Energy Research and Development Division
FINAL PROJECT REPORT

CARBON NANOTUBE MEMBRANES FOR ENERGY-EFFICIENT CO_2 SEPARATION

Prepared for: California Energy Commission
Prepared by: Porifera Inc

NOVEMBER 2013
CEC-500-2014-064

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ACKNOWLEDGEMENTS

Porifera appreciates the California Energy Commission's match support for demonstrating the potential that Porifera's CNT technology has for energy efficient carbon capture. The DOE, under its ARPA-E program, has been a solid supporter of these efforts as well. Our Energy Commission Contract Manager, Cheryl Closson, did an excellent job. She was supportive, knowledgeable, and helpful in guiding us through the many steps needed to administer the Commission contract.

PREFACE

The California Energy Commission Energy Research and Development Division supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

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Carbon Nanotube Membranes for Energy-Efficient CO_2 Separation is the final report for the Carbon Nanotube Membrane for Energy-Efficient CO_2 Separation project (contract number PIR-10-036) conducted by Porifera Inc. The information from this project contributes to Energy Research and Development Division's Energy Systems Integration Program.

For more information about the Energy Research and Development Division, please visit the Energy Commission's website at www.energy.ca.gov/research/ or contact the Energy Commission at 916-327-1551.

ABSTRACT

Carbon dioxide emissions from power generation have significant negative environmental consequences. Carbon capture and sequestration may allow using fossil fuels for power generation with substantially reduced contributions to greenhouse gas emissions. Current carbon capture technologies; however, are generally cost prohibitive and have their own set of environmental impacts. Although membrane technologies for carbon capture promise to be an improved method for separating carbon dioxide from post-combustion flue gas, current carbon capture membranes do not meet the performance capabilities necessary to be considered a feasible technology.

This project developed a high flux (quick flow) and highly carbon dioxide selective carbon nanotube (one atom thick cylinder structure) membrane for capturing carbon dioxide from post-combustion flue gas. Porifera Inc. fabricated carbon nanotube membranes that capture carbon dioxide. Vertically aligned carbon nanotubes were grown and integrated with polymeric materials for membrane production. The membranes were tested and optimized for flux and selectivity. Porifera Inc.'s carbon nanotube membranes were demonstrated to selectively separate carbon dioxide from a mixed gas, and could be used to reduce greenhouse gas emissions at power plants. In addition, the membrane can maintain performance in humid environments. This advantage is particularly important for the humid conditions present in flue gas. The project developed new laboratory-scale carbon nanotube membranes that may potentially be used to capture carbon, reduce greenhouse gas emissions, and improve local and global air quality.

The United States Department of Energy Advanced Research Projects Agency – Energy funded this project and the California Energy Commission contributed matching funds.

Keywords: Carbon nanotube membrane, carbon dioxide selectivity, carbon capture

Please use the following citation for this report:

Bakajin, Olgica; Klare, Jennifer; Mendelssohn, Jeffrey; Noy, Aleksandr. (Porifera Inc.). 2013. ***Final Report of Carbon Nanotube Membranes for Energy-Efficient CO_2 Separation.*** California Energy Commission. Publication number: CEC-500-2014-064.

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EXECUTIVE SUMMARY

Introduction

Carbon dioxide (CO_2) emission is a widespread consequence from combustion technologies used in energy generation. The United States Energy Information Administration (EIA) reports that the United States alone produces nearly 6 billion metric tons of CO_2 per year, which is about 20 percent of the world's CO_2 emissions (EIA, 2009). Growing concern about global warming is generating an increasing sense of urgency about reducing CO_2 emissions. Today, the necessity for combustion flue gas CO_2 separation technology is well recognized.

Carbon capture is a promising method for reducing the negative impacts of fossil fuel power generation. Current CO_2 capture technologies; however, depend on chemical absorption, which is expensive, energy-intensive, and produces its own negative environmental impacts. Membrane-based CO_2 separations could potentially deliver better efficiencies, resulting in less expensive carbon capture and less energy consumption.

