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

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U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management and Natural Gas & Oil Research Project Review Meeting

Virtual Meetings August 2 through August 31, 2021

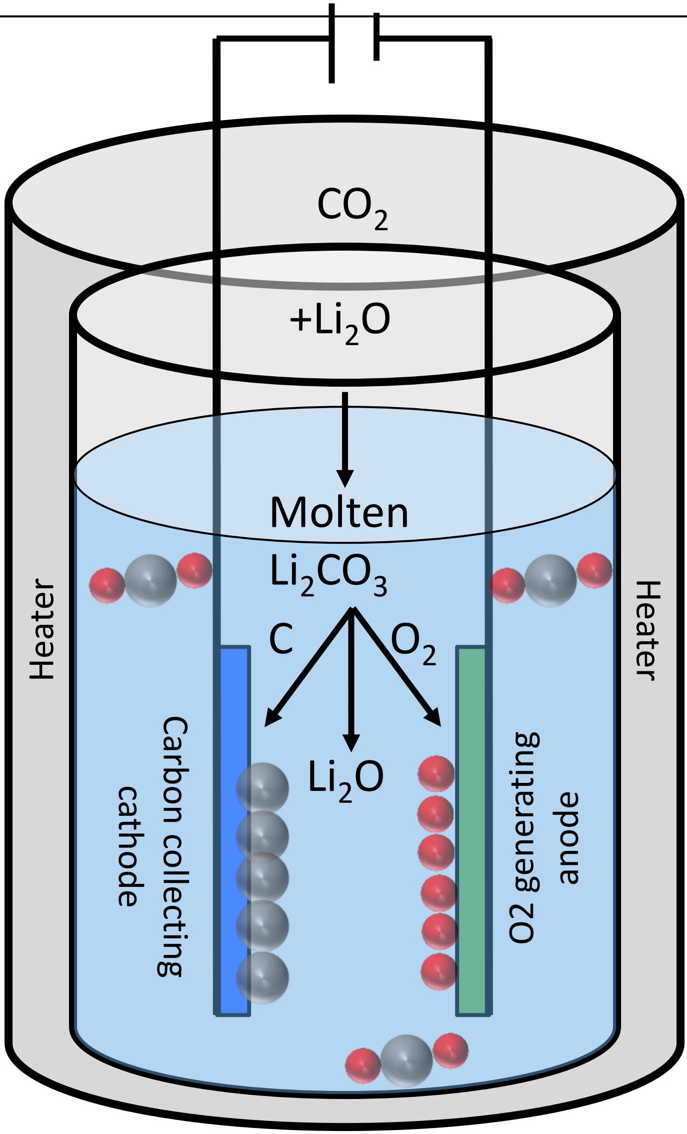
Project Overview

- Project Funding
  - Total: $2,587,339
  - Federal: $2,000,000
    - $1,750,000 contract to SkyNano
    - $250,000 contract to NREL
  - Cost Share: $587,339
- Project Performance: 10/1/2020-09/30/2023
- Project Participants
  - SkyNano
  - NREL
  - TVA

Project Overview

- Overall Project Objectives
  - Demonstration of core technology at scale of 0.2 kg_{CNT}/hr
  - Net reduction in CO_2 → CO_2 sourced from a flue gas provided by utility
  - CNTs exhibiting market-ready materials properties at costs 80-90% lower than industrial standard
  - median diameter < 30nm
  - ID/IG <1
  - purity > 95%

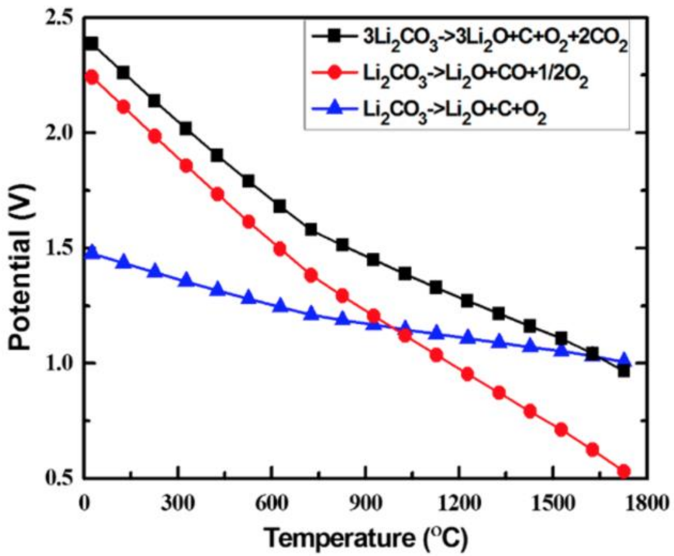
Electrolytic CO_2 Reduction Chemistry



$Li_2CO_3 \rightarrow Li_2O + C + O_2$

$Li_2O + CO_2 \rightarrow Li_2CO_3$

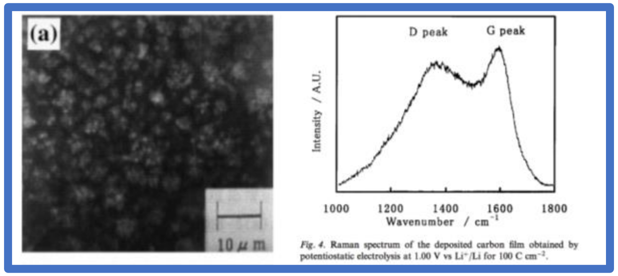
NET: $CO_2 \rightarrow C + O_2$



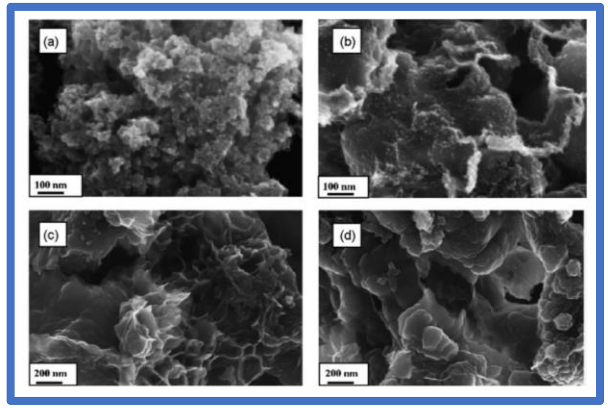
		Reduction Potential (V)	
Molten Salt	MP (C)	Alkali Metal	Carbon
Li2CO3	723	-2.964	-1.719
Na2CO3	851	-2.546	-2.551
K2CO3	891	-2.612	-3.083

