ORNL/TM-2020/1545
CRADA/NFE- NFE-17-06843

CRADA Final Report: CRADA Number NFE1706843 with SkyNano LLC

Dr. Anna Douglas, Ph.D.
Dr. David Geohegan, Ph.D.

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OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

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1. Abstract

Cooperative Research and Development Agreement (CRADA) NFE-17-06843 between Oak Ridge National Laboratory (ORNL) and SkyNano LLC focused on studying and developing a better fundamental understanding of SkyNano's technology to capture and convert CO_2 into solid carbon nanostructures, including carbon nanotubes (CNTs), using electrochemistry at elevated temperatures in molten salts. The project focused on developing a fundamental scientific understanding of how electrochemistry influences the dynamic catalytic processes that drive the formation of CNTs on electrodes, while developing synthesis and processing technology relevant to implementation of the technology – including chemical engineering to aid in recapturing the lithium carbonate electrolyte essential to the process, and the modeling and testing of systems with the required thermal management at practical scales.

2. Statement of Objectives

The aim of this project is to address an understanding of the fundamental mechanisms governing the growth of carbon nanostructures, and primarily carbon nanotubes, using carbon dioxide as a feedstock gas that is scavenged from an open-air environment. In contrast to well-studied gas-phase growth processes, the liquid-phase electrochemical growth of carbon nanotubes, arising from the splitting of CO_2 between two electrodes immersed in a molten carbonate electrolyte, has only recently been reported. First observations of carbon nanotube growth from this process relied on a corrosive Ni anode, which was the basis for catalyst particle formation and resulting catalytic carbon nanotube growth. However, this technique leaves little to no control over the size and structure of the carbon nanotube products. More recently, our team has controlled the electrode composition to yield controlled synthesis of carbon nanotubes from CO_2 dissolved in molten carbonate electrolytes leading to the first observation of electrochemically-grown carbon nanotubes with diameters ~ 27 nm. However, significant questions remain towards the growth small diameter and single-walled carbon nanotubes using this generalized approach. Overall, this project will answer critical questions that remain for this system that may draw from understanding in gas phase synthesis approaches such as how precursor chemistry, catalyst size and structure, and processes such as Ostwald ripening and catalyst coarsening affects synthesis outcomes. The results of this effort will guide an effort to produce highly functional small diameter carbon nanotubes using an open system that leverages ambient carbon dioxide as the growth feedstock.

The proposed research tasks under the CRADA at ORNL Center for Nanophase Materials Science (CNMS) included all preliminary electrode fabrication, experimental synthesis with in-situ Raman spectroscopy characterization, and ex-situ characterization techniques including scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The first phase of the project involved studying how electrochemical parameters influenced catalyst size, structure, and chemistry influence growth process, all of which are critical parameters in conventional gas phase growth techniques. The second phase of the project involved scaling of the novel electrochemical growth cell, and performing an initial design exercise on a scaled-up growth reactor. Lastly, the project considered the full system of CNT production through electrochemical CO_2 utilization and considered all post-growth processing needed to accompany this production technique, including experimental tasks related to Li_2CO_3 recovery from washing residual carbonates from the carbon product.

3. Benefits to the Funding DOE Office's Mission

The mission of EERE is to create and sustain American leadership in the transition to a global clean energy economy. The strategic goals relevant to this project include:

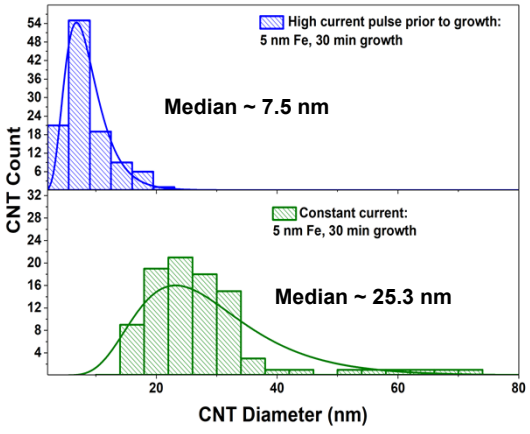
• ***Accelerate the development and adoption of sustainable transportation technologies*** The development of low-cost advanced carbon structures (such as MWCNTs) that can be used to enable fast-charging of Li-ion batteries is extremely relevant to this mission, which accelerates the development and deployment of electric transportation technologies.
• ***Stimulate the growth of a thriving domestic clean energy manufacturing industry*** The development of a manufacturing technology that utilizes atmospheric carbon dioxide to produce high value materials useful to a host of advanced technological products is well-aligned with this goal of a thriving domestic clean energy manufacturing industry.

