.00 | 3.4 | 6.8[j] | 15 |
| Propionaldehyde | 16 | EC | 1.6[k] | 5.8 | 0.6[l] | 1.4 |
| Propylene | 18 | TC | 1.07 | 2.5 | 117 | 367 |
| 1-Propanol | 18 | EC | 1.43 | 4.8 | 0.2 | 0.4 |
| Isopropanol | 18 | BC | 1.07 | 3.6 | 1.9[f] | 4.2 |




**SkyNano targeting carbon black additive-based markets, representing a 8.1 MMT/y market**

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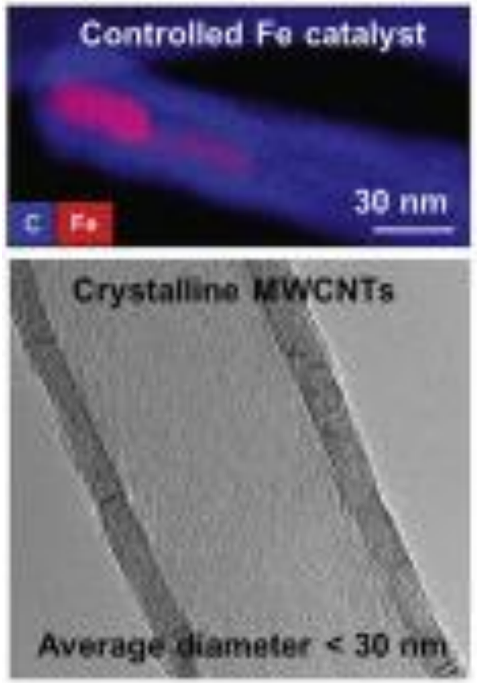
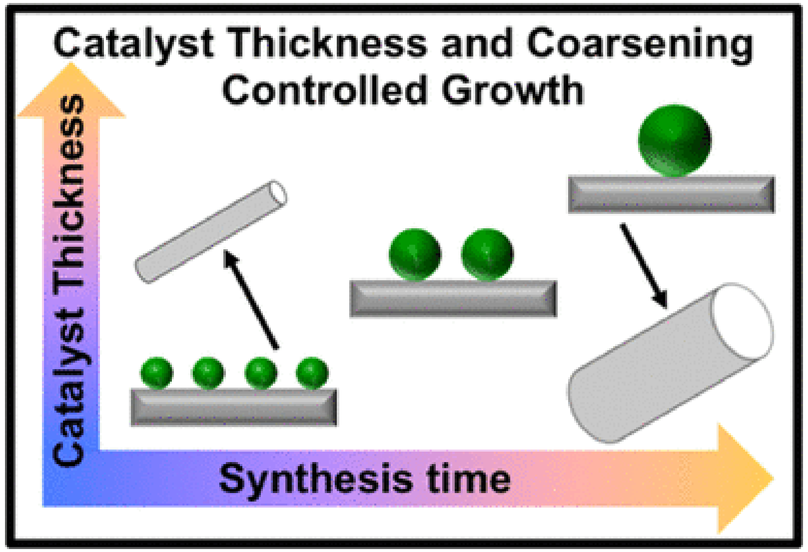
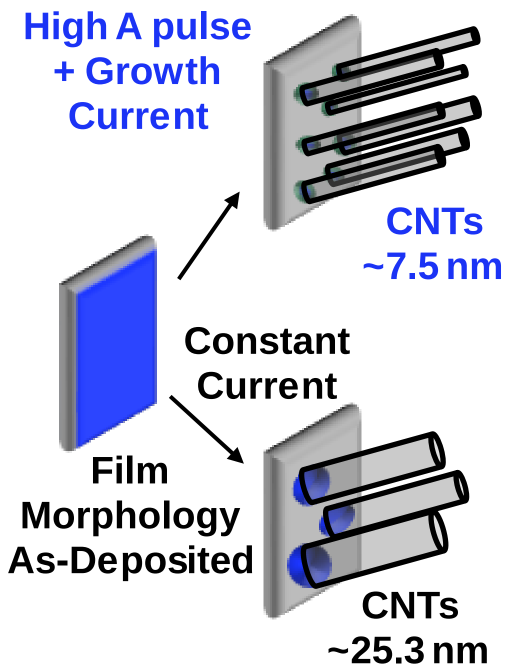
# SKYNANO TECHNOLOGY ADVANCEMENTS




Engineered anode w/ surface passivity that enables catalyst on cathode to be active

Mitigating Ostwald Ripening to control MWCNT diameter + structure




Utilization of electrochemical controls such as current pulsing to modulate MWCNT product structure

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Douglas, A. *et. al*. *Carbon*, 2017, 116, 572-578
Douglas, A. *et. al*. *ACS Appl. Mater. Int.*, 2018, 10 (22), 19010-19018

# TECHNICAL APPROACH OVERVIEW

- Task 2 + 3 focused on closed e-cell demonstrating CNT growth from $CO_2$ gas inputs
  - pure $CO_2$
  - synthetic flue gas
  - TVA-provided flue gas
- Task 4 focused on scaling e-cell to $0.05kg_{CNT}$/hr + system of 4 cells totaling $0.2kg_{CNT}$/hr
- Task 5 focused on integrating all systems required for fully continuous operation