To capture CO_2 from power plant flue gas, CO_2 must be selectively removed from a mixture of gases that is primarily comprised of nitrogen and CO_2. The membrane must pass the CO_2 quickly (high flux) and reject most or all of the nitrogen gas (high selectivity). Membrane-based CO_2 separation has been hampered by a lack of membranes that combine sufficiently high flux with high CO_2 selectivity.

For this project, Porifera, Inc. developed an aligned carbon nanotube (one atom thick cylinder structure) membrane with high flux and selectivity for CO_2. Aligned carbon nanotube membranes have higher flux compared to conventional membranes due to the unique transport properties of carbon nanotubes. Porifera proposed using these properties advantageously in a membrane for carbon capture.

The United States Department of Energy Advanced Research Projects Agency – Energy (ARPA-E) funded this project and the California Energy Commission contributed matching funds. The ARPA-E project was a collaborative effort lead by Porifera Inc., with support from researchers at Lawrence Livermore National Laboratory and the University of California, Berkeley. The Energy Commission funding was used to support Porifera scientific personnel and allowed all research and development efforts to take place in California.

Project Purpose

This project developed a CO_2 selective carbon nanotube membrane with high flux for carbon capture. Porifera, Inc. proposed to produce an aligned carbon nanotube membrane and modify the membrane surface so that it could achieve CO_2 selectivity. Covalent attachment or the depositing of coatings on the surface that are specifically designed for CO2 selectivity chemically modified the membrane. A carbon nanotube membrane with a CO_2 selective layer resulted in a membrane with high flux and high selectivity.

Project Activities and Results

Porifera, Inc. developed new methods for fabricating aligned nanotube membranes that avoided problematic defects in the membrane and achieved the high selectivity necessary for

gas separations. Porifera, Inc. also explored different methods of selectivity enhancement, including molecular modifications and ultra-thin-film deposition. The membrane performance used single gas and mixed gas studies on test setups developed for this project. Laboratory-scale membranes were successfully produced that had excellent flux, good selectivity and maintained performance in humid conditions.

Project Benefits

This project resulted in a significantly better understanding of how to successfully produce aligned carbon nanotube membranes and how to best modify them for CO_2 selectivity. It also provided insights into the gas transport behavior of carbon nanotube membranes. The carbon nanotube membranes produced by the project have excellent performance in laboratory-scale studies. These membranes may potentially be used to capture CO_2 from power plant emissions after scale-up. In addition, the Department of Energy and Energy Commission funding supported creating jobs at Porifera, Inc. and helped the company maintain its dedication to high quality breakthrough research in membrane development.

CHAPTER 1:
The Technology

1.1 Introduction

Carbon dioxide (CO_2) emission is a widespread consequence from combustion technologies used in energy generation. The United States Energy Information Administration (EIA) reports that the United States alone produces nearly 6 billion metric tons of CO_2 per year, which is about 20 percent of the world's CO_2 emissions (EIA, 2009). Growing concern about global warming is generating an increasing sense of urgency about reducing CO_2 emissions. Today, the need for combustion flue gas CO_2 separation technology is well recognized.

The majority of CO_2 removal (carbon capture) processes currently used in industrial settings is based on reversible solvent absorption technologies. For these processes, solvents such as alkyl amines, methanol, or glycol ethers enable selective CO_2 removal by interacting physically or chemically with the CO_2 in the flue gas. While effective, the need for solvent regeneration makes this process energy and capital intensive. An economic assessment of amine-based CO_2 capture from power plant flue gases estimates the costs of capture to be \$30-\$75 per ton of CO_2 avoided, with a 20 percent increase of capital costs (Rao and Rubin, 2002). The process also uses about 27 percent of a 500 megawatt plant's energy production capacity. Other studies report costs of \$32-\$45 per ton of CO_2 avoided (Ho, 2006). Even though solvent-based processes offer an undeniable environmental benefit by reducing CO_2 greenhouse gases, they also have a significant negative environmental impact associated with toxic solvent and chemical additive losses, process wastes, and degradation products (Rao and Rubin 2002; Thitakamol, 2007).

