Ultrahigh-Efficiency Capacitive Devices For Continuous Water Deionization

DE-SC0011909

Phase II: 7/2015 to 7/2017

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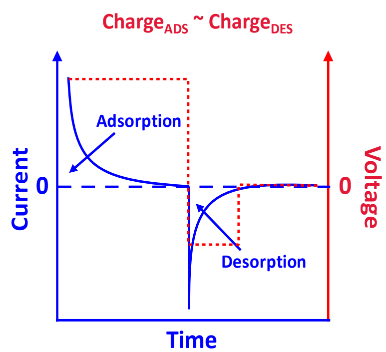
Project Objective

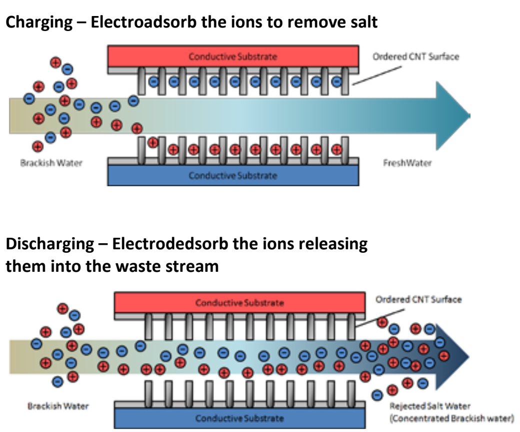
- The overall project objective is to develop a membrane free high efficiency system for desalination of brackish water based on capacitive electrode structures.
  - Current small scale reverse osmosis based systems are energy inefficient, require high pressure pumps and are susceptible to membrane fouling.
  - Capacitive deionization provides a path to low power requirement, energy efficient low maintenance modular systems that can easily be deployed in remote locations.
  - The major barriers is the design and control of the electrode structures.
    - Electrode structures are needed that provide highly controlled and uniform porosity to maximize the ion removal rate and efficient.
- In Phase I we demonstrated the benefits of controlled porosity for ion removal providing a 50 time improvement in extraction level per g of carbon
- The objective of Phase II is to scale up the electrodes both size and production rate and develop a prototype stack and system design

Technical Innovation

- Reverse osmosis is currently the most common method of desalination
  - Most economic in large plants collocated with power plants in coastal areas
  - Major issues include
    - Highly energy intensive with high pressure pump – 55% of operating cost
    - Labor and maintenance intensive
    - High pressure requirements make safety a concern
    - Susceptible to fouling
    - Creates large volumes of concentrate effluent which must be disposed safely
  - Does not represent as good a solution for the large volumes of brackish water
- Capacitive Deionization (CDI) offers a good solution for small scale and distributed inland applications

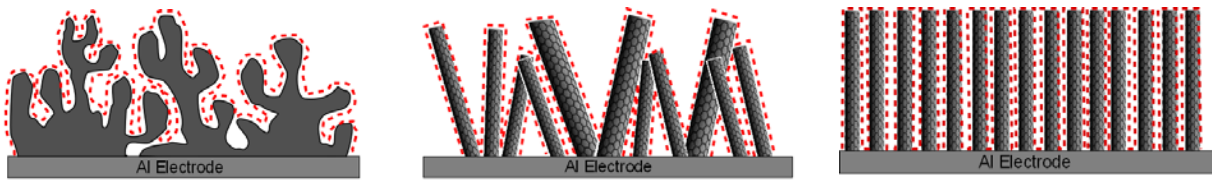
- CDI use a low applied voltage to pull the ions out of solution
- Operates a low pressure
- Creates a low volume of concentrate – improved waste management
- Is modular and can be applied to a wide range of applications and sizes
- Can be readily automated





Technical Innovation

- CDI needs different electrode structures than energy storage based electrodes
  - Ions must be actively removed from the flowing solution with a sufficiently high flux
  - Electrodes must be optimized to remove and store the ions not just surface charge
  - Conventional high surface area carbons for capacitors have a high surface area but poor availability for the ions



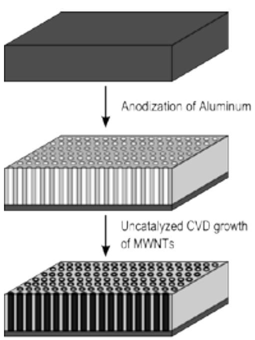
Activated Carbon Electrode	Non-templated MWNT Electrode	Templated MWNT Electrode
* Industry standard		*Mainstream's approach
SSA: <2,000 m^2/g	SSA: < 450 m^2/g	SSA: 1,320 m^2/g
κ: 0.28 W/m-K	κ: >200 W/m-K	κ: >200 W/m-K