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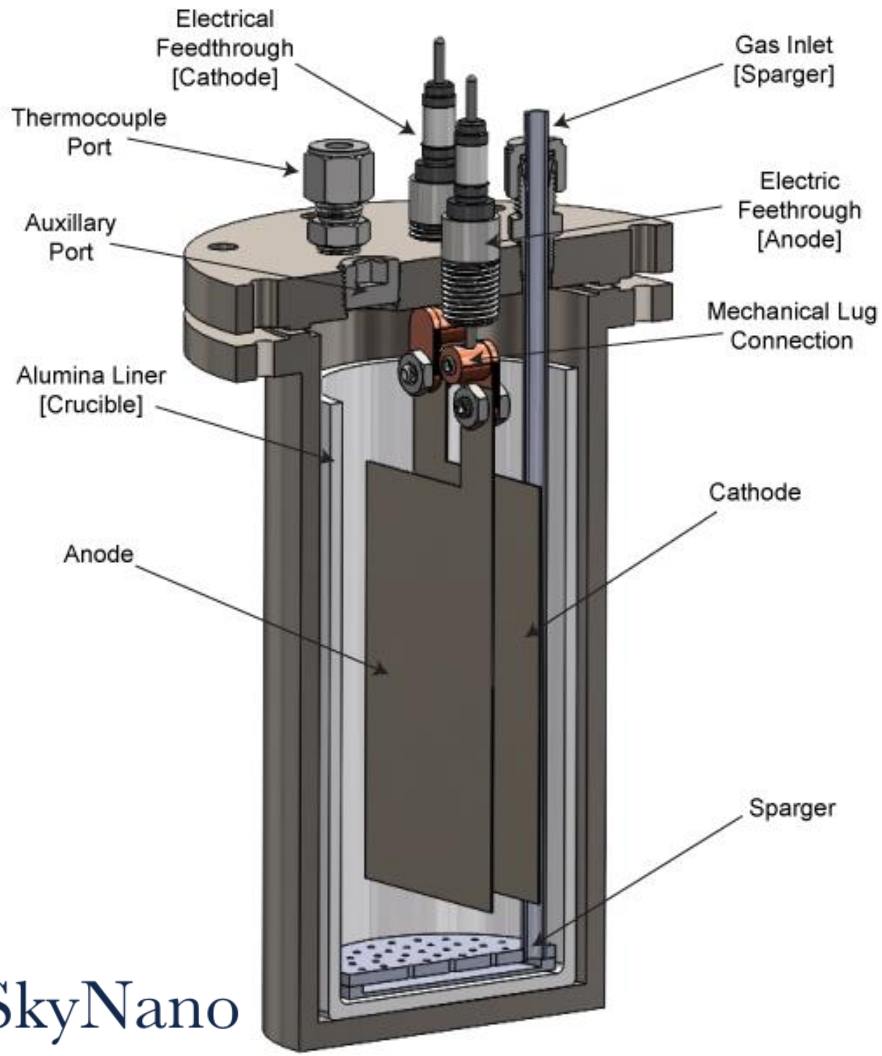
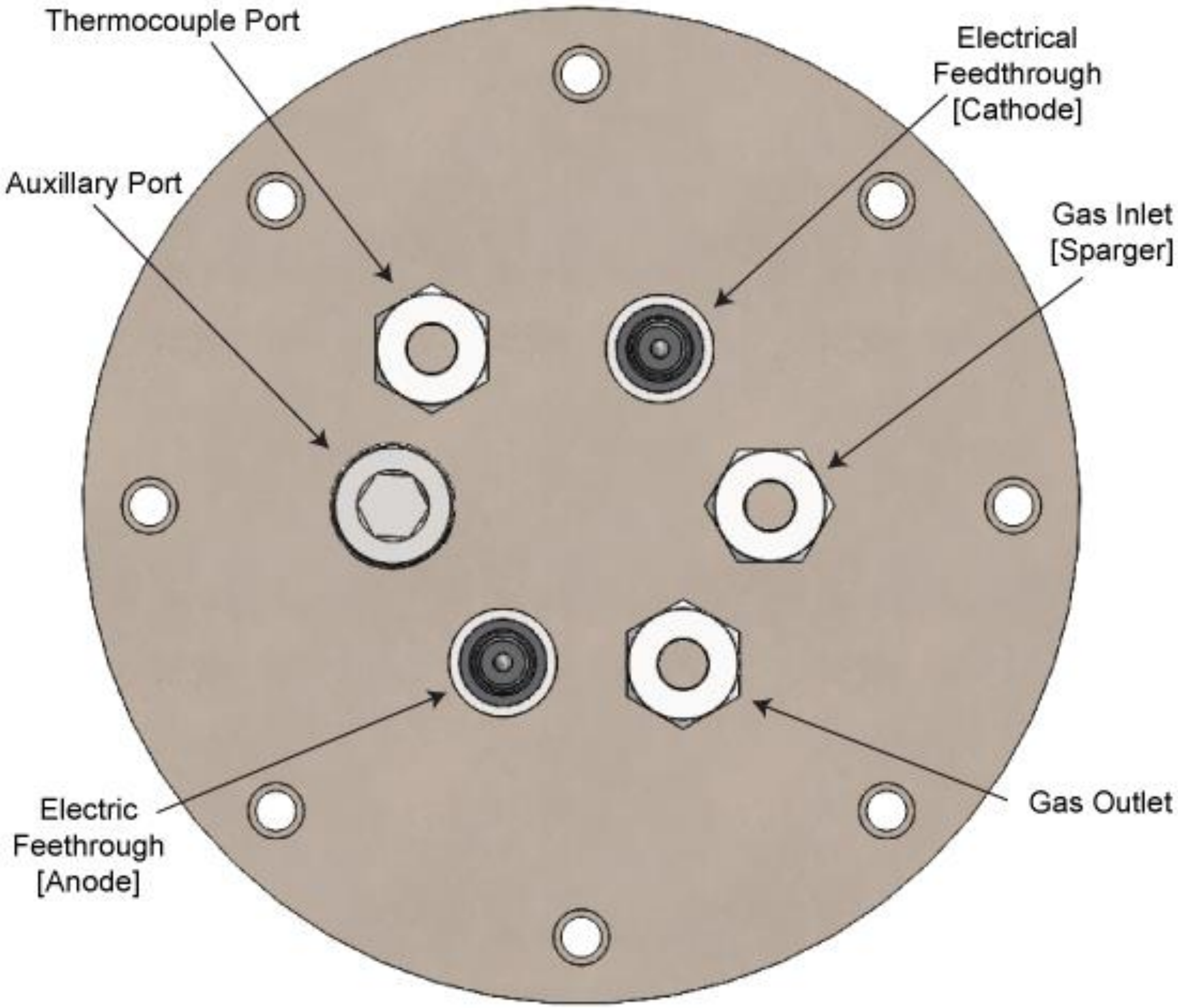
# TASK 2: DESIGN

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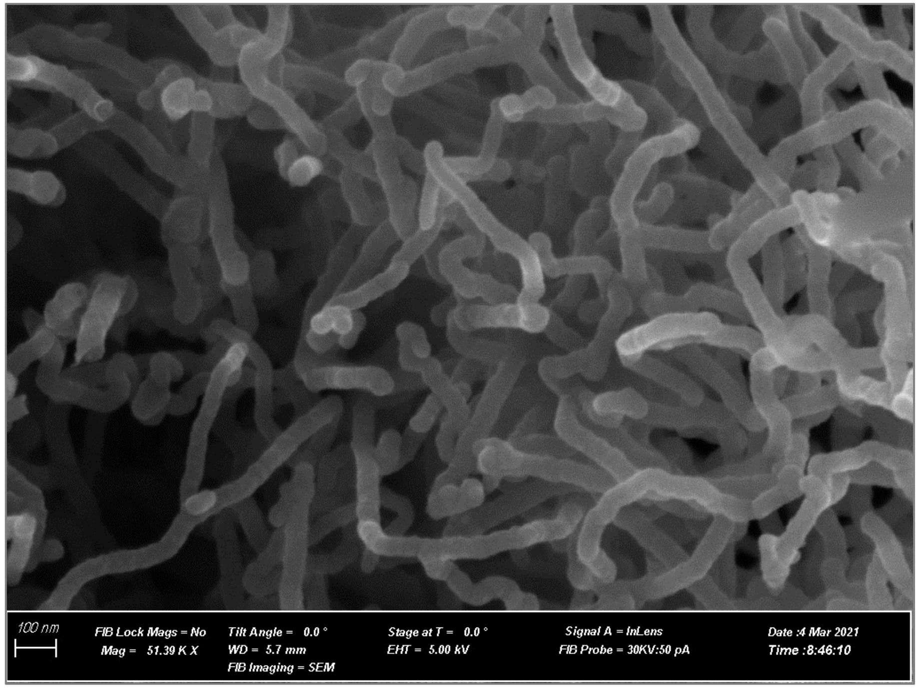
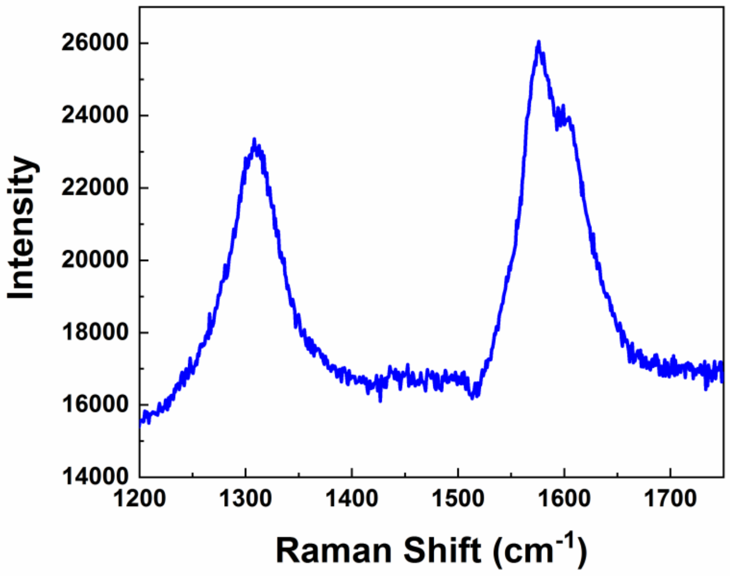
# TASK 2: BUILD + VERIFY