Membrane separation of CO_2 from flue gas streams is extremely attractive for a number of reasons. First, there is no need for chemicals or solvents, which eliminates the high costs associated with solvent regeneration. Second, membrane processes do not require energy intensive chemical process phase changes and, therefore, require considerably less energy. Third, the membrane units have small footprints and low maintenance costs. Their lightweight and inherently modular nature facilitates cost-effective unit design, scale-up, and retrofitting of existing power plants or manufacturing facilities.

To capture CO_2 from combustion flue gas, CO_2 must be selectively removed from a mixture of gases that is primarily comprised of nitrogen and CO_2. The membrane needs to pass the CO_2 quickly (high flux[1]) and reject the nitrogen gas (high selectivity). Membrane-based CO_2 separation has been hampered by a lack of membranes that combine sufficiently high flux with high CO_2 selectivity. They are either high flux, with poor selectivity, or highly selective, with poor flux.

[1] Flux of a membrane is defined as the amount of permeate produced per unit area of membrane surface per unit time. Generally, flux is expressed as Liters per square Meter per Hour (LMH).

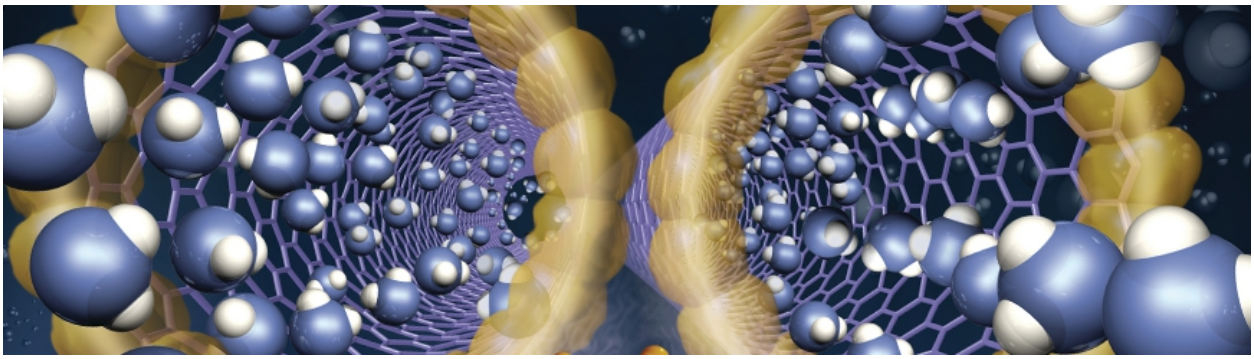
1.2 Purpose and Approach

Porifera, Inc. (Porifera) proposed a research program to the United States Department of Energy (DOE) Advanced Research Projects Agency – Energy (ARPA-E) to develop and demonstrate a comprehensive set of chemical and physical modifications of carbon nanotube membranes with high flux and high selectivity. These combined performance characteristics would enable energy-efficient CO_2 capture. DOE funded this project and the California Energy Commission (Energy Commission) contributed matching funds through the Public Interest Energy Research program. The project was a collaborative effort lead by Porifera with support from researchers at Lawrence Livermore National Laboratory (LLNL) and the University of California, Berkeley (UC Berkeley).

Carbon Nanotubes (CNTs)