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

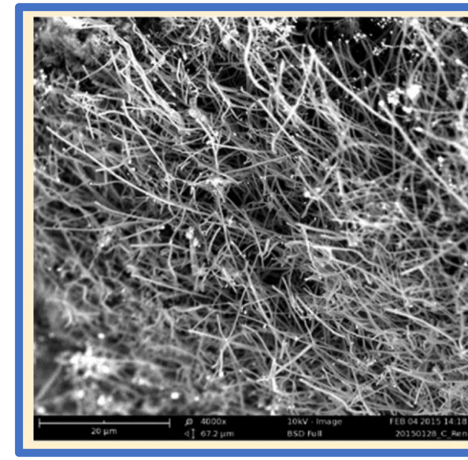
Carbon Products Previously Observed



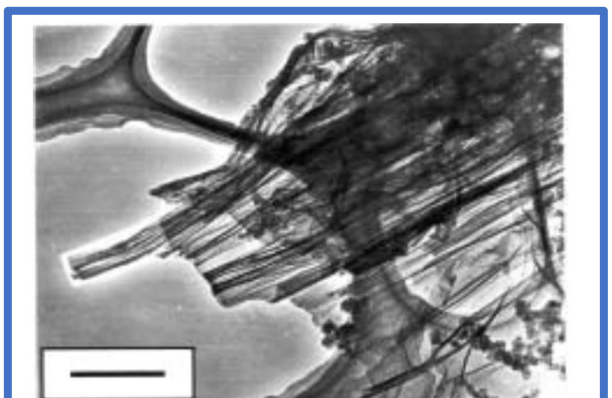
Carbon film electrodeposited onto aluminum electrode 1999



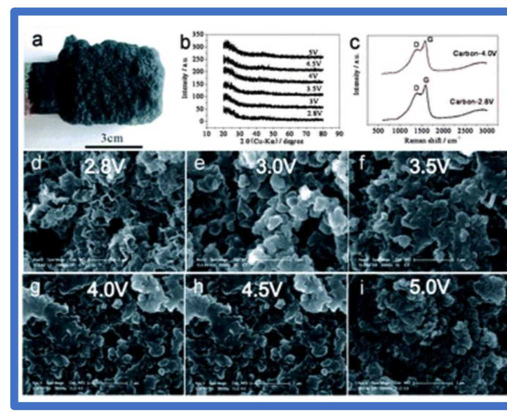
Porous carbon nanopowders 2002



CNFs 2015



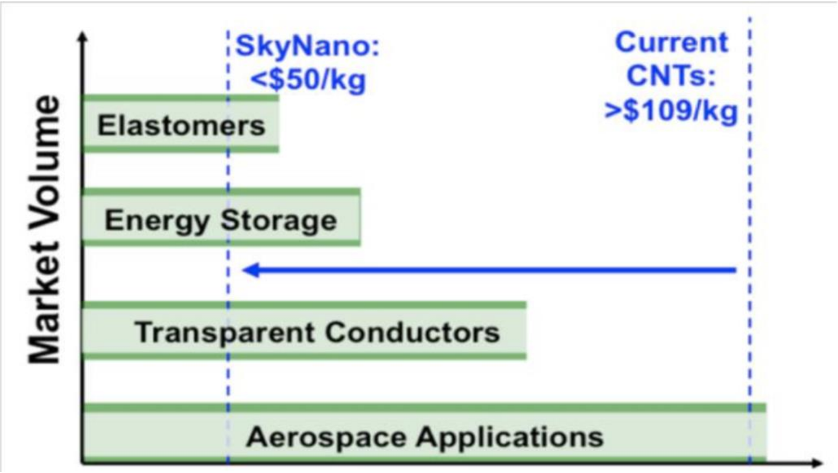
Nanostructured carbon ropes 2001



High surface area carbon 2013

CNTs: High CO_2 Value

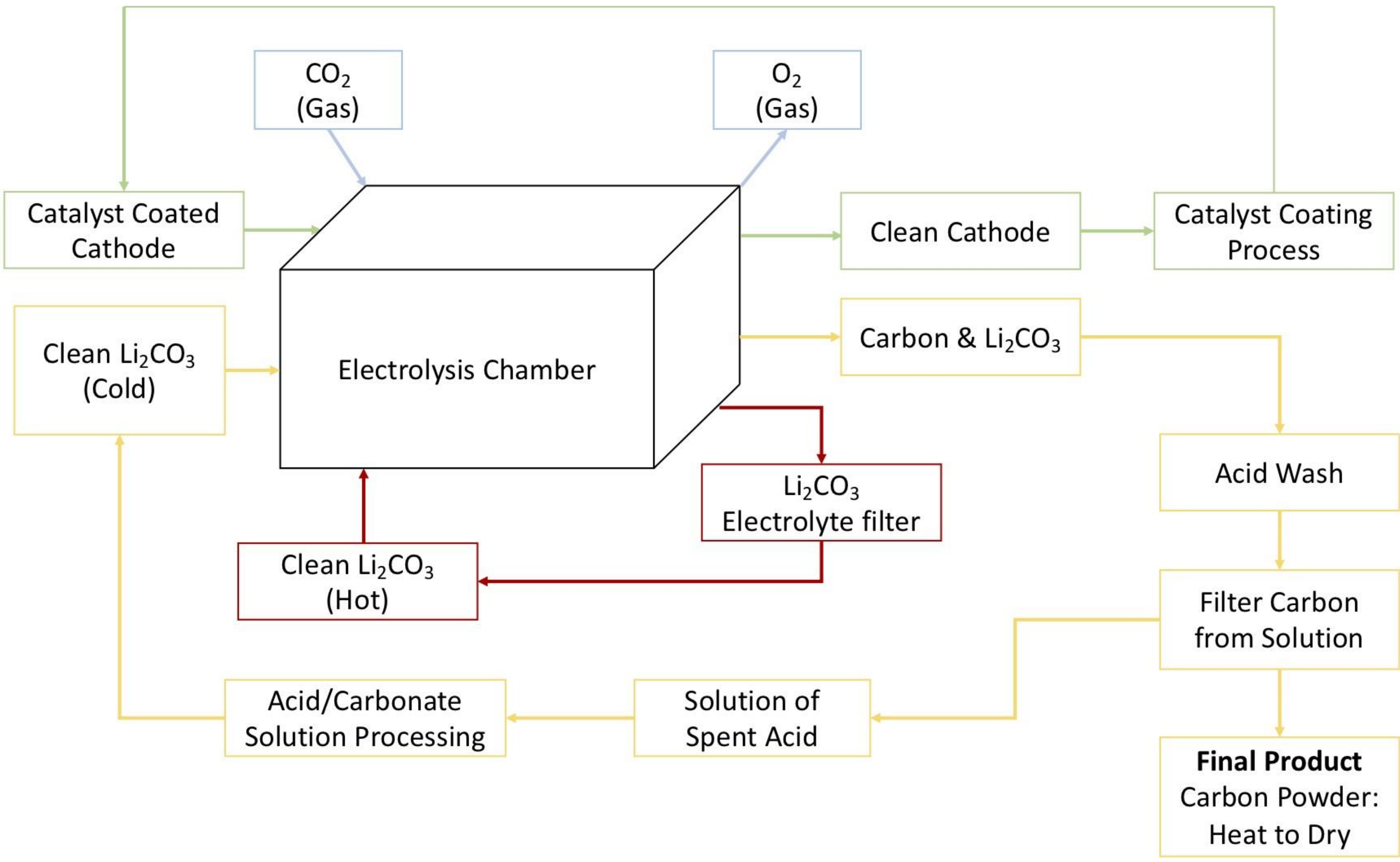
Species	#e-	Pathway	US Market Price ($/kg)[a]	$/e- req. (x10[3])[b]	Global Production (MMT/y)	CO_2ec (MMT CO_2/y)
Carbon Monoxide	2	EC, TC	0.18	2.6	150	236
Formic Acid	2	EC, TC	0.66[d]	15.2	0.6	0.60
Carbon Nanotubes	**4**	**EC**	**110.2**	**331.0**	**0.003[e]**	**0.01**
Methanol	6	EC, TC	0.35	1.9	91.8[f]	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