Things we noted:

1. $Li_2CO_3$ was splashing onto the lid and top part of electrochemical feedthroughs and required a cleaning procedure to be developed and executed between electrolysis experiments
2. Observation of carbon growth on front and back side of cathode, indicating some e-fields were reaching back of cathode and causing carbon growth
3. $Al_2O_3$ crucible was experiencing cracking and leaking $Li_2CO_3$ – unable to determine failure mechanism but switched to metal crucible

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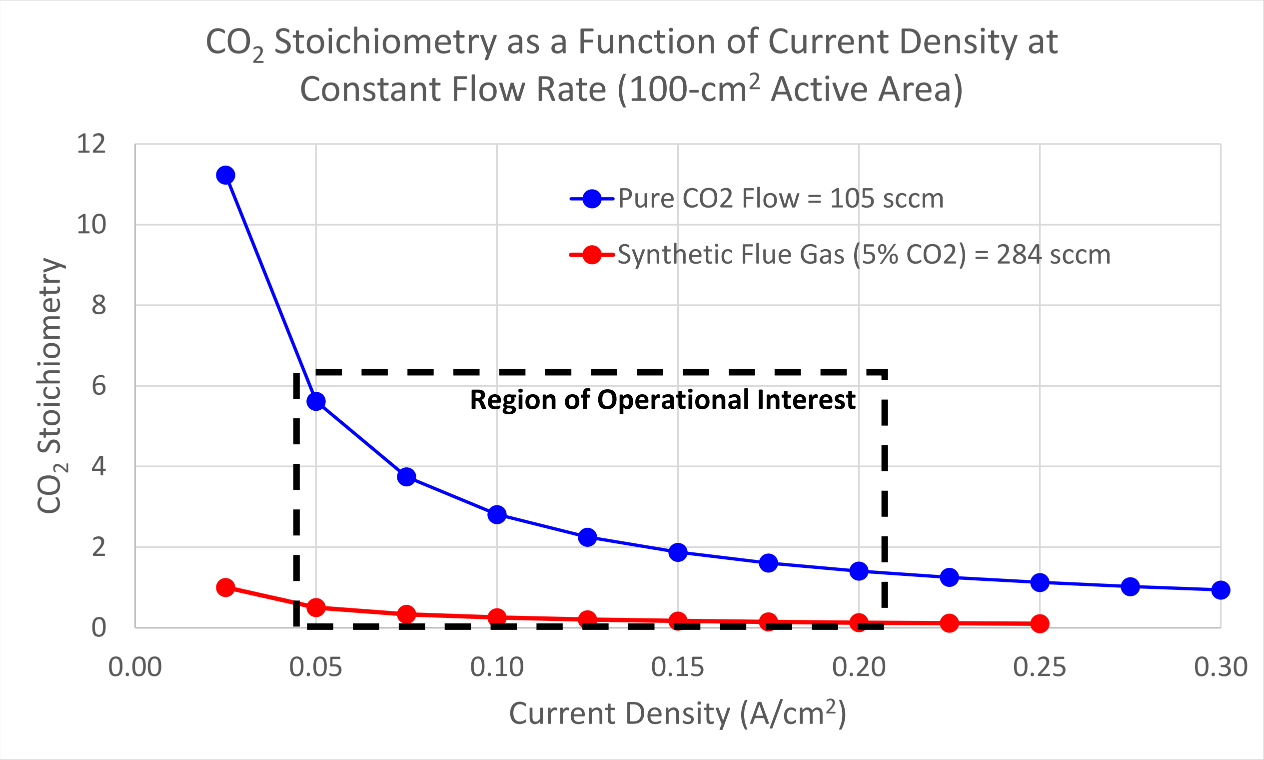
# TASK 2: GAS FLOW RESULTS FROM 100% $CO_2$


$$CO_2\ Utilization\ (\%) = \frac{CO_2\ Uptaken}{Total\ CO_2\ Inlet\ Flow} \times 100$$

$$CO_2\ Conversion\ (\%) = \frac{moles\ CO_2\ Uptaken}{Th.moles\ CNTs\ (80\%\ C.E)} \times 100$$

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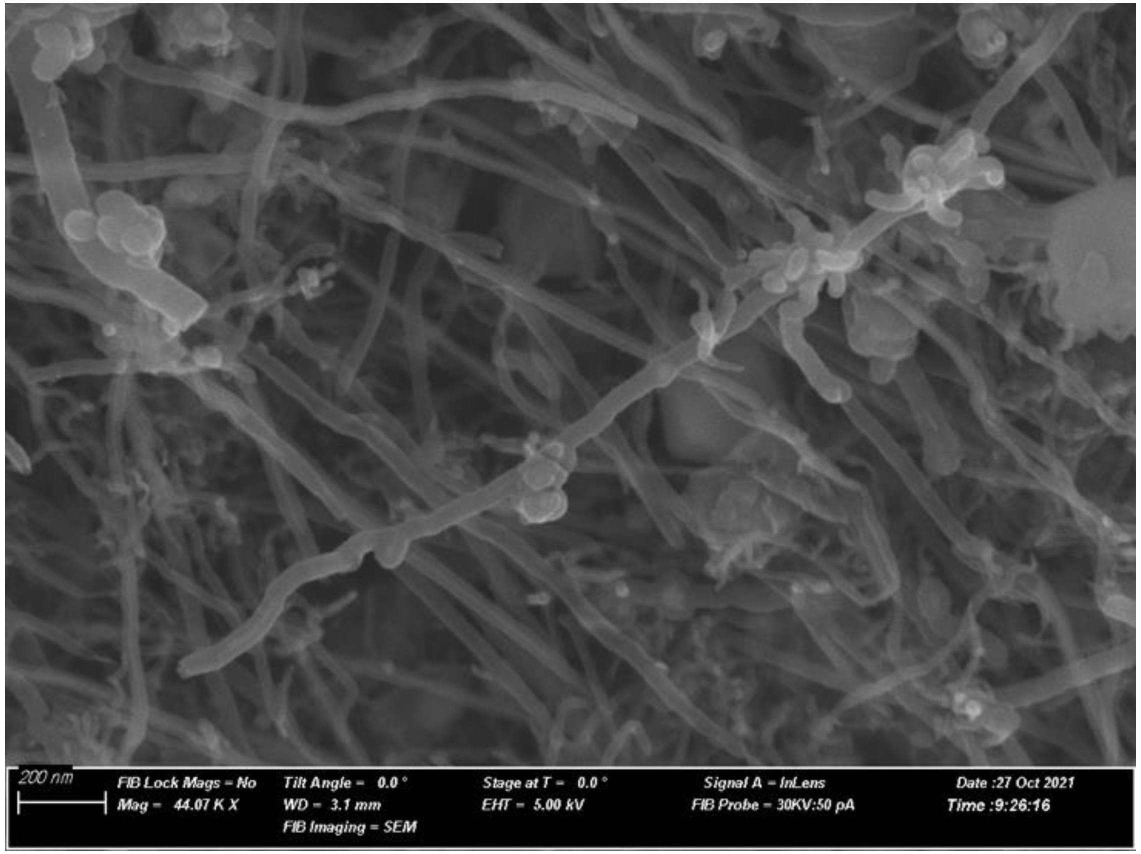
# TASK 2: UTILIZING SYNTHETIC FLUE GAS