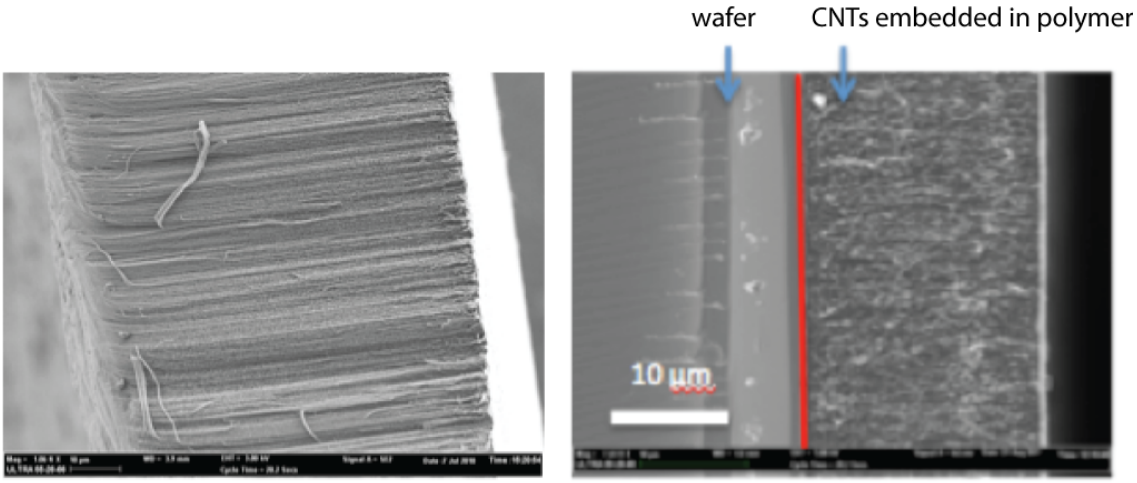
CNTs are elongated graphitic tubes with diameters on the molecular scale (1 - 5 nanometers). CNT membranes are known for their extremely fast mass transport of water and gas molecules due to their atomically smooth walls.

Figure 1. CNT Membranes Have Fast Transport



Single wall carbon nanotubes (SWNT) have a single layer of graphitic carbon while double wall nanotubes (DWNT) have two layers, and multiwall nanotubes (MWNT) have greater than two layers of graphitic carbon. For this project, Porifera pursued two basic approaches. The first approach was to create a membrane with aligned carbon nanotubes that serve as pores whose end tips are functionalized to enhance CO_2 selectivity. The second approach was to create a nano-structured composite membrane that combines ultra-permeable nanotube support with ultra-thin selective layers at the surface of the membrane.

Figure 2: Images of CNTs



Left: Image of aligned CNTs. Right: Image of aligned CNTs embedded in polymer on a silicon wafer.

Previous research work by LLNL researchers demonstrated that a ceramic-based CNT membrane with aligned DWNT pores embedded in a silicon nitride matrix provides extraordinarily high gas fluxes. Nitride-based membranes are mechanically and chemically robust, and heat-resistant. However, in practical terms, they are limited in that they are expensive to make and are very fragile.

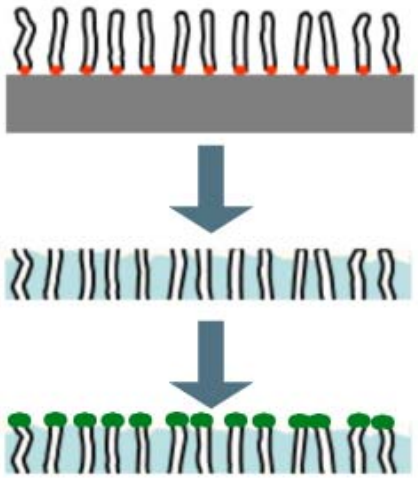
Porifera proposed an alternate way to create CNT membranes whereby the CNT would be embedded within a polymer matrix. For CNT membrane fabrication, matrix encapsulation of CNT arrays preserves the CNT alignment and results in a void-free membrane film. While the infiltration of dissolved polymers into CNT arrays may provide flexible and high-density composite films, the liquid phase processing of polymeric solutions often results in CNT collapse. CNT collapse causes the clustering of the CNTs into islands of CNT mats. Once such CNT collapse occurs, a CNT membrane cannot be produced due to the large voids between the mats and between tubes. CNT collapse generally occurs during solvent infiltration or during the solvent evaporation step. To overcome this limitation, Porifera proposed different methods to embed the CNTs in a polymeric matrix and produce a CNT membrane. After producing a polymeric aligned CNT membrane, functionalization of the membrane surface would achieve CO_2 selectivity.