EC = Electrochemical, TC = Thermochemical, BC= Bioelectrochemical; a: 2014-2018 average price in United States unless otherwise noted; b: Normalized price calculated based on mole of electrons required per mole of product; c: United States EPA 2017 emissions data.[16] 324 total operating coal fired power plants in U.S. producing a total of 3.30 GT/y of CO_2 yielding average of 1.02 MMT/y carbon per plant; d: Average of 2014 and 2016 price; e: 2015 global consumption; f: Average 2017-2018 global consumption; g: Assumes natural gas price and market size; h: Average 2016-2017 global consumption; i: Average Chinese spot price in 2014-2018 converted to USD; j: 2016 global consumption; k: Average Western European price in 2008; l: 2017 global consumption.

Process Diagram



Challenges Remaining

- Technical questions remaining as we scale up:
- What concentration of CO_2 is required for high quality CNTs?
- Can we increase current density to enable high throughput CO_2 conversion while maintaining CNT quality?
- What are the effects of various impurities that may be present in flue gas or other concentrated CO_2 source?
- Engineering challenges remaining as we scale up:
- highly efficient thermal management
- materials/device choices for high temperature electrochemistry
- optimized reactor design including CO_2 inputs, outputs, carbon collection, electrolyte flow system, etc.

Technical Approach of Project

- 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 0.05 kg_{CNT}/hr + system of 4 cells
- Task 5 focused on integrating all systems required for fully continuous operation

Project Schedule/Milestones

- Updated PMP 10/31/2020
- Updated TMP 12/31/2020
- Design + assembly of e-cell 1/31/2021
- Demonstrate CNT growth from e-cell 3/31/2021
- Demonstrate CNT growth from CO_2 gas inputs 9/31/2021
- Complete design + build of pilot cell prototype 0.05 kg/hr 12/31/2021
- Demonstrate functionality + CNT growth from single cell 0.05 kg_{CNT}/hr 3/31/2022
- Demonstrate optimized thermal management 6/30/2022
- Validate functionality of 4-cell system total of 0.2 kg_{CNT}/hr 9/30/2022
- Functionality of all auxiliary systems needed for a fully integrated process with 10+ hrs continuous operation 9/30/2023

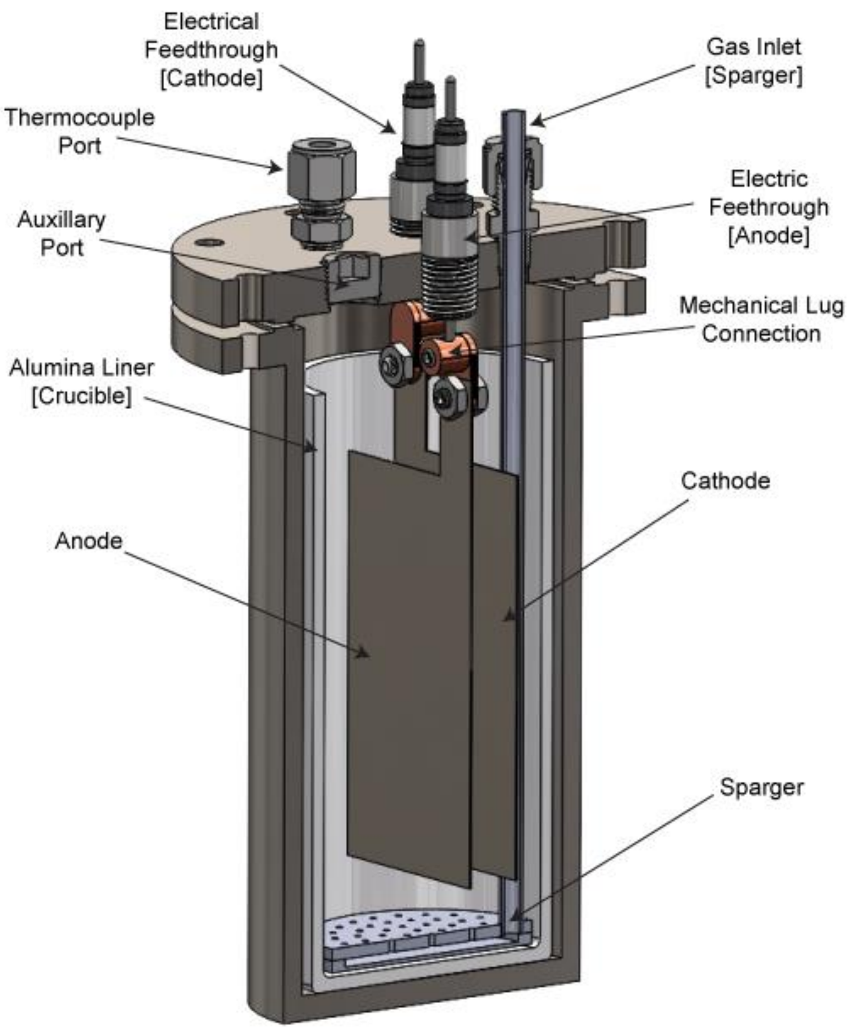
Success Criteria

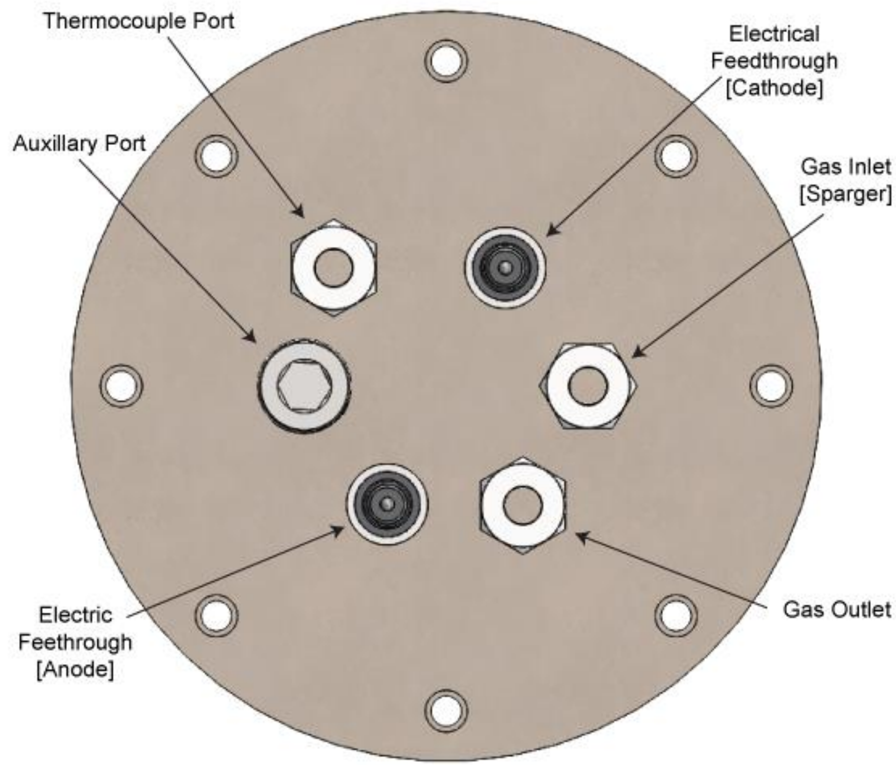
- BP1
  - demonstrate CNT growth from CO_2 gas inputs + optimized flow rates
  - CNT median diameter < 30nm (SEM)
  - ID/IG < 1 (Raman)
  - Coulombic efficiency > 80% (moles e- in / moles C out)
  - CO_2 efficiency > 80% (moles C out / moles CO2 in)
- BP2
  - functionality of 4 cell system using CO_2 gas inputs
  - CNT growth @ 0.2 kgCNT/hr w/ same quality criteria as above
  - based on Aspen model, demonstrate minimum selling price (2020$) << market value ($109/kg)
- BP3
  - functionality of auxiliary systems including electrolyte flow, carbon collection, and carbon processing
  - fully optimized system demonstrating CNT growth @ 0.2kgCNT/hr
  - demonstration of 10+ hr continuous operation
  - demonstrate net negative carbon balance from LCA study