- Selected flue gas blend based on feedback from TVA's historian data on output concentrations of CO2, O2, & N2 from natural gas combined cycle power plants
- 83% $N_2$, 12% $O_2$, 5% $CO_2$, and 12 ppm NO
- High CO2 uptake (93%) + MWCNT product with diameters ~30nm

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# TASK 2: COLLECTING REAL FLUE GAS

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# TASK 2: COLLECTING REAL FLUE GAS

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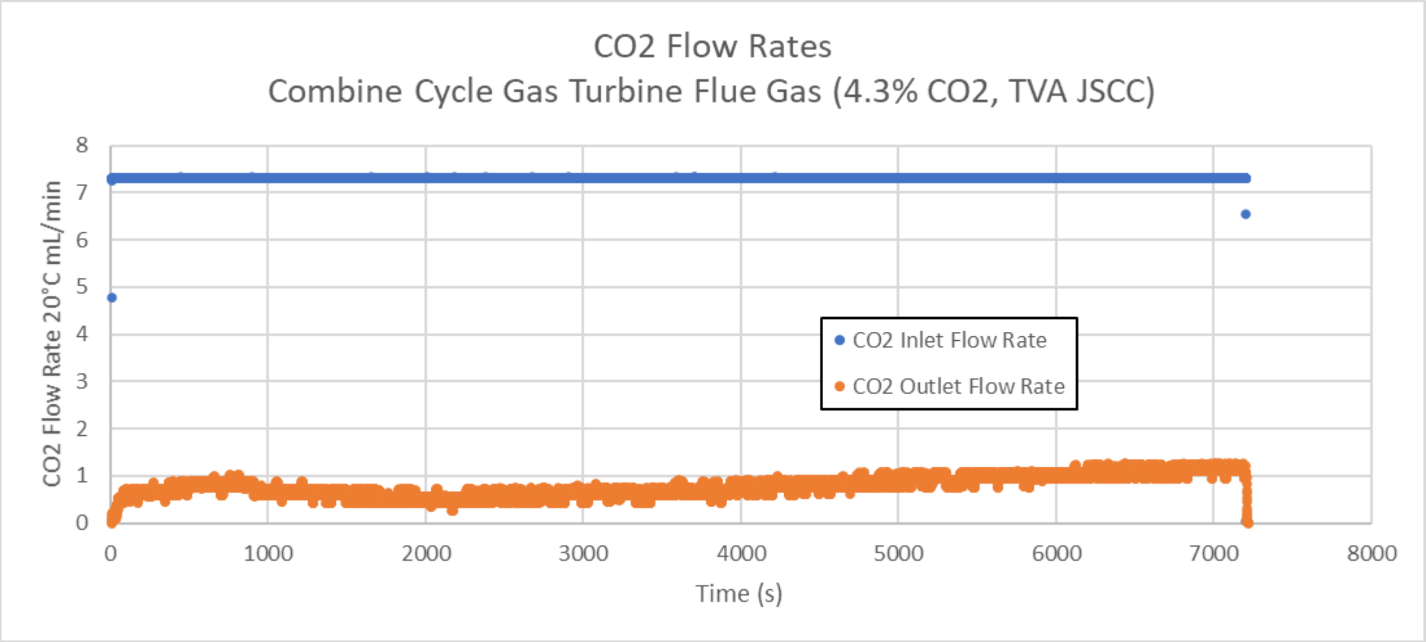
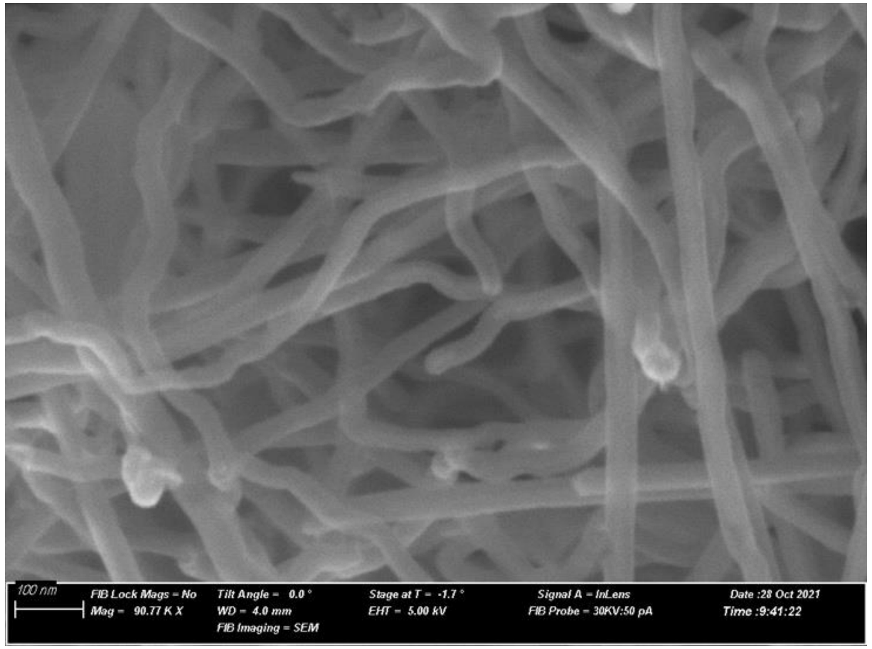
# TASK 2: UTILIZING TVA FLUE GAS

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# TASK 2: MILESTONE E

| Gas Composition | Average CNT-Diameter Range (nm) | $I_D/I_G$ Ratio | Coulombic Efficiency (%) | $CO_2$ Utilization (%) | Carbon Conversion Percent ($CO_2$ to CNT) |
|---|---|---|---|---|---|
| Pure $CO_2$ | ~ 30 nm | N/A | 74.1 | 44.4 | 83.5 |
| Airgas Synthetic Flue Gas | ~ 30 nm | N/A | 89.95 | 93.19 | 91.13 |
| TVA John Sevier Combined Cycle (JSCC) Unit 2 Flue Gas | ~ 26 nm | ~1 | 87.88 | 87.91 | 87.89 |