4. Technical Discussion of Work Performed by All Parties

Task 1. Progress towards understanding electrochemical controls on catalyst structure that determines CNT properties such as diameter:

Prior to the start of the project at ORNL, we developed techniques to tune the electrode design and system parameters to grow highly crystalline few-walled CNTs, achieved through electrode design to activate nanoparticle catalysts for CNT growth at the electrode-electrolyte interface by passivating the anode used in this system, which produces CNTs as small as 30 nm in diameter. We also developed the ability to tune the diameter of the CNTs through electrode engineering to produce CNTs with a median diameter as small as 22 nm. As we began the research project at ORNL, the main goals were to establish process controls to continue to decrease the median diameter of CNTs produced with this technique, and to begin to study applications that use CNTs based on what our market research revealed as most promising potential markets.

To study process controls, we first began by studying the effects of electrochemical high current pulsing, as electrochemical controls are entirely unique to this method of carbon nanotube growth and present an opportunity to tune the growth in a way that has never been done.



Throughout the course of the project, we further reduced the median diameter of CNTs produced in this system by implementing electrochemical process controls to enable rapid reduction of the catalyst and produce CNTs with a median diameter of 8 nm. This was achieved through high-pulsed electrochemical reduction prior to carbon deposition, which enabled electrochemical "pinning" of catalyst particles that mitigates catalyst coarsening and leads to smaller diameter CNTs.

Task 2. Progress towards developing protocol for Li_2CO_3 recovery from residual Li_2CO_3 that is embedded in carbon product post-electrochemical growth

The rationale for this task is the realization that the Li_2CO_3 electrolyte, when utilized as a consumable for this growth technology, presents a great deal of risk in potential supply chain challenges and price volatility, due to the need for Li_2CO_3 as a raw ingredient towards the production of Li-ion battery materials, and the exponentially increasing demand for such materials for Li-ion battery production. Therefore, the ability to utilize Li_2CO_3 as a fixed capital asset, and the recovery any "spent" electrolyte that is used in our typical experimental process, will be paramount towards our futures success in commercializing this technology.

After an initial survey of the existing literature on Li_2CO_3 recovery from LiCl, a protocol was developed in house throughout the course of this project, which was then implemented to ultimately demonstrate **99.7% recovery**, which demonstrates excellent promise towards a commercially viable process to be implemented in the overall process flow of this production technology.

The following protocol was developed for a typical 40g batch of Li_2CO_3 utilized in a small electrochemical MWCNT growth reaction:

LI_2CO_3 RECYCLING PROCEDURE

1. React spent Li_2CO_3 with$HNO_3$to form aqueous $LiNO_3$ and dilute the resulting solution down to 10M concentration by adding DI water.
2. Add NaOH to reach a solution ratio of 25mmol OH/mol of Li.
3. Allow the solution to sit for 48 hours to allow for the precipitation of metal hydroxides to occur.
4. Filter off the precipitates and raise the solution temperature to 60°C.
5. Add 4M Na_2CO_3 to the solution while stirring. Once completed, allow 10m for the crystallization of Li_2CO_3 to occur and filter and wash with DI water.
6. Collect the formed Li_2CO_3 and add to DI water to form a slurry.
7. Transfer the slurry into a Parr non-stirred pressure vessel and subject the product to a high-pressure CO_2 environment. Allow the system to sit for 1hr.
8. Depressurize the pressure vessel and decant the solution into a 50mL beaker. Slowly heat the slurry to a final temperature of 90°C at a rate of 1°C/min, allowing the solvent to evaporate. Wash the final product with DI water.

Task 3. Initial design of scaled-up electrochemical cell

Building upon our initial electrochemical cell design, which relied on ceramic cylindrical crucibles surrounded by vacuum-formed cylindrical resistive wire heaters, where 2 electrodes are submerged vertically, we designed a scaled-up electrochemical cell that has a working size of 6"x4" and is intended for horizontal electrodes, where the anode would rest on the bottom of the cell and the cathode would be suspended above for MWCNT growth. This cell was particularly designed and constructed to study thermal phenomena, due to the high temperature nature of this process and a lack of industrial understanding of working with this particular molten salt system. An example of the thermal modeling we performed using SolidWorks software as shown in **Figure**

1, where we measured the temperature at various spatial locations throughout the electrochemical cell to ensure uniform temperature distribution and efficient and effective insulation. Also included below is an image of our reactor 2.0 design, which includes a heating method which uses cartridge heaters embedded along the bottom of the cell chamber, almost like a hot plate, and was able to efficiently heat the entire electrolyte bath very uniformly – **Figure 2** below shows the hot glowing electrolyte in the middle of a heat-up experiment, where one can still see some portions of electrolyte that remain in a solid state but will eventually fully melt.