→ **Ordering of material increases**

Mainstream templated electrode structures provides excellent approach to controlling both the pore size and the pore availability for maximizing ion removal

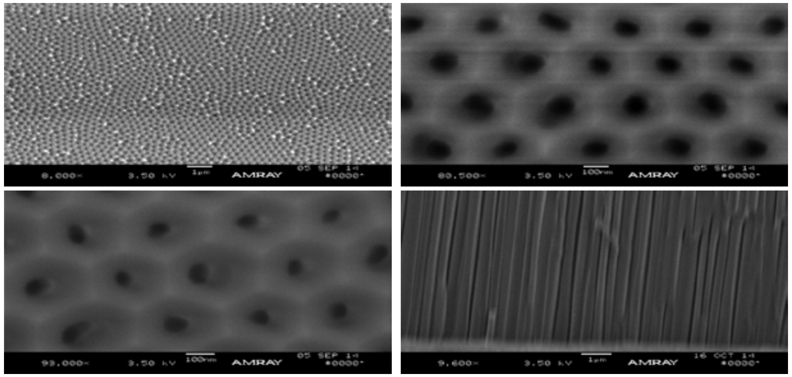
Technical Approach

- Mainstream's approach to capacitor electrode design uses templated growth of highly stable multiwall carbon nanotube (MWCNT) to produce high stability electrodes
  - Controlled potential anodization of aluminum provides a path to tunable pore size and depth due to controlled self ordering of the pore growth
  - Uncatalyzed growth of high stability MWCNTs provides a path to high stability electrode structures



- **Controlled anodization produces vertically aligned, HCP pores**
- **Pores catalyze CVD CNT growth**
- **CNTs adopt template morphology**
- **Highly scalable and tunable fabrication method**

Self ordering anodization and catalyst free MWCNT growth produces high stability tunable electrode



SEMs show highly ordered pore vertically aligned structures

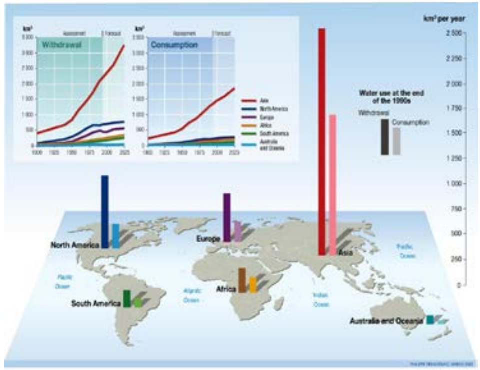
- Phase I demonstrated high efficiency ion removal from water with small 3.8 cm^2 electrodes using a single cell

Technical Approach

- The technical approach in Phase II is to scale up the electrode structures and build them into a multicell stack and system
  - Scale up electrode fabrication size and production rate
  - Optimize the electrode pore size and depth to maximize the rate for a range of target ions
  - Incorporate the electrodes into a multi cell stack
  - Develop system controls to maximize both the rate and the overall efficiency of the system

Transition and Deployment

- Plentiful water supply is essential for human survival but only 0.65% is available as freshwater and withdrawals are outstripping supply
  - Brackish water represents a significant source of water
- Tunable scalable Modular design enable local point of use water
  - Commercial opportunities
    - Remote communities (mobile or stationary)
    - Individual whole house supply
    - Inland communities where disposals of the concentrate water is an issue
    - Areas where the integration with renewable energy sources is advantageous
    - Industrial water clean up and concentrate water volume reduction
    - Mobile disaster and emergency back up water supply
  - Military
    - Small portable desalination units for forward operating bases
    - Mobile applications
    - Waste water clean up (removal of toxic chemicals)



Measure of Success

- Existing small scale Reverse Osmosis systems
  - Have a high energy and power requirement (2.2 to 5 kWh/m^3 of water)
  - High operator and maintenance costs
  - Requires high pressures – a maintenance and safety issue
  - Large volume of concentrate waste which must be disposed of– a significant issue with inland applications
- Capacitive Deionization
  - Low energy and power requirements (<1.5 kWh/m^3 of water produced)
  - Lower voltage application and low pressure pumping requirements
  - Can integrated with renewable energy sources
  - Easier to adapt to remote monitoring and operator free operation
  - Low waste production (10 to 20% of the volume of the produced water)
  - Can be applied to the clean up and recovery of enviromantal ionic contaminates
    - Phosphates, nitrates and a wide range of toxic metals