Risk Management

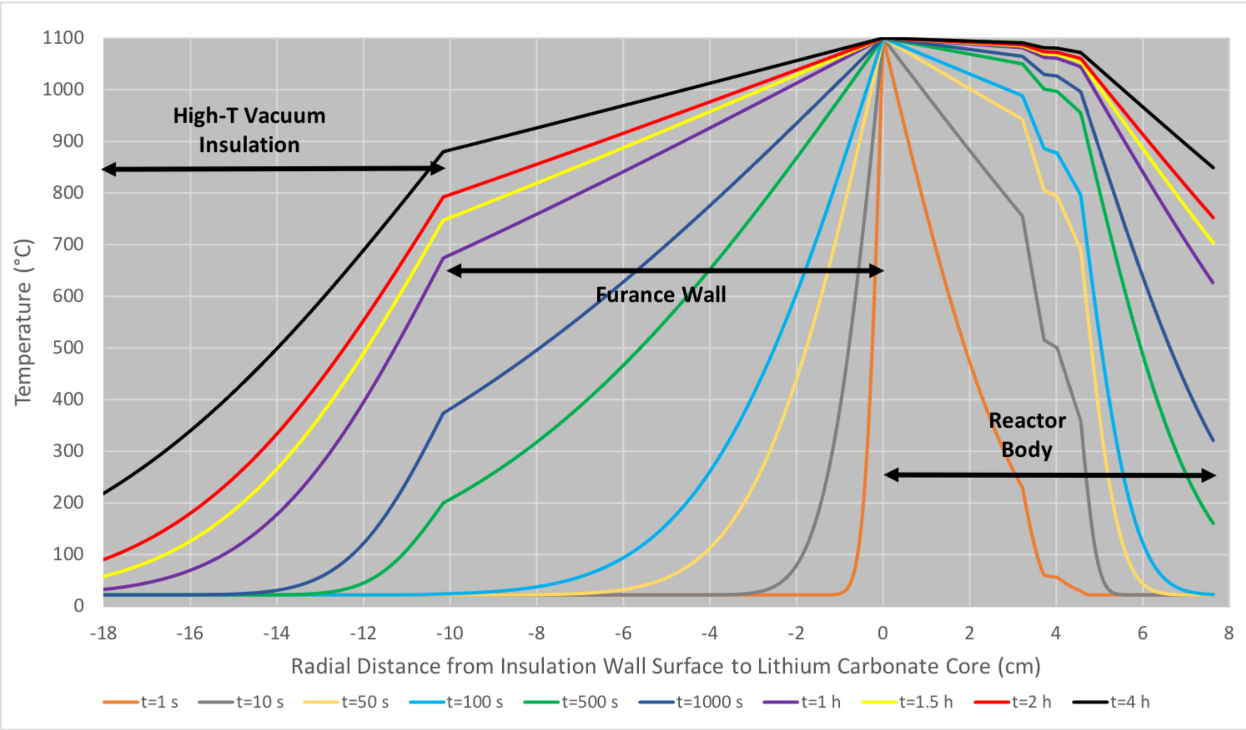
- Cost/Schedule
  - cost of labor and/or pilot cell higher than anticipated – mitigation strategy includes early design and/or increase SkyNano contribution
- Technical
  - risk of CNT quality observed at small scale not achievable at larger scales – mitigation strategy includes TEA/LCA on carbon products produced
  - flue gas impurities negatively influencing electrochemistry – mitigation strategy includes closely monitoring effects at small scale to design around any influences in BP2 and BP3
- Management/Planning
  - staying on schedule – mitigation strategy includes weekly progress meetings
- External
  - access to key resources/lab space at UT in light of ongoing COVID-19 pandemic – mitigation strategy includes at-home work strategy and advocate for us within the UT system