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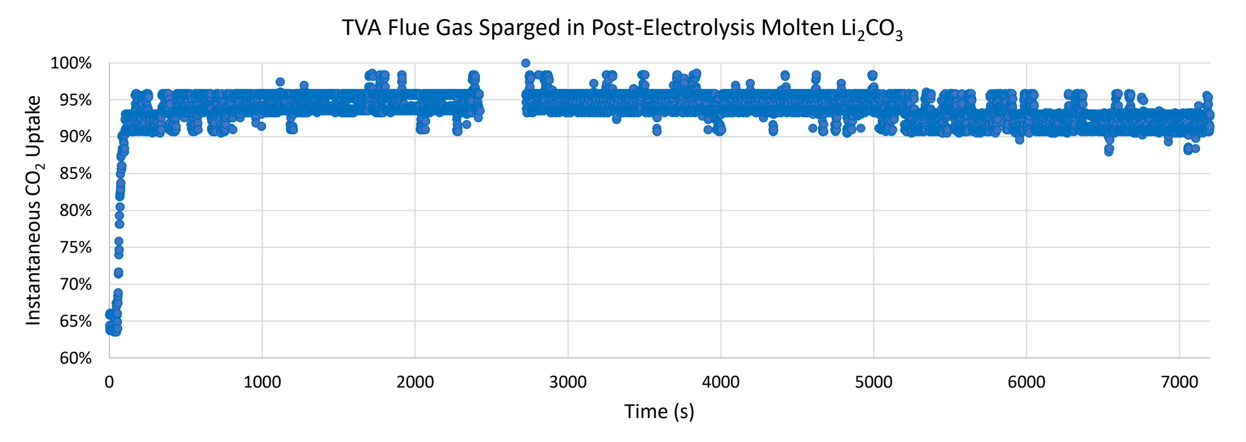
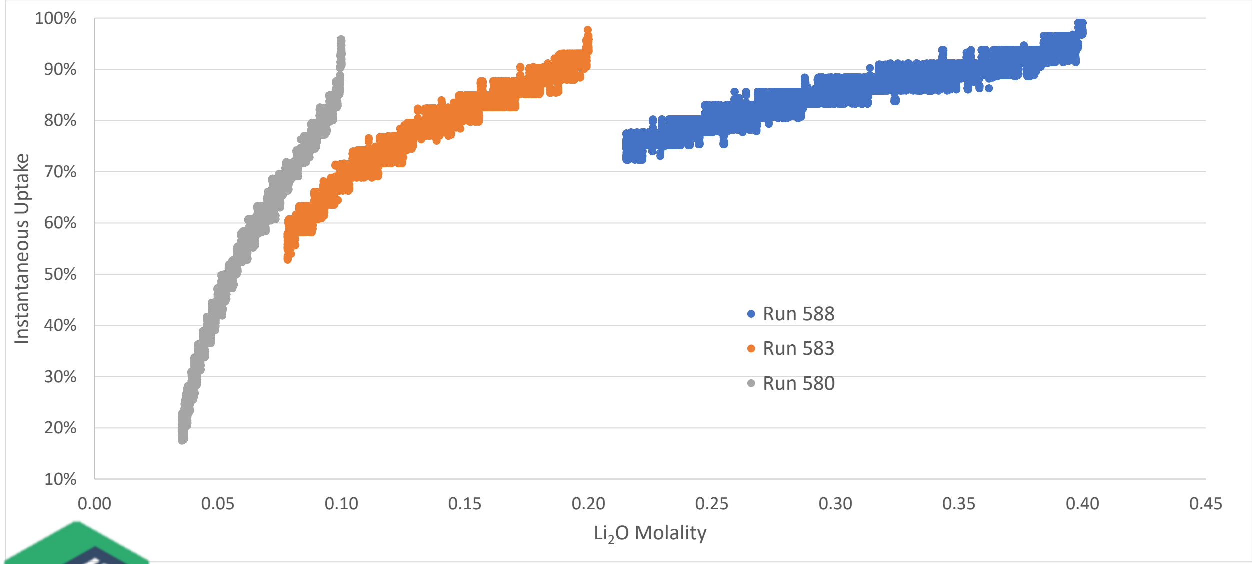
# TASK 3: IMPROVED CO2 UPTAKE PROTOCOL




Varying CO2 uptake measurements previously lead to questions about the effects of exposure to atmospheric CO2 or possibly Li2O crystals getting stuck within the carbon cake on the cathode surface.

While we awaited for parts to arrive for new E-cell, we devised a set of experiments to elucidate the effects of various Li2O molar concentrations on CO2 uptake kinetics.

Starting with known concentrations of Li2O from powdered precursors in Li2CO3 melts, we were able to measure uptake over time for 3 different starting concentrations.