1.3 Activities Performed and Results

First, CNT growth was optimized to produce high quality vertically aligned nanotubes. CNTs are grown using a metal catalyst, such as iron, in a high temperature furnace in the presence of a carbon source gas, such as acetylene. Nanotube growth optimization was achieved by varying the catalyst deposition (i.e., the composition and deposition recipe) and the carbon nanotube growth recipe (i.e., the temperature, pressure, and gas mixture). The quality of the CNTs was quantified using spectroscopic and high-resolution imaging techniques.

To fabricate the membranes, the CNTs were grown to be vertically aligned on silicon wafers, and then embedded in polymer. After specialized processing, the CNT composite material was removed from the wafer. To enable CO_2 selectivity, the surface of the membrane was either functionalized or coated with small molecules or polymers.

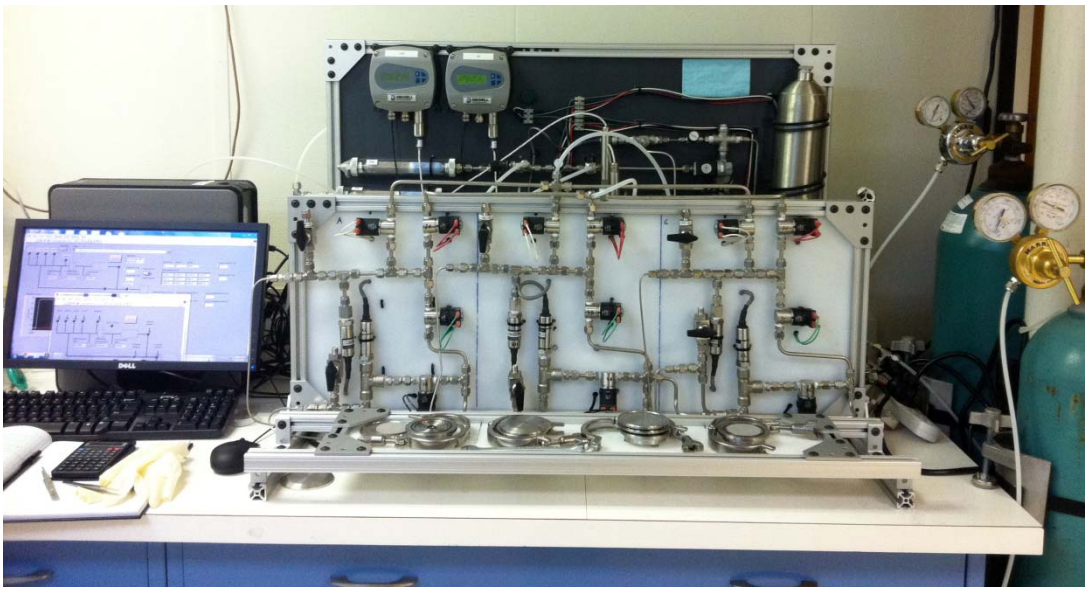
Figure 3: Schematic of Aligned CNT Infiltration and Functionalization



Aligned CNTs (top), infiltrated with polymer to form a membrane (middle), and functionalized for CO_2 selectivity (bottom).

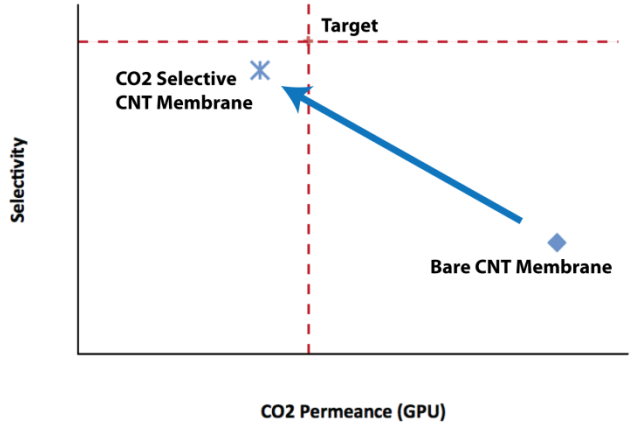
CNT membrane performance is dependent on a variety of factors including pressure, concentration, humidity, and temperature. Pure gas, or single gas, studies of nitrogen and CO_2 were measured at Porifera to initially gauge the membrane's performance using the system shown below.