Project Management & Budget

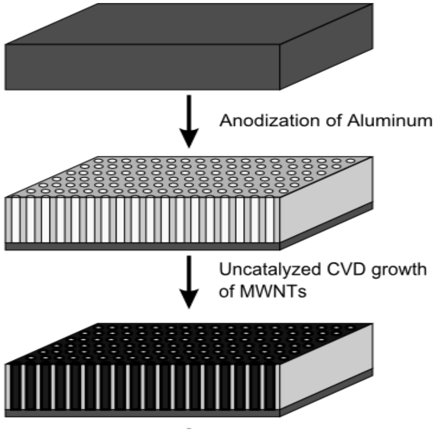
- Project: start 7/2015 (Phase II) Completion 7/2017

Milestone	Status
Scale up electrode structures to two sides 162 cm^2 electrodes with controlled porosity	Complete 5/2016
Scale up the CVD process to produce multiple two sides electrodes per run	Complete 5/2016
Optimize the electrode structure for pore size and depth	In process (10/2016)
Build a multicell stack and demonstrate scaled up ion removal	In process (8/2016)
Optimize system controls for ion removal	12/2016
Build subscale prototype system with integrated controls for continuous deionization of target waste stream	2/2017

Total Project Budget	
DOE Investment	$1.14M (Phase I and II)
Cost Share	0
Project Total	$1.14 (Phase I and II)

Results and Accomplishments : Electrode Scale Up

- Scaled the electrodes up by a factor of 42 from the 3.8 cm^2 electrodes developed in Phase I
  - Scaled the electrodes to 10 cm by 10 cm
  - Anodization of both sides of the aluminum – to increase the area and allow a smaller stack
- Scaled up and optimized the process conditions without losing control of the pore size, pore density or pore depth

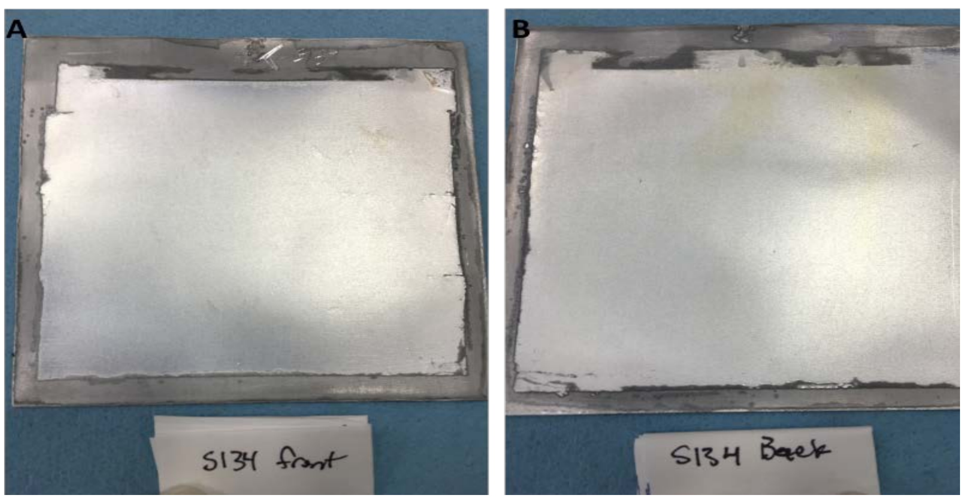


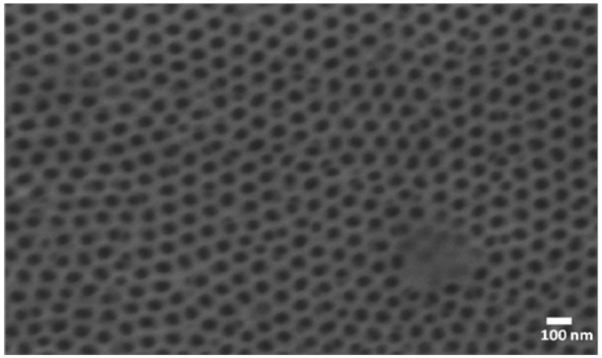
Phase I: single sided 3.8 cm^2

Scaled to 2 sided large area electrodes 81 cm^2 per side

Results and Accomplishments : Anodized Electrode Structures

- Scaled up by a factor of 80 without loss of uniform pore distribution
  - Optimized anodization for multiple samples per run
  - Improvements in the masking technique to obtain square samples in process