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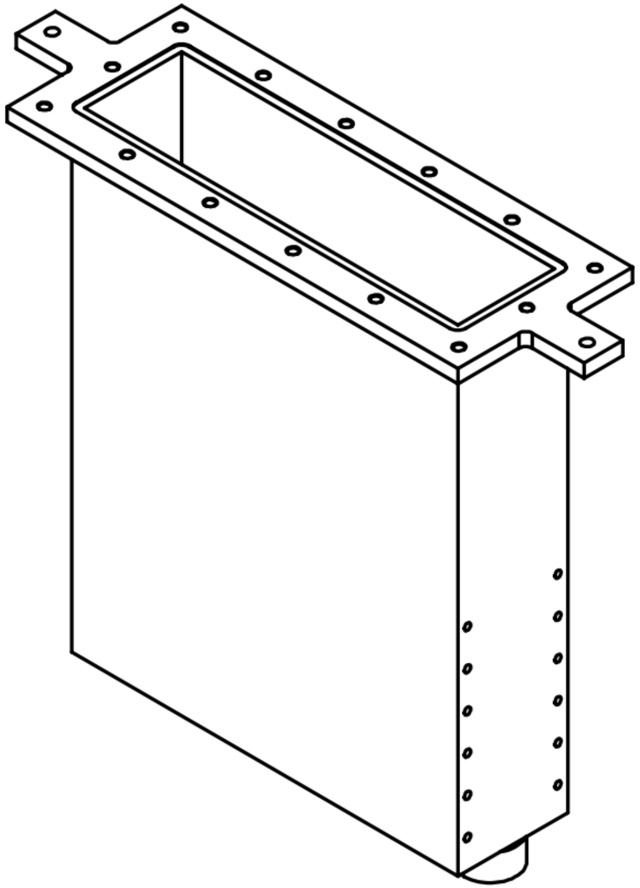
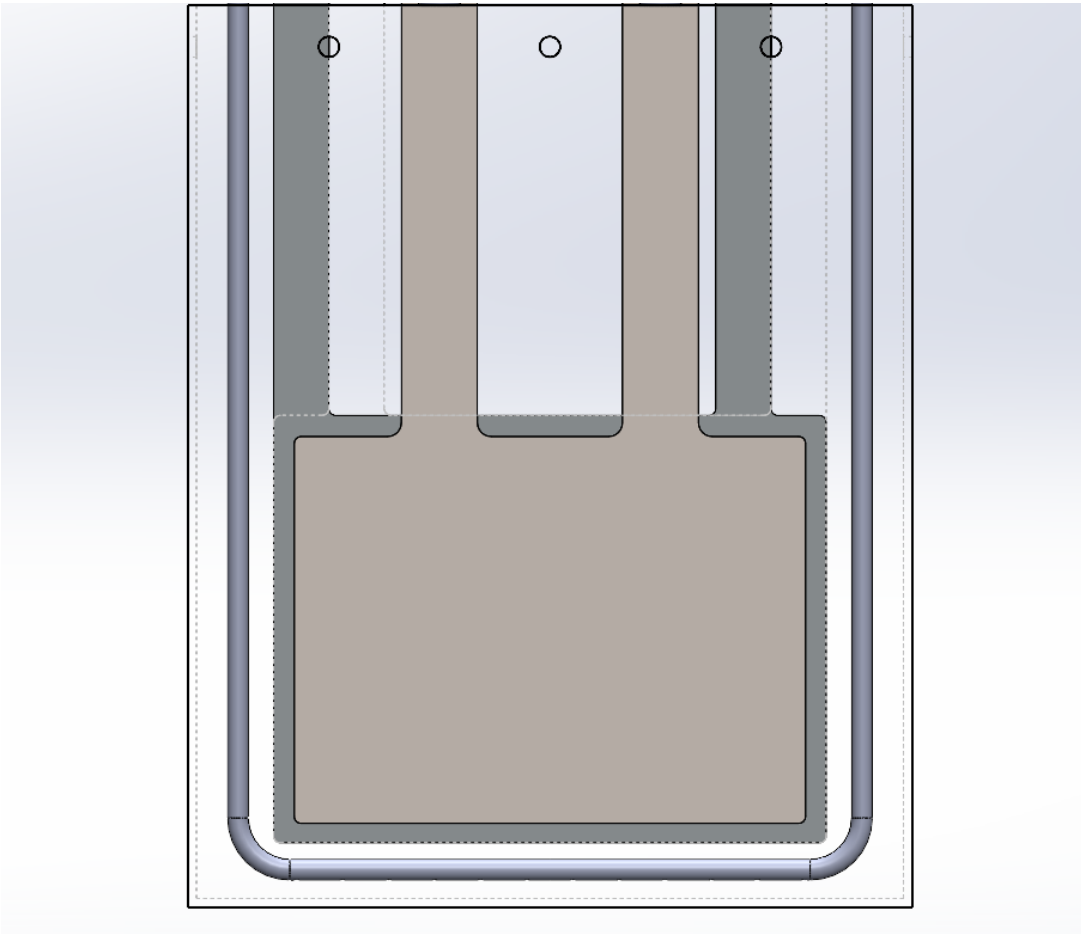
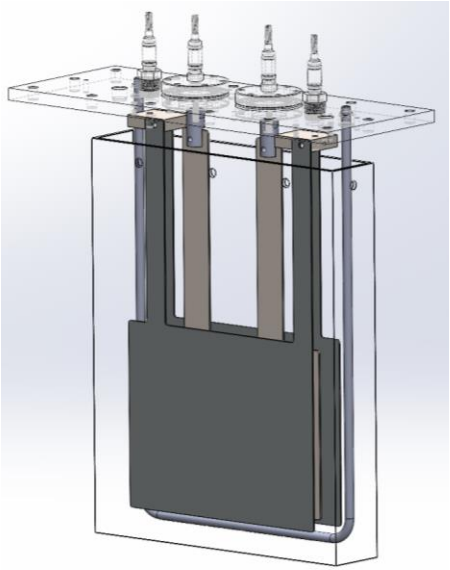
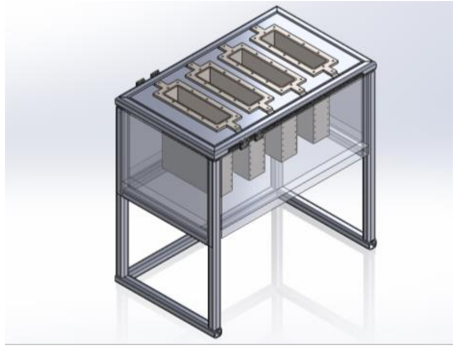
# TASK 4: SCALING THE DESIGN









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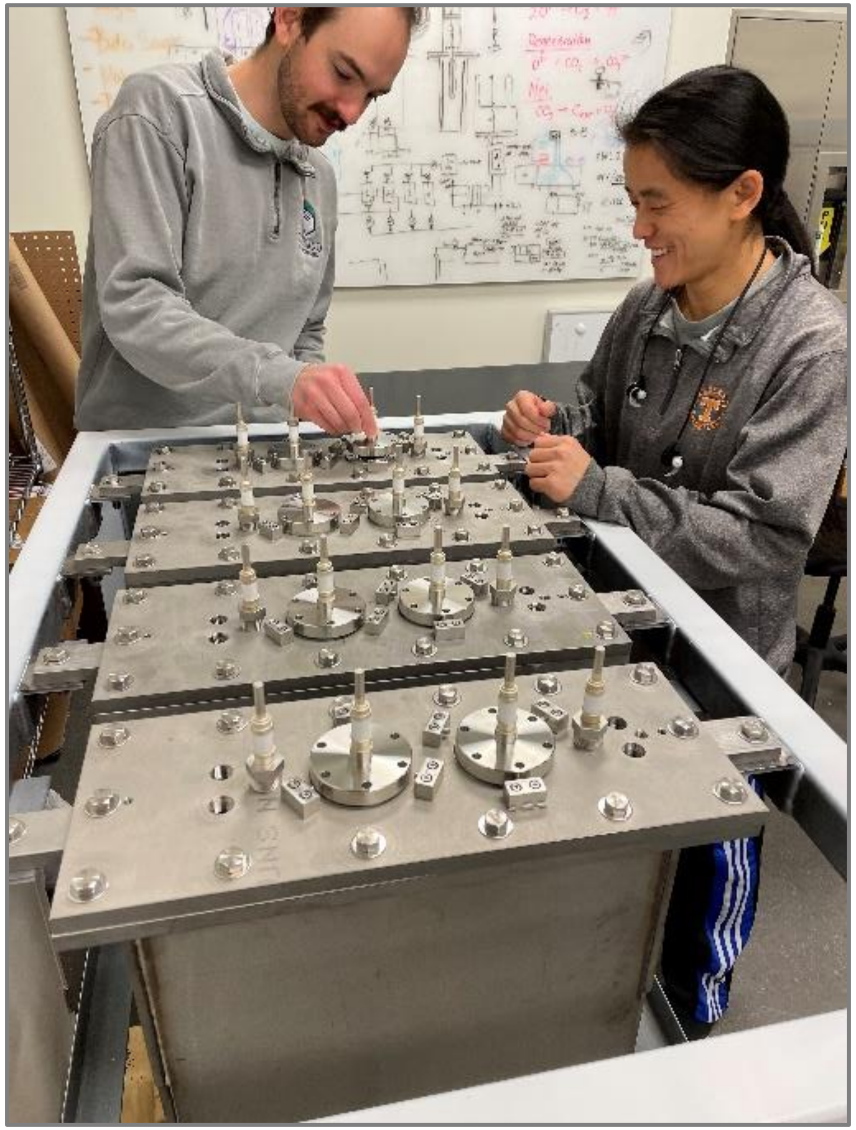
# TASK 4: BUILDING THE CELLS



