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LLNL-TR-403910

# Q1 Report for CADWR Project: Desalination using carbon NAnotube Membranes

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May 15, 2008

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**Quarterly Technical Progress Report**  
**Covering Period** March 6th, 2008 to May 3rd, 2008  
**Date of Report** May 6<sup>th</sup>, 2008

**Agreement Number:** 4600007449

**DWR ID Number:**

**Project Title:** Desalination using Carbon Nanotube Membranes

**Recipient Organization:** Lawrence Livermore National Laboratory; 7000 East Ave; Livermore, CA 94550

LLNL

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**Date Submitted:**

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Signed, Reviewed by **NAME, TITLE** Date

**1. Project Objective:**

In this research and development project, LLNL will leverage the process for fabrication of the membranes developed by our internally funded effort (LLNL Laboratory Directed Research and Development). LLNL will then employ chemical manipulations to modify charge at the ends of the nanotubes and make the membranes more selective to either positive or negative ions through a combination of size and charge selectivity. LLNL's goal is to demonstrate ion exclusion while preserving high permeabilities and low energy use. Success of this research and development project may warrant further developments in the fabrication of membranes.

**2. Project Description / Background:**

Over the period of 1 year Lawrence Livermore National Laboratory (LLNL) proposes to demonstrate anion and cation selectivity using sub-2nm membranes that have carbon nanotubes (CNTs) as pores. LLNL will demonstrate feasibility of desalination using our membranes whose pore sizes are in the range of some traditional RO membranes. LLNL is uniquely positioned to do this because the laboratory is home to the first group in the world to fabricate carbon nanotube membranes with diameters <2nm and directly measure its transport properties(J.K. Holt, H.G. Park, Y. Wang, M. Stadermann, A. B. Artyukhin, C. P. Grigoropoulos, A. Noy, and O.

Bakajin, *Fast Mass Transport Through Sub-2nm Carbon Nanotubes*, **Science**, 312(2006), 1034, (**COVER**). This study revealed up to 2 orders of magnitude higher permeabilities than those of other desalination membranes, including some used for RO.

- LLNL will fabricate and functionalize the membranes
- If necessary to achieve performance metrics, LLNL will refine the nanotube growth process to produce monodisperse tubes in < 1 nm pore size regime; this will largely involve tailoring of the metallic catalyst recipe used
- LLNL will increase the number of active carbon nanotube pores in our new membrane chip design to obtain more than 2 orders of magnitude larger membrane area.
- LLNL will use a flow cell and conduct reverse-osmosis experiments
- LLNL will conduct analysis of ion composition and concentration The results of this study will be summarized in report form and a manuscript will be prepared for submission to a high-profile scientific journal

**3. Progress and Status:**

Over the first two months of the project we have fabricated several 1<sup>st</sup> generation membranes and started working on the development of the second generation of the membrane with increased open area.

Fabrication of the 1<sup>st</sup> generation membranes for use in this project:

We have used a previously developed a fabrication process for sub-2 nm CNT pore membranes using catalytic chemical vapor deposition (CVD) growth of a dense, vertically-aligned array of DWCNTs on the surface of a silicon chip, followed by conformal encapsulation of the nanotubes by a hard, low-pressure chemical vapor deposited (LPCVD) silicon nitride (Si<sub>3</sub>N<sub>4</sub>) matrix. The excess silicon nitride is removed from both sides of the membrane by ion milling and the ends of the nanotubes are opened up with reactive ion etching.

Development of the second generation membranes

We are developing a process based on encapsulation of carbon nanotubes with a vapor deposited polymer – parylene. We have demonstrated that the parylene coats the carbon nanotubes well and that we can create a free standing film of parylene/CNT composite.

Project meetings have been conducted weekly.

**4. Percent Complete of Total Project:**

18%

**5. Deliverables:**

**a. Publications / Presentations:**

Olgica Bakajin gave an invited presentation in the panel on Emerging Technologies for water purification, which was part of the Water and the Developing World conference held at Stanford University on 04/11/08

6. **Expenditures:** Provide a budget with detailed listing of expenditure items. Specify grantee agency's share and State's share. If invoicing for this period, submit invoice with the report. Note that the balance is the amount remaining of the funds not yet paid out.

Expense Report from \_\_03/06/08\_\_ to \_\_05/03/08\_\_

Expense Items (Budget Category )	State Share		
	Previous Quarter's Balance A	Current Quarter's Expenses B	Quarter's Ending Balance A – B = C
Effort	0	\$15.5K	
Procurements & Travel	0	\$2.3K	
Facilities	0	\$7.3K	
Indirect	0	\$20.8K	
<b>Totals</b>	<b>\$64K</b>	<b>\$45.9K</b>	<b>\$18.1K</b>

LLNL is providing analytical equipment, materials fabrication facilities and the value of information and methods in excess of \$500,000.

**7. Schedule Status:**

Over the first two months of the project we have fabricated several 1<sup>st</sup> generation membranes and started working on the development of the second generation of the membrane with increased open area. The project is progressing according to the plan as detailed in the chart below.

		Year 1			
	Task	Q1	Q2	Q3	Q4
1	Membrane Fabrication and Functionalization				
2	Increase of open area on the chip (Gen2)				
3	Development of membranes with smaller diameter pores				
4	Anion selectivity measurements				
5	Cation selectivity measurements on sub 2nm membranes				
6	Testing of the membranes with smaller pore diameters (flux ion and selectivity)				
7	Summary report				

**8. Plans for Next Quarter (and the remainder of Q1):**

We will focus our activities on the following tasks:

- 1) Exploration of surface treatments to functionalize the membranes
- 2) demonstration of the increased permeability with 2<sup>nd</sup> generation membranes
- 3) setup of the ion selectivity measurements using CE electrophoresis
- 4) Optimization of carbon nanotube synthesis

*All quarterly reports should be publicly disclosable and not contain confidential, proprietary or business sensitive information.*

Agreement Number 4600007449		Starting Date:3.6.08		Completion Date: 3.05.09		Quarter - Year 1-2008		Report Number 1		PERCENT OF									
Grantee Agency Name: Lawrence Livermore National Laboratory				% Time Elapsed 17		Total Grant Funds used \$43.9K		Grant funds this Quarter \$43.9K		Project	Task Complete Last Report	Task Complete This Report	Project Complete						
Name of Project: Desalination using Carbon Nanotube Membranes																			
TASKS		YEAR		2007		2008								2009					
		MONTH		Qtr 4		Qtr 1		Qtr 2		Qtr 3		Qtr 4		Qtr 1					
Task 1: Membrane Fabrication and Functionalization																10	0	67%	0.067
Task 2: Increase of open area on the chip (Gen2)																15	0	67%	0.1005
Task 3: Development of membranes with smaller diameter pores																30	0	0%	0
Task 4: Ion selectivity measurements																35	0	0%	0
Task 5: Testing of the membranes with smaller pore diameters																10		0%	
Show Progress by Use of Bar Chart		Scheduled =														100			0.1675
		Completed =																	