Progress/Current Status



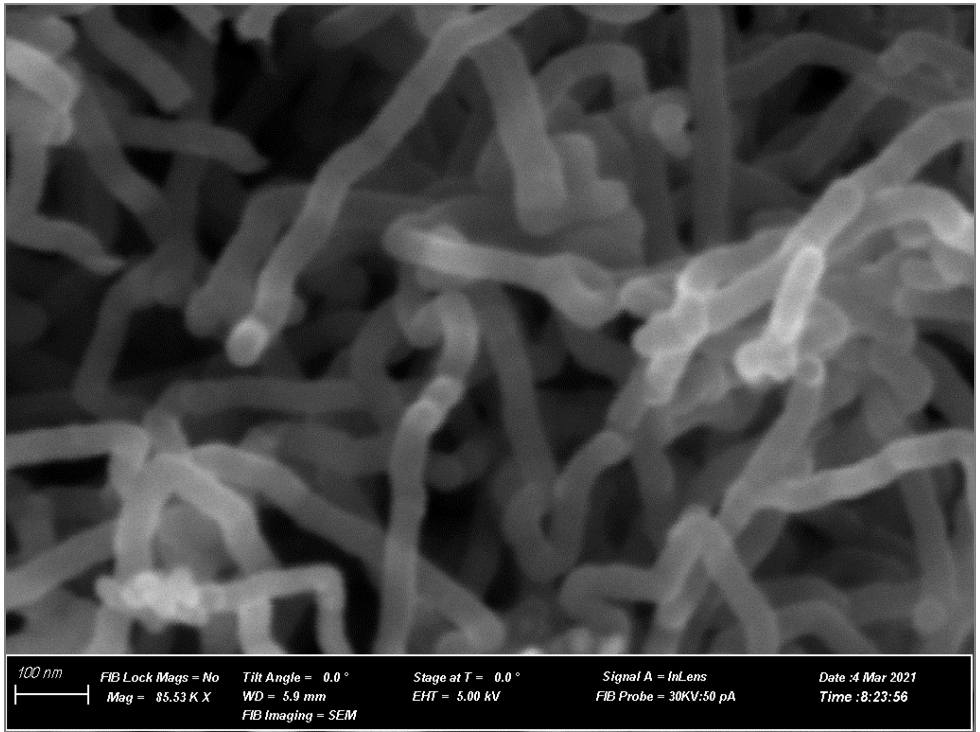


Progress/Current Status



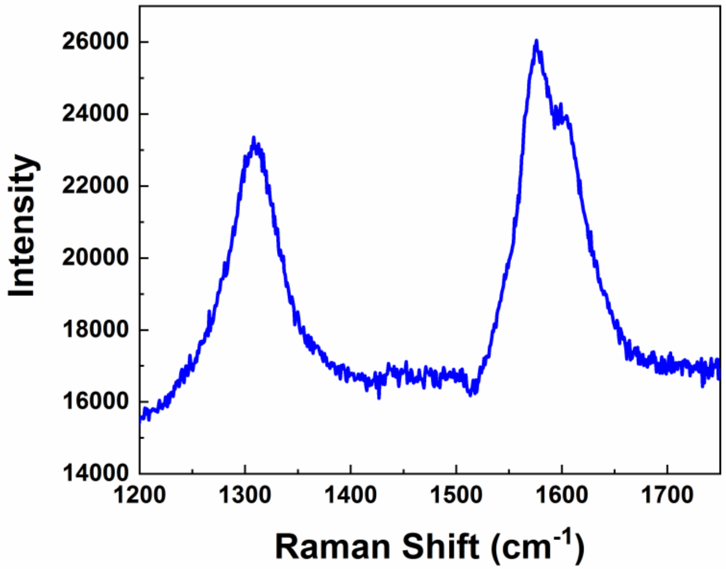
Progress/Current Status

First experiments in GFC: no gas flowing; ambient pressure
Plain stainless steel cathode vs. Al_2O_3-coated Ni shim anode
Operating conditions: 100mA/cm^2, 60min

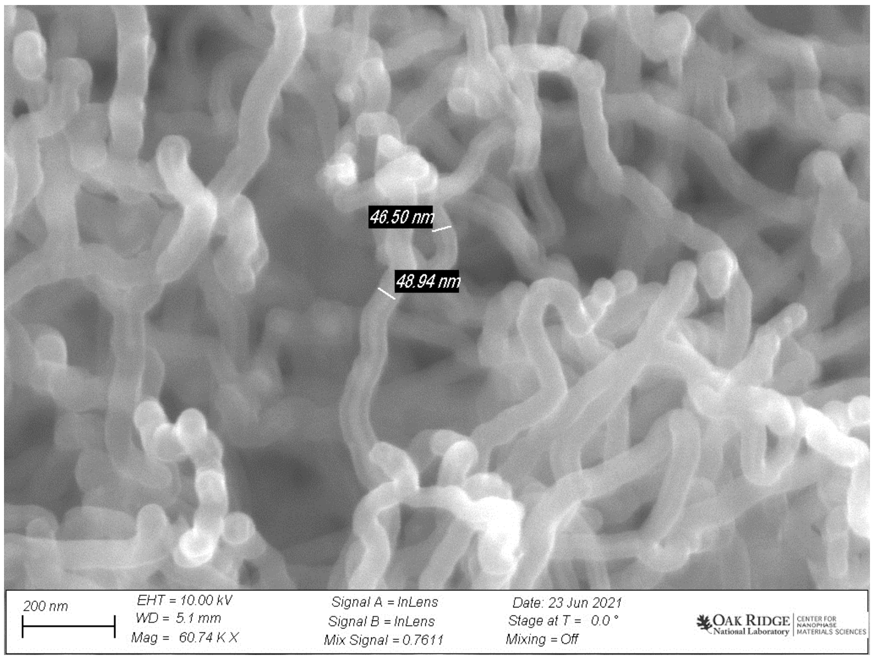


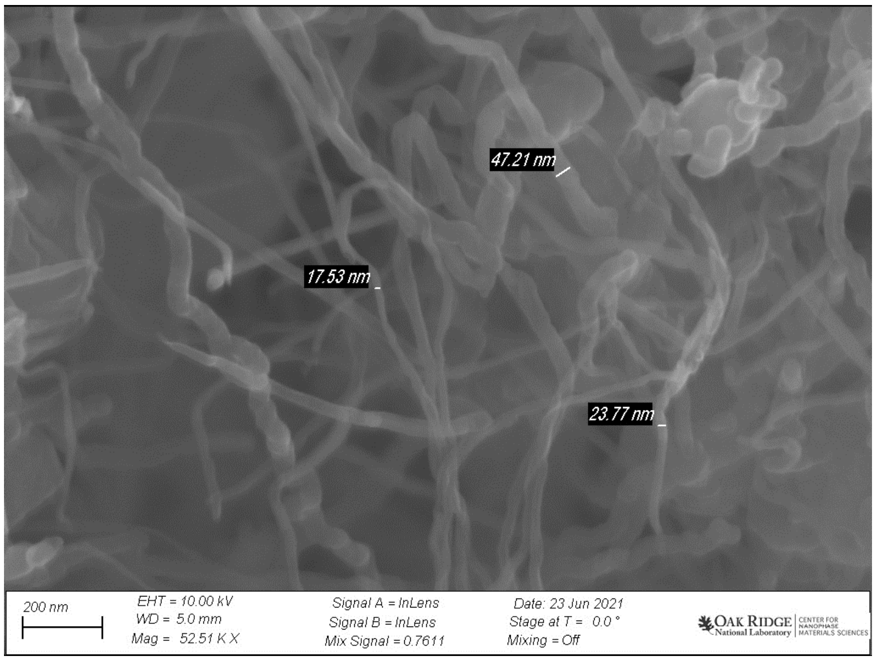
Success Criteria Achieved

- 82.9% Coulombic efficiency at 93 mA/cm^2 for a 1 hour run; 0.864 g CNT produced
- SEM images shown here
- I_D/I_G = 0.89 from Raman spectroscopy shown below