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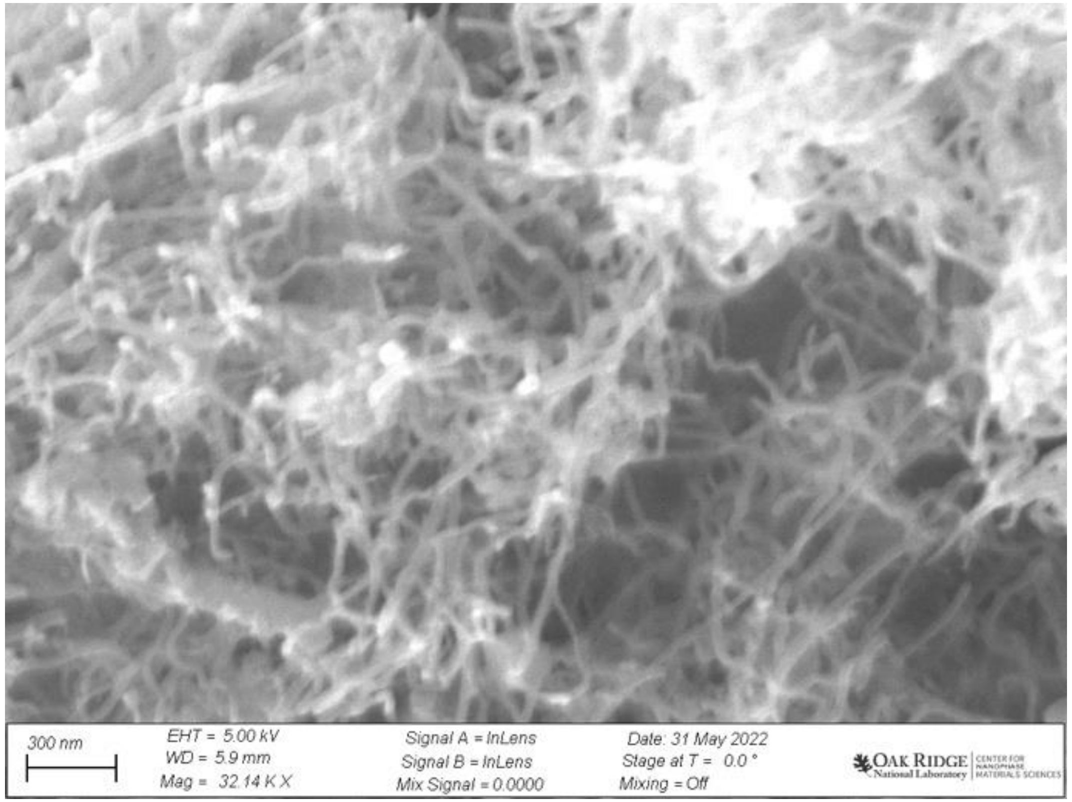
# TASK 4: CHARACTERIZING CARBON PRODUCT





**BP2.0 Electrochemical cell functionality <u>VALIDATED</u>**
**CNT diameter median ~30**
**ID/IG ~1**
**Coulombic efficiency 80%**

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# TASK 4: THERMAL BUDGETING

**4-8X improvement in thermal efficiency normalized to mass C product**

| System Parameter (Single Cell Configurations) | BP1 (GFC) (kWh/g-C) | BP2 (kWh/g-C) |
|---|---|---|
| Sustaining Heat Load (100 mA/cm$^2$) | 0.687 | 0.199 ± 0.048 |
| Sustaining Heat Load (150 mA/cm$^2$) | 0.783 | 0.103 ± 0.018 |

**Ratio of electricity for heat input : electricity for electrolysis IMPROVED**

| Reactor | Heat Load (kWh/g-C) | Electrolysis Load (kWh/g-C) | Heat/Electrolysis Load Ratio (Target <1) |
|---|---|---|---|
| BP1 GFC (100 mA/cm$^2$) | 0.687 | 0.0401 | 17.1 |
| BP1 GFC (150 mA/cm$^2$) | 0.783 | 0.0601 | 13.0 |
| BP2 (100 mA/cm$^2$, single cell) | 0.199 | 0.0489 | 4.07 |
| BP2 (150 mA/cm$^2$, single cell) | 0.103 | 0.0565 | 1.82 |

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# TASK 6: TEA w/ NREL

## Assumptions

| Parameter | Value |
|---|---|
| **Inlet $CO_2$ Concentration (%)** | 4.3 |
| **$CO_2$ Price ($/tonne)** | 0 |
| **Electricity Price ($/kWh)** | 0.03 |
| **Electrolyzer CAPEX Cost ($/kW)** | 4,000 |
| **Electrolyzer CAPEX Cost ($/m2)** | 20,000 |
| **Electrolyzer Replacement Interval (years)** | 5 |
| **Electrolyzer Replacement Fraction (%)** | 25 |
| **Capacity Factor (%)** | 90 |
| **Voltage (V)** | 5 |
| **Faradaic Efficiency (%)** | 85 |
| **Current Density (mA/cm2)** | 100 |

## TEA Methodology

- Decided to use NREL resources to model a larger pilot plant
- Assumed a 50kg/hr plant, @ 90% capacity equating to 394 tonnes CNT/year (1,418 tonnes CO2)