Figure 4: Gas Test Setup Developed at Porifera



While single gas data is a good first characterization of separation, mixed gas studies provide a more detailed picture. Mixed gas studies were performed at LLNL using a system tailored for this project. Porifera determined that the CNT membrane maintains performance under humid conditions by measuring flux and selectivity of the membrane under both dry and wet conditions.

Figure 5: Porifera's CNT membrane Approached DOE's Target.



The initial DOE target for the project was to demonstrate a CO_2 permeability of 10,000 barrer (1 barrer = 10^{-10} cm^3 (STP) cm/(sec cm^2 cm-Hg)) and a CO_2/N_2 selectivity equal to or greater than 100. However, these targets were modified mid-project during the development of Porifera's composite membrane. Composite membranes are more appropriately quantified by permeance in gas permeation units (GPU), with 1 GPU = 10^{-6} cm^3(STP)/cm^2(scmHg), instead of permeability in barrer. These final milestone targets are business sensitive and have not been included in this

report. CNT membrane performance approached the final milestone targets set by the DOE under dry and wet conditions.

The table below lists the tasks for this project and were completed within the scope and budget of this project.

Table 1: Project Tasks and Work Completed

DOE Task	Activity	Degree of Completion
Fabrication of polymer-fill membranes using Method 1	Fabricated membranes	Completed
Fabrication of polymer-based membranes using Method 2.	Fabricated membranes	Completed
Fabrication of polymer-based membranes using Method 3.	Developed faster fabrication method using this technique	Completed
Identify the most promising membrane fill material and technique.	Studied different polymers and chose the most promising material	Completed
Fabrication of large-scale membranes	Increased size of samples	Completed
CNT end-tip functionalization	Studied different methods of nanotube functionalization	Completed
Functionalization of CNT membranes with CO_2-selective polymeric skin layers	Developed CO_2 selective layers for fabrication of a composite membrane	Completed
CNT membrane functionalization with branched amines	Attached small molecule amines	Completed
Evaluation of CO_2 selectivity	Built test setup and measured membranes	Completed
Evaluation of CO_2 permeability	Built test setup and measured membranes	Completed
Evaluation of membrane fouling by water (H_2O), SOx, NO_2	Added humidity sensors to gas test setups	Completed H_2O

1.4 Conclusions

This project resulted in a significantly better understanding of aligned CNT membrane development, functionalization of CNT membranes to produce selective aligned nanotube membranes, and gas transport behavior of aligned CNT membranes. The CNT membranes generated by the project have been shown to have excellent performance in laboratory-scale studies, within the limited environments that were tested.

While further work is required, industrial scale-up of CNT growth and membrane fabrication was shown to be technically feasible. Industrial volume production will enable reduction in membrane manufacturing costs and may provide opportunity to monitor long-term membrane performance measurements for improvements. Pilot testing of the membranes on-site at a power plant using flue gas will be required to validate the technology and reveal any potential problems with chemical stability.

CHAPTER 2:
The California R&D project

2.1 The Benefits to California

As of 2012, 7.5 percent of California's total system power comes from coal and 43.4 percent from natural gas (Nyberg, 2013). While natural gas power plants produce about half the amount of CO_2 emissions as coal, increasing rates of natural gas power generation within the state contribute significant greenhouse gas emissions into the atmosphere.

The United States Environmental Protection Agency (EPA) estimates that the average emission rate from a single natural gas power plant is 1,135 pounds of CO_2 per megawatt-hour of power generated (EPA, 2000). In 2012, California's natural gas plants generated a sum total of more than 121,716 gigawatt hours of power, releasing more than 69 million tons of CO_2 into the atmosphere.