Progress/Current Status

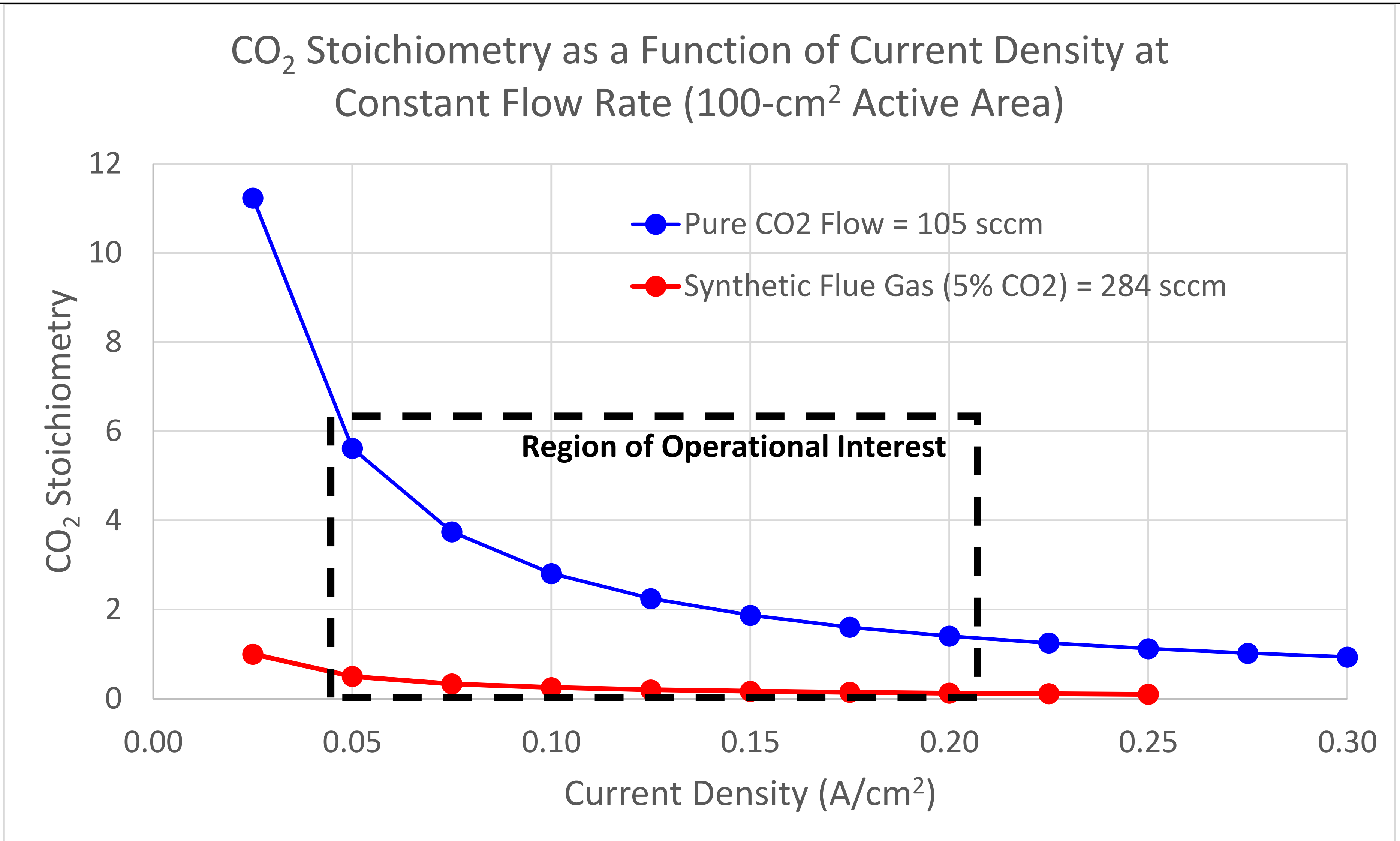




SEM of MWCNTs produced with pure CO_2 flowing through headspace of GFC cell at 300 sccm

No characterization on if these CNTs were produced from the CO_2 flowing through headspace – uptake needs to be measured to fully characterize this phenomena

Progress/Current Status



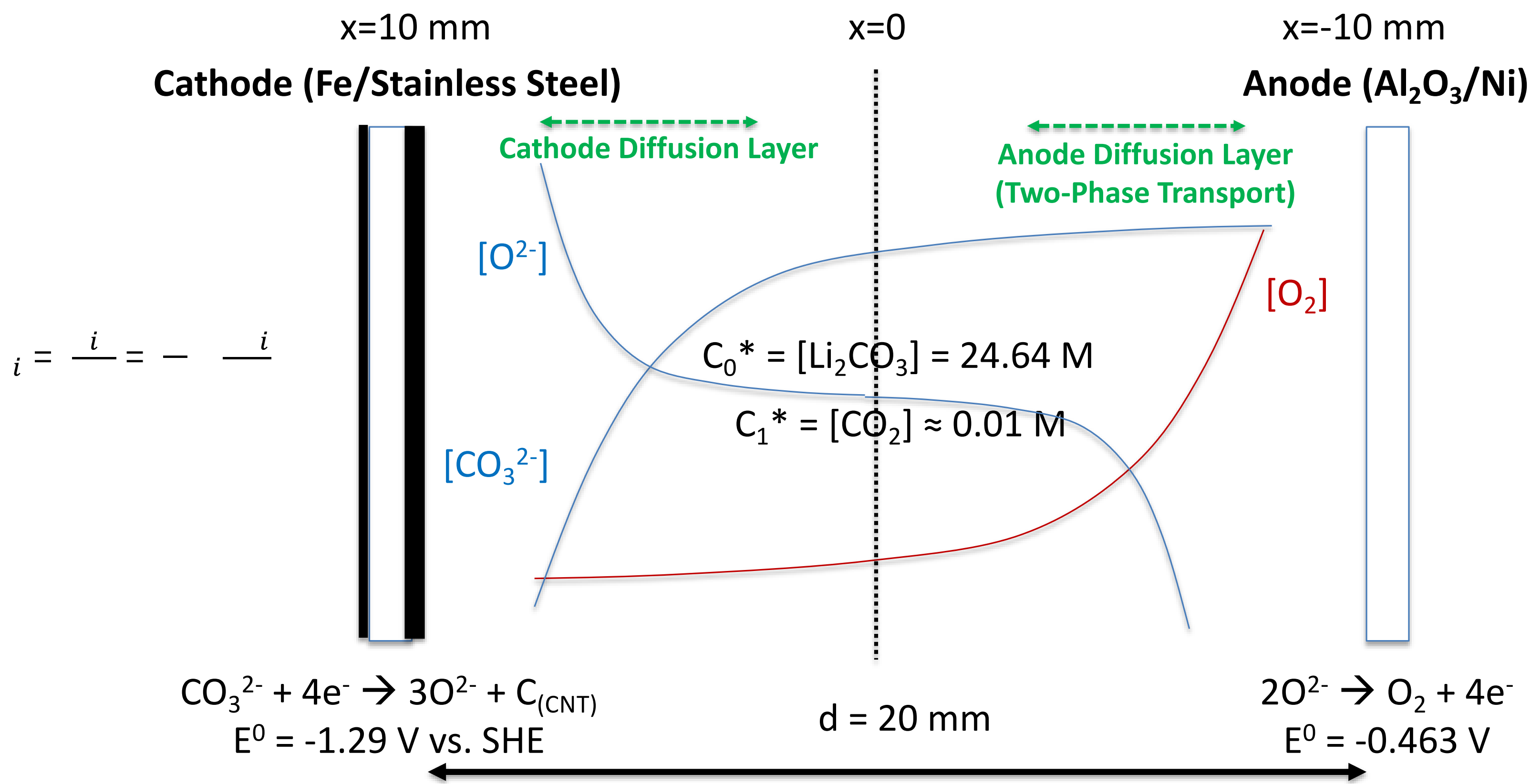
Progress/Current Status

- Observations related to CO_2 and N_2 sparging pre-electrochemistry may indicate some effect of dissolved elemental CO_2 in Li_2CO_3
  - undesirable CO formation at cathode?
  - mitigation strategy may include oxide-rich carbonate electrode
- Active sparging vs. pre-sparging gasses
  - active sparging of CO_2 and N_2 at high current density is
- Outlet measurement and characterization system
  - Quantek instruments CO_2/O_2 analyzer + MFC

Progress/Current Status

GFC helping fundamental understanding of driving electrochemistry

DESIRED REACTIONS



Yin et al., *Energy & Environmental Science*, **6**, 1538 (2013).