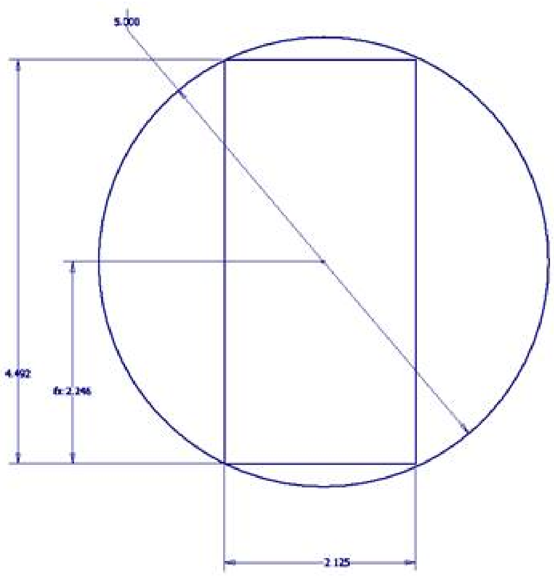




SEM of multiple locations on both sides show uniform pore distribution

Results and Accomplishments : Scale up of CNT growth

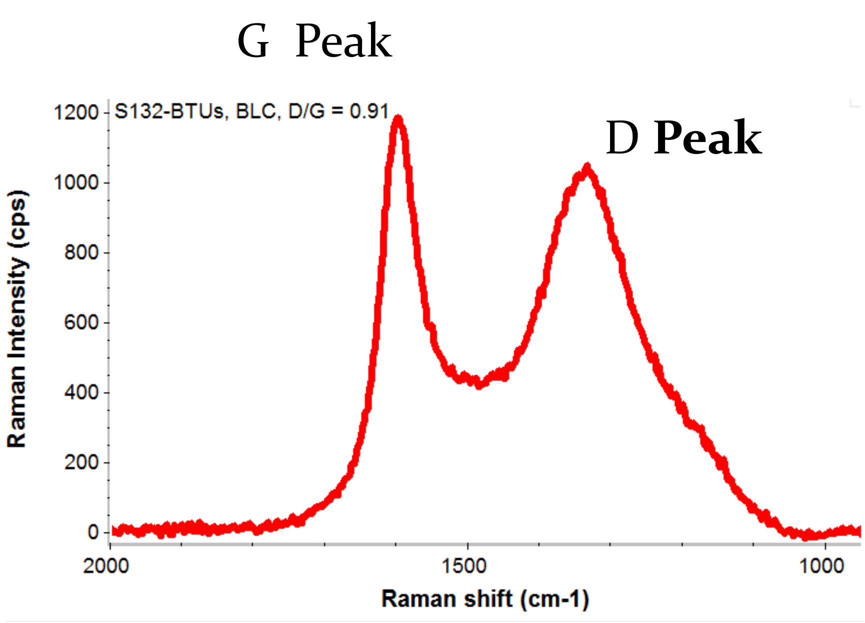
- Process scale up performed at CVD equipment for both area and number of samples per run
- Electrode size maximized for the available process tube size is 8 in diameter
- Titanium fixture designed to allow MWCNT growth on 5 electrodes per run
    - can be increased to 9 electrodes per run with existing equipment