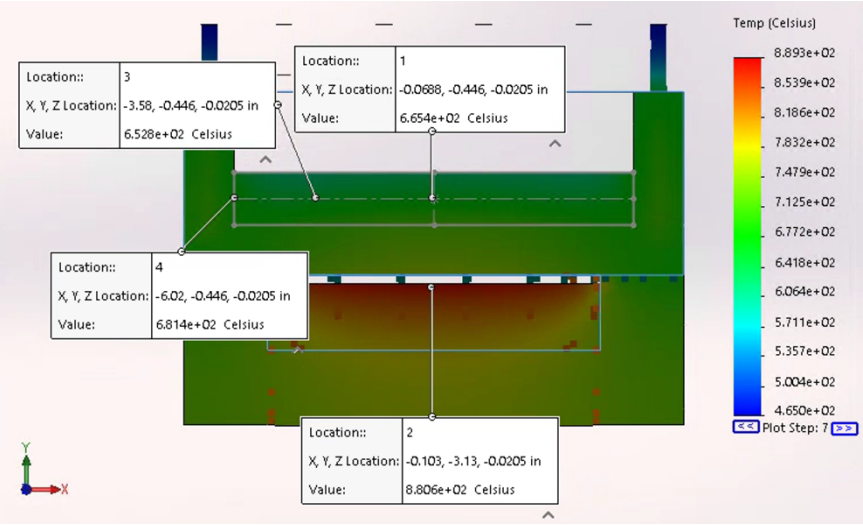


Figure 1: Thermal modeling of the temperature distribution within the electrochemical cell used for the electrocatalytic growth of carbon nanotubes on metal electrodes, which relies upon maintaining molten Li_2CO_3 salt at concstant temperature.

Figure 2: The electrochemical growth reactor (version 2.0) for carbon nanotubes constructed in the project, showing the 6" x 4" bath of glowing, molten Li_2CO_3 salt at 700°C and immersed electrodes and thermocouples within a firebrick insulation.

5. <u>Subject Inventions (As defined in the CRADA)</u>

None.

6. Commercialization Possibilities

As a result of the work performed under the CRADA towards scaling SkyNano's electrochemical production of MWCNTs, we are currently selling initial products into a variety of customer markets including battery companies, composite manufacturers, aerospace, automotive, tire manufacturers, and coatings. Since the conclusion of the CRADA work, SkyNano has raised over $4M in funding from federal, state, and customer sources. This follow-on funding has allowed us to grow our team to 7 scientists and engineers, scale our electrochemical reactor 20X, demonstrate the utilization of flue gas from a combined cycle natural gas power plant as the basis for CO_2 to grow MWCNTs, and demonstrate our products in Li-ion battery cathodes with a 60% improvement in high rate charging with only a 10% replacement of state-of-the-art conductive additives with our MWCNTs.

7. Plans for Future Collaboration

Throughout the course of this CRADA project, SkyNano has developed great working relationships with scientists and engineers at CNMS and across ORNL as a whole. As a result of this initial work, we were able to form a great working collaboration with scientists at the battery manufacturing facility at the NTRC campus, which resulted in a DOE STTR Phase I project, with a significant portion of the work being performed under a subcontract to ORNL. We plan to continue submitting proposal projects in collaboration with this group at ORNL to demonstrate the utilization of our MWCNT materials in Li-ion batteries. Further, we have developed a greater understanding of the facilities, resources, and expertise available at CNMS and have maintained active user proposals throughout our time at ORNL and plan to continue using this vehicle to perform cutting edge research in collaboration with ORNL. CNMS has unique capabilities in electrochemistry, materials science machine learning, in-situ nanomaterials growth characterization, and unparalleled microscopy capabilities. SkyNano has remained in the greater Knoxville region specifically due to the capabilities and collaboration at ORNL, and is extraordinarily grateful for the CRADA's role in catalyzing these working relationships.

8. Conclusions

During this CRADA, SkyNano made significant progress towards developing a more fundamental understanding of the electrochemical growth of MWCNTs from CO_2, demonstrated the control of MWCNT properties such as diameter through electrochemical controls, developed an initial protocol for Li_2CO_3 recovery from residual carbonate salt that was washed from the carbon product, and demonstrated initial efforts towards scaling the electrochemical cell, with a great deal of progress made towards understanding best methods for heating a rectangular cell, materials that are compatible with our corrosive molten salt electrolyte, and methods for efficient thermal management. Overall, we made critical progress towards the further development of technical advances of this technology and have achieved critical progress towards commercialization.