H.V. Ijije et al., *Faraday Discussions*, **172**, 105 (2014).

Progress/Current Status

GFC helping fundamental understanding of driving electrochemistry

UNDESIRED REACTIONS

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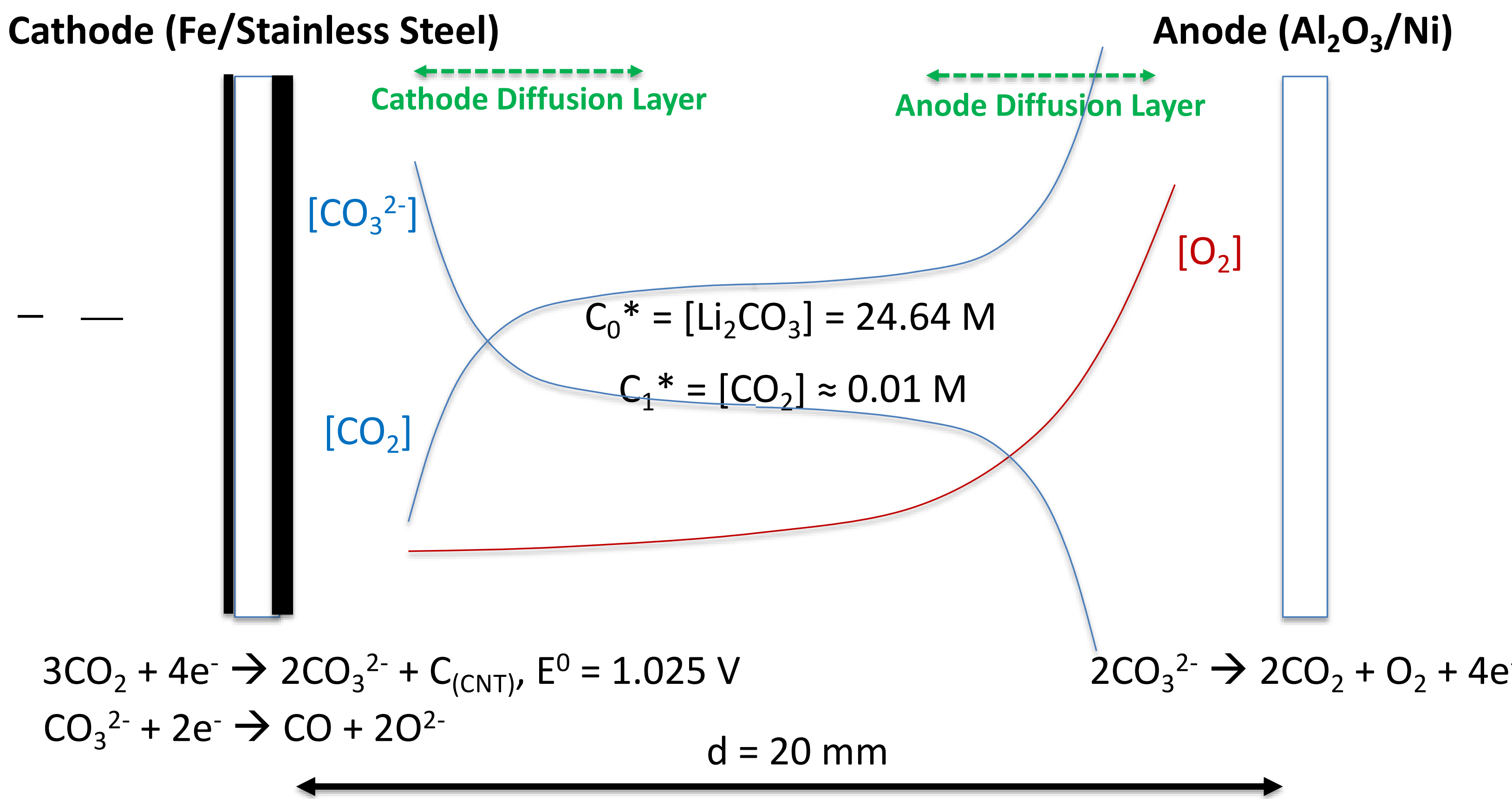


M.D. Ingram and G.J. Janz, *Electrochimica Acta*, **10**, 783 (1965).

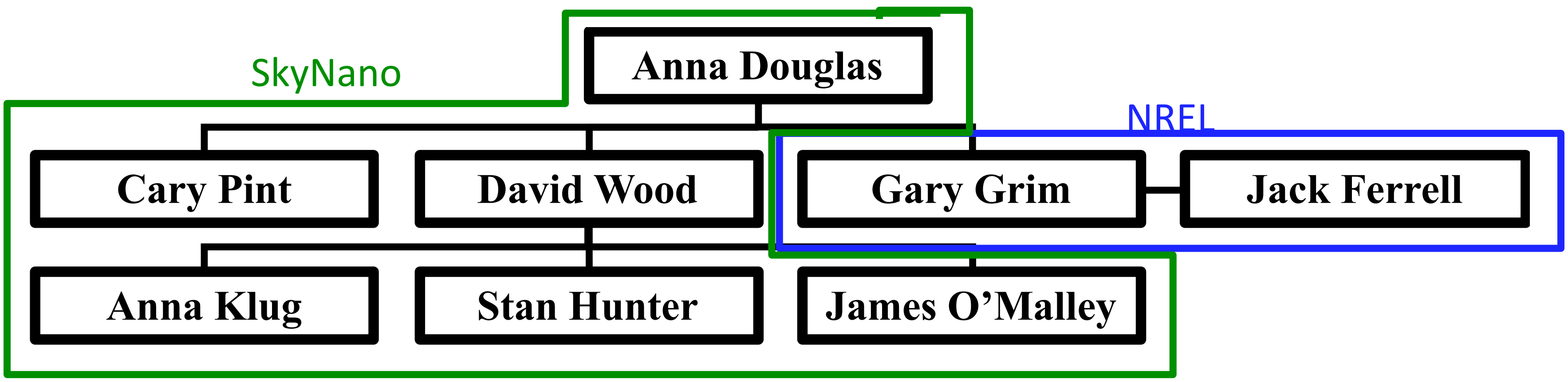
H.V. Ijije et al., *Faraday Discussions*, **172**, 105 (2014).