Once taken from laboratory to industrial scale, the potential of the CNT membranes developed for this project to reduce CO_2 emissions by 85-90 percent could have a very large impact within the state and beyond. In addition, CNT membrane-based CO_2 separations could potentially deliver better flue gas separation efficiencies for California power plants and manufacturing facilities, resulting in less expensive carbon separation and capture and less energy consumption.

2.2 Financial Details

Total costs for the project were budgeted at $1,442,469 (Table 1). Actual project costs were about $1,470,493. Labor costs comprised 82 percent of actual costs and supported work performed directly in California at Porifera (located in Hayward, California), LLNL (located in Livermore, California), and UC Berkeley (located in Berkeley, California).

The project received match funds of $115,397 from the Energy Commission's R&D program (Table 2). These funds equaled 10 percent of the funds awarded by the DOE. LLNL and UC Berkeley contributed match funds of $75,000 and $45,000 respectively. Porifera had an original cost share budget of $53,097. Actual project costs that exceeded the original budget were provided by Porifera, increasing the total match contribution to $81,121.

Table 2: Project Costs

Project Costs	Budget ($)	Actual Cost ($)	Spending
Direct	1,197,327.00	1,206,923.52	101%
G&A	245,142.00	263,569.98	108%
Total Project Costs	1,442,469.00	1,470,493.50	102%

Table 3: Project Funding

Project Funding Sources	Budget ($)	Actual Funding ($)	Spending
University of California, Berkeley	45,000.00	45,000.00	100%
Porifera, Inc.	53,097.00	81,121.51	153%
Lawrence Livermore National Lab	75,000.00	75,000.00	100%
State of California (PIER Funding)	115,397.00	115,396.99	100%
United States Department of Energy	1,153,975.00	1153,975.00	100%
Total Project Funding	1,442,469.00	1,470,493.50	

The DOE and PIER project funding combined supported California's economic recovery through the direct support of ten staff scientists, professors, graduate students, and postdocs at Porifera, UC Berkeley, and LLNL. Eighty-eight percent of the project was underwritten with state and federal funds, which supported more than 6,100 person-hours of research and development work performed exclusively within California.

2.3 Observations and Recommendations

What has become apparent is that no matter how good these technologies are, they will not reach their commercial potential unless there are state and federal mandates that create economic incentives for companies engaged in developing carbon capture solutions. California's cap and trade system—as run by the California Air Resources Board—is a good start, but the economic incentives at this point are too weak to stimulate and support self-sustained technology development. Until this happens, any company, including Porifera, must rely on continued and committed state and federal support further advancements in carbon capture technologies.

Research frequently has applications for society in associated areas. For example, the potential for treating water at lower energy costs. As the California Energy Commission describes on its website, water and energy are "inextricably connected" (CEC, 2013), with water-related

electricity accounting for "nearly 20 percent of California's total electricity consumption." Porifera would like to see state and federal support of promising technologies that have the potential to reduce these costs. Porifera believes that water-energy technologies will achieve widespread adoption more quickly than carbon capture technologies.

GLOSSARY

Term	Definition
ARPA-E	Advanced Research Projects Agency - Energy
cm	centimeter
CNT	carbon nanotube
CO_2	carbon dioxide
DOE	United States Department of Energy
DWNT	double wall carbon nanotube
EIA	United States Energy Information Administration
Energy Commission	California Energy Commission
EPA	United States Environmental Protection Agency
GPU	gas permeation unit
H_2O	water
Hg	mercury
LLNL	Lawrence Livermore National Laboratory
MWNT	multi wall carbon nanotube
N_2	nitrogen gas
NO_2	nitrogen dioxide
PIER	Public Interest Energy Research
Porifera	Porifera, Inc.
RD&D	research, development and demonstration
sec	second
SO_x	sulfur oxide
STP	standard temperature and pressure
SWNT	single wall carbon nanotube

UC Berkeley	University of California, Berkeley

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