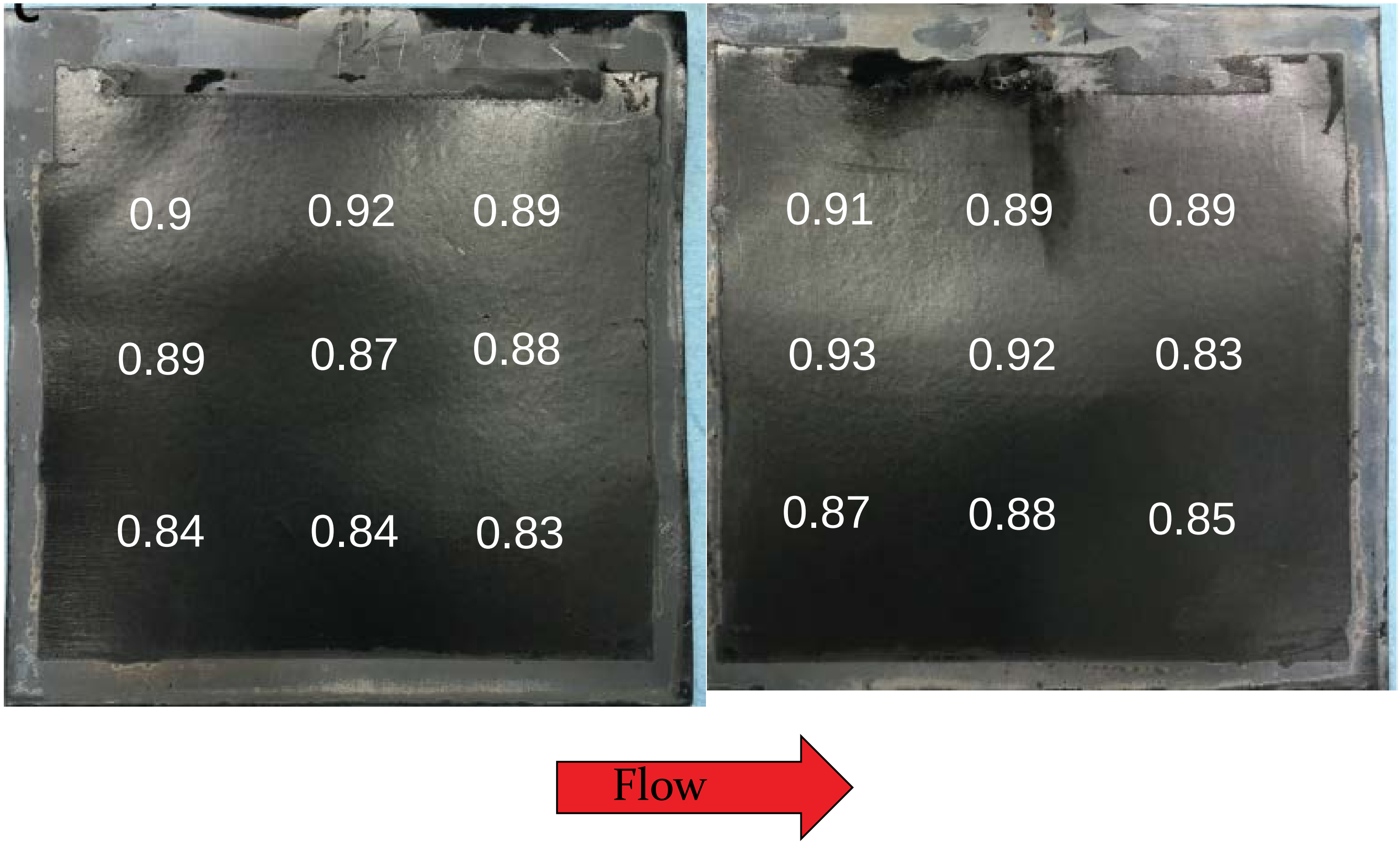
Initial fixture designed with a 5 mm spacing to ensure no depletion of reactant gasses

Results and Accomplishments : Raman Spectroscopy of CNT Coated Electrodes

- Raman Spectroscopy provides a measure of the CNT carbon quality
  - higher quality provides improved stability and durability
  - The lower the ratio the higher the level of ordered graphitic structure
- Typical Raman spectra of scaled up electrodes shows improved graphitic CNT carbon compared to Phase I



Results and Accomplishments : Uniform CNT Growth Over Electrode Surface

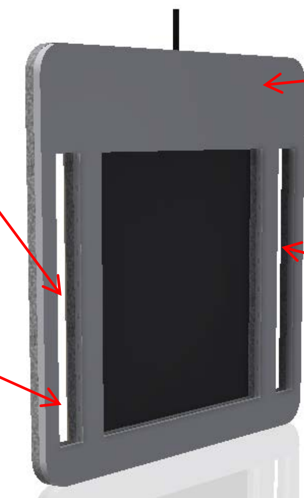


- Excellent CNT quality over the entire surface of both sides of the electrode
  - Produces a high stability electrode structure
- Less than ~5% variation in D/G ratio across the sample

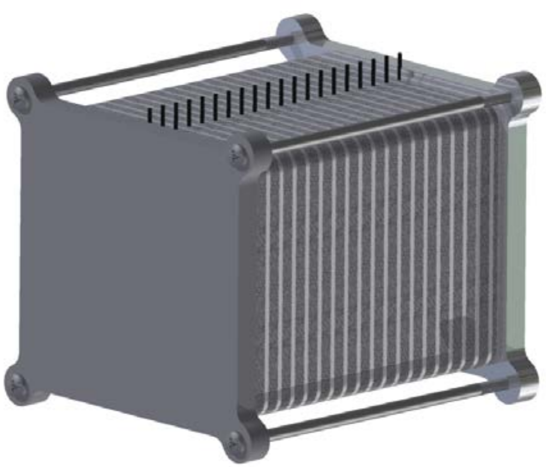
Stack and Seal Design

- Stack and seal design completed
  - 10 cm by 10 cm electrodes
- Design incorporates two sided electrodes
- Flexible Stack sizing
  - Stack testing underway with large electrodes

Front Side



Back Side



20 Cell Stack