Summary Slide

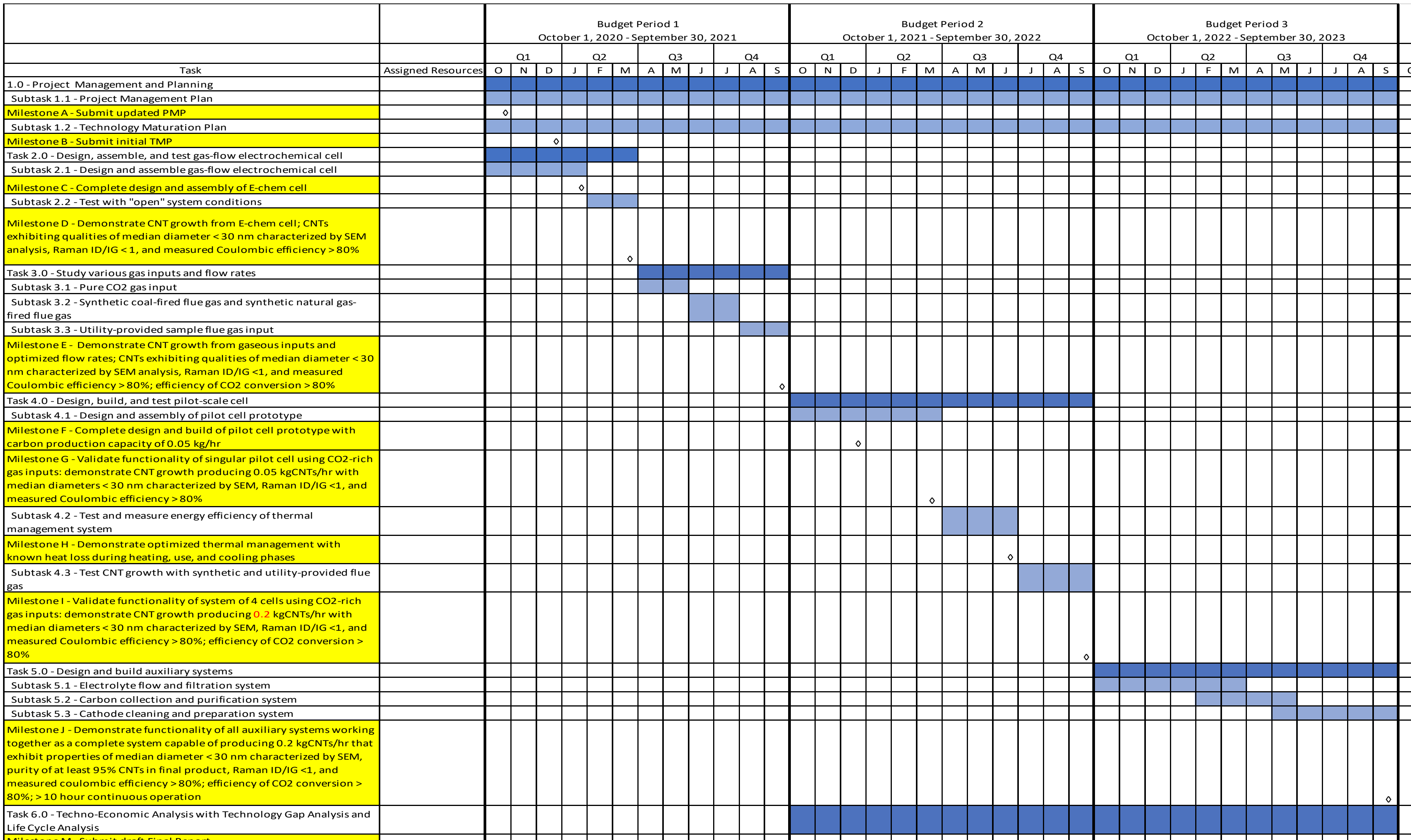
- Designed and built an electrochemical cell capable of accommodating flowing gasses through the electrolyte and headspace
- Results so far have demonstrated the ability to produce MWCNTs from Li_2CO_3 in the GFC-designed reactor that will be utilized for flowing pure CO_2, synthetic flue gas, and real flue samples from TVA
- Designed and built system to analyze gas outputs from off the headspace of GFC to characterize CO_2 uptake

Appendix

Organizational Chart



Gantt Chart



Budget Period 1
October 1, 2020 - September 30, 2021
Budget Period 2
October 1, 2021 - September 30, 2022
Budget Period 3
October 1, 2022 - September 30, 2023
Q1 Q2 Q3 Q4
Task
Assigned Resources
O N D J F M A M J J A S O
1.0 - Project Management and Planning
Subtask 1.1 - Project Management Plan
Milestone A - Submit updated PMP
Subtask 1.2 - Technology Maturation Plan
Milestone B - Submit initial TMP
Task 2.0 - Design, assemble, and test gas-flow electrochemical cell
Subtask 2.1 - Design and assemble gas-flow electrochemical cell
Milestone C - Complete design and assembly of E-chem cell
Subtask 2.2 - Test with "open" system conditions
Milestone D - Demonstrate CNT growth from E-chem cell; CNTs exhibiting qualities of median diameter < 30 nm characterized by SEM analysis, Raman ID/IG < 1, and measured Coulombic efficiency > 80%
Task 3.0 - Study various gas inputs and flow rates
Subtask 3.1 - Pure CO2 gas input
Subtask 3.2 - Synthetic coal-fired flue gas and synthetic natural gas-fired flue gas
Subtask 3.3 - Utility-provided sample flue gas input
Milestone E - Demonstrate CNT growth from gaseous inputs and optimized flow rates; CNTs exhibiting qualities of median diameter < 30 nm characterized by SEM analysis, Raman ID/IG <1, and measured Coulombic efficiency > 80%; efficiency of CO2 conversion > 80%
Task 4.0 - Design, build, and test pilot-scale cell
Subtask 4.1 - Design and assembly of pilot cell prototype
Milestone F - Complete design and build of pilot cell prototype with carbon production capacity of 0.05 kg/hr
Milestone G - Validate functionality of singular pilot cell using CO2-rich gas inputs: demonstrate CNT growth producing 0.05 kgCNTs/hr with median diameters < 30 nm characterized by SEM, Raman ID/IG <1, and measured Coulombic efficiency > 80%
Subtask 4.2 - Test and measure energy efficiency of thermal management system
Milestone H - Demonstrate optimized thermal management with known heat loss during heating, use, and cooling phases
Subtask 4.3 - Test CNT growth with synthetic and utility-provided flue gas
Milestone I - Validate functionality of system of 4 cells using CO2-rich gas inputs: demonstrate CNT growth producing 0.2 kgCNTs/hr with median diameters < 30 nm characterized by SEM, Raman ID/IG <1, and measured Coulombic efficiency > 80%; efficiency of CO2 conversion > 80%
Task 5.0 - Design and build auxiliary systems
Subtask 5.1 - Electrolyte flow and filtration system
Subtask 5.2 - Carbon collection and purification system
Subtask 5.3 - Cathode cleaning and preparation system
Milestone J - Demonstrate functionality of all auxiliary systems working together as a complete system capable of producing 0.2 kgCNTs/hr that exhibit properties of median diameter < 30 nm characterized by SEM, purity of at least 95% CNTs in final product, Raman ID/IG <1, and measured coulombic efficiency > 80%; efficiency of CO2 conversion > 80%; > 10 hour continuous operation
Task 6.0 - Techno-Economic Analysis with Technology Gap Analysis and Life Cycle Analysis
Milestone M - Submit draft Final Report