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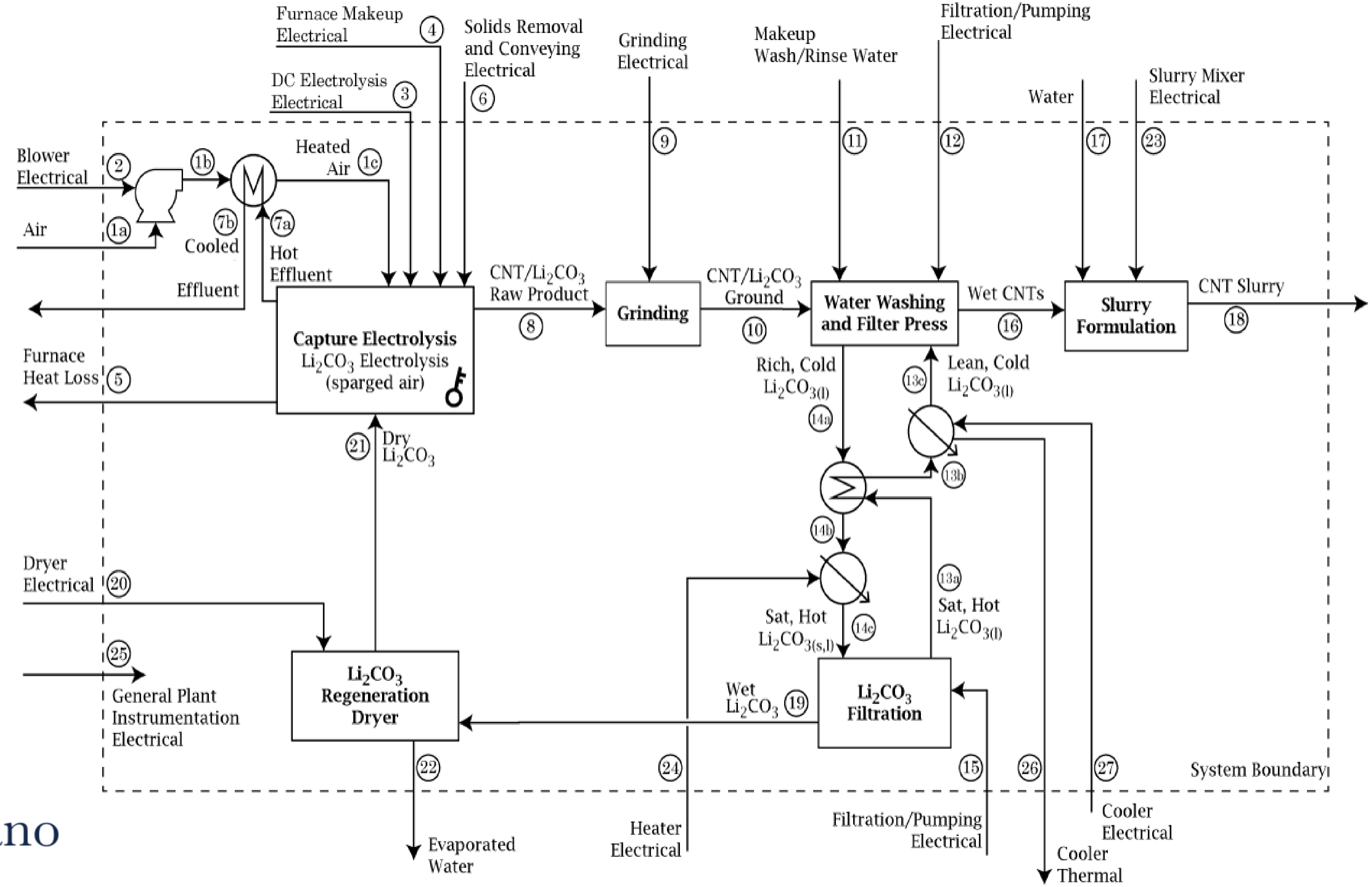
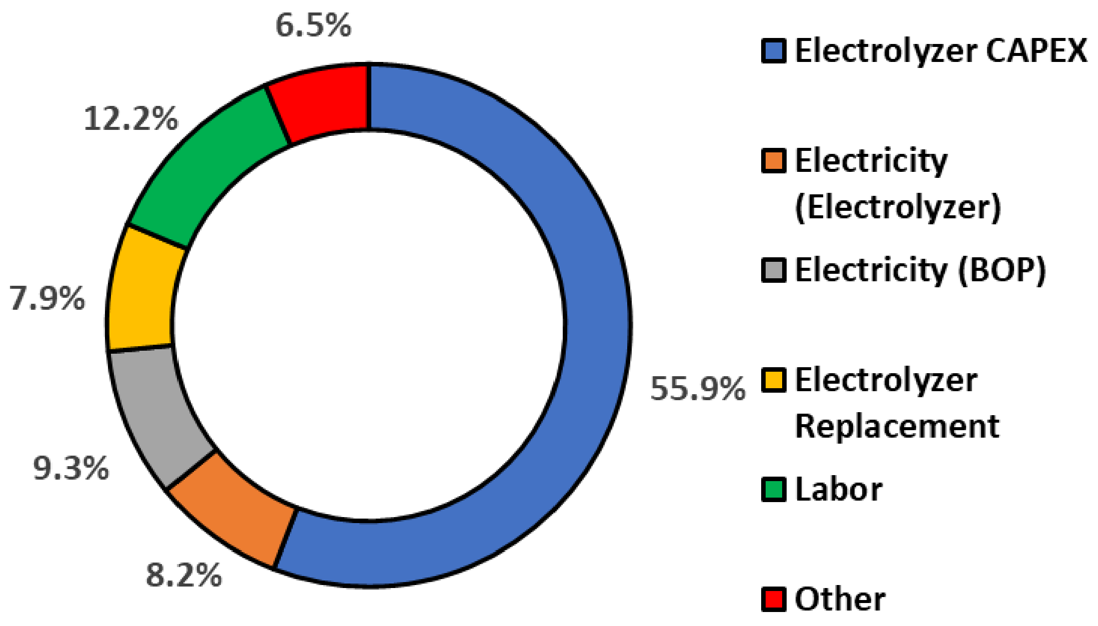
# TASK 6: TEA PFD



# TASK 6: ASPEN-PLUS MODEL




- Preliminary results demonstrate a MSP of \$19.16/kg at a scale of 50kg/hr
- Electrolyzer makes up overwhelming majority of cost, with labor making up 2$^{nd}$ highest cost – used molten carbonate fuel cell pricing as model

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# NEXT STEPS

- Finalizing CO2 uptake experiments with larger BP2.0 cell
- Very quickly evaluate any improvements from BP2.0 cell design to integrate into BP2.9 design; incorporate electrolyte flow system into design
- Design + order components for BP2.9 (200g/hr)
- Work with TVA to collect increased amount of flue gas
- Scale-up of auxiliary systems required for full-system 10-hr continuous operation

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# QUESTIONS?

**NETL Program Manager:**
Natalie Iannacchione
**DOE HQ PM:**
Amishi Claros
**DOE Tech Manager:**
Joseph Stoffa

NREL
NATIONAL RENEWABLE ENERGY LABORATORY
TVA
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# APPROACH

| | Units | Measured/Current Performance | Projected/Target Performance |
|---|---|---|---|
| Reaction[3] | | Li2CO3 --> Li2O + O2 + C<br>Li2O + CO2 → Li2CO3 | |
| Chemical Equation | $mol^{-1}$ | Balanced chemical equation | |
| $\Delta H^\circ_{rxn}$ | kJ/mol | -393.5 | |
| $\Delta G^\circ_{rxn}$ | kJ/mol | 615 @ 700C | |
| ***Reaction Conditions*** | | | |
| $CO_2$ Source[4] | - | Natural gas flue gas | Natural gas flue gas |
| Catalyst[5] | - | Fe (CNT growth) | Fe (CNT growth) |
| Pressure | bar | 1 | 1 |
| $CO_2$ Partial Pressure | bar | N/A | N/A |
| Temperature | ℃ | 750 | 750 |
| Nominal Residence Time[6] | sec | 3600 | 3600 |
| ***Once-Through Performance[7]*** | | | |
| $CO_2$ Conversion[8] | % | 93% | 80% |
| Selectivity to Desired Product[9] | % | 90% | 80% |
| Yield of Desired Product[10] | % | 90% | 80% |
| ***Product Composition*** | | | |
| Desired Product[11] | - | MWCNTs | MWCNTs |
| Main Product Impurities[12] | - | other C structures | Other C structures |
| Purity of Finished Product[13] | % | 90% | 80% |
| Product Production[14] | kg/hr | 0.04kg/hr | 0.2kg/hr |
| Co-Products[15] | - | O2 | O2 |
| Co-Product Production[16] | kg/hr | 1.04kg/hr | 0.52kg/hr |
| ***Product Properties[17]*** | | | |
| Density | $kg/m^3$ | 90 | 170-220 |
| Particle Size | (microns) | <30nm diameter | <30nm diameter |
| Surface Area | $m^2/g$ | 25-40 | 30-300 |
| ***Commercial Product Properties[18]*** | | **Current** | |
| Density | $kg/m^3$ | 220 | |
| Particle Size | microns | .02 | |
| Surface Area | $m^2/g$ | 300 | |
| U.S. Market Size | Tonnes/yr | 1542 | |
| Global Market Size | Tonnes/yr | 77089 | |
| Market Price | $/kg | 110 | |

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