3-D Nanofilm Asymmetric Ultracapacitor

Annual Merit Review, DOE Vehicle Technologies Program

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Project ID: ES141

Overview

Timeline

- Project Type: STTR
- Phase I Start: 10/2009
- Phase II Start: 10/2010
- Phase II End: 09/2012
- Completion: 75%

Budget

- Funding FY10: $100K
- Funding FY11: $375K
- Funding FY12: $375K
- DOE Share: $850K
- Contractor: N/A (STTR)

Barriers Addressed

- Energy Density: 10Wh/kg,20Wh/L
- Materials Cost: $10/kg
- Mfg Cost: Reduction
- Environmental: Benign

Partners

- Florida State University STTR RI
  - Dr. Jim P. Zheng
  - Dr. Qiang Wu
- Yardney Technical Products
  - Cell Package Co-Design
- Nilar, Inc.
  - Bipolar Stack Concept

Relevance: Ultracapacitor HEV

Strengths

High Rate	→	Charge Acceptance/Delivery (Ch. Sustaining)
Long Cycle Life	→	Last The Full Life Of The Vehicle
Low Temp Operation	→	Broad Market Geography

Weaknesses

Low Energy	→	5Wh/L, 4Wh/kg Too Large, Too Heavy
Electrolyte Safety	→	Toxic, Flammable ACN Electrolyte
Cost/System Complexity	→	**10x Worse** vs. USABC Target

USABC
UNITED STATES ADVANCED BATTERY CONSORTIUM

FreedomCAR

System Attributes	12V Start-Stop (TSS)		42V Start-Stop (FSS)		42V Transient Power Assist (TPA)	
Discharge Pulse	4.2 kW	2s	6 kW	2s	13 kW	2s
Regenerative Pulse	N/A		N/A		8 kW	2s
Cold Cranking Pulse @ -30°C	4.2 kW	7 V Min.	8 kW	21 V Min.	8 kW	21 V Min.
Available Energy (CP @1kW)	15 Wh		30 Wh		60 Wh	
Recharge Rate (kW)	0.4 kW		2.4 kW		2.6 kW	
Cycle Life / Equiv. Road Miles	750k / 150,000 miles		750k / 150,000 miles		750k / 150,000 miles	
Cycle Life and Efficiency Load Profile	UC10		UC10		UC10	
Calendar Life (Yrs)	15		15		15	
Energy Efficiency on UC10 Load Profile (%)	95		95%		95%	
Self Discharge (72hr from Max. V)	<4%		<4%		<4%	
Maximum Operating Voltage (Vdc)	17		48		48	
Minimum Operating Voltage (Vdc)	9		27		27	
Operating Temperature Range (°C)	-30 to +52		-30 to +52		-30 to +52	
Survival Temperature Range (°C)	-46 to +66		-46 to +66		-46 to +66	
Maximum System Weight (kg)	5		10		20	
Maximum System Volume (Liters)	4		8		16	
Selling Price ($/system @ 100k/yr)	40		80		130	

- Energy Density: 3Wh/kg, 3.75Wh/L
- Power Density: 650W/kg, 812W/L
- Cycle Life: 750,000
- Operating Temp: -30 to +52ºC
- Survival Temp: -46 to +66ºC
- Selling Price: 2.17$/Wh

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Project Objective

Objective

Develop an asymmetric ultracapacitor combining the 3-D Nanofilm oxide cathode ("3DN") with an activated carbon anode in an aqueous electrolyte that preserves the cycle life and temperature performance of an EDLC while providing the following characteristics at the multi-cell module level:

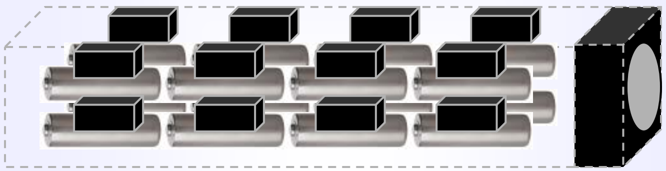
	3DN	USABC	Improvement
Energy Density (Wh/L)	20	3.75	>500%*
Specific Energy (Wh/kg)	10	3	>300%
Power Density (W/L)	2500	812	>300%
Specific Power (W/kg)	1500	650	~250%
Selling Price ($/Wh)	2.2-3.5	2.17	10x better vs. EDLC**
Environmental	Non Toxic		Safe

* LIC-like energy density but lower cost, less toxic and more scaleable.

** Depending on electrode configuration.

Approach: Device

EDLC Module Today

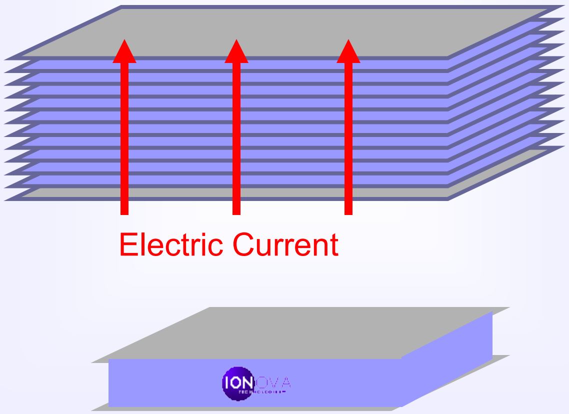


Cell voltage balancing electronics

Cylindrical cells

Cooling fan

Bipolar Module



Feature	Benefit
Single vs. Multi-Step Mfg Process	Reduces System Cost, Increase Reliability*
Scaleable Small To Large Format Devices	Enables New (Large Volume) Applications
Lower Inductance/Resistance	Increase Power Density, Reduce Heat

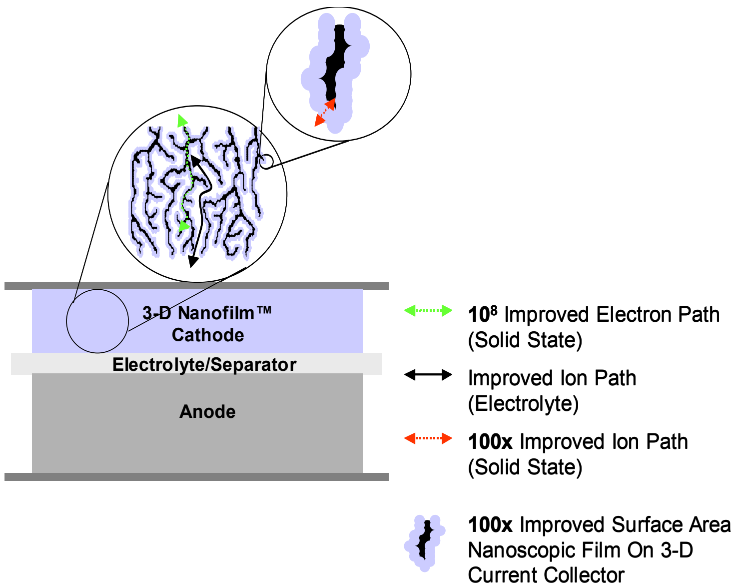
* Main challenge: seal.

Approach: Technology Strategy

Problem

The use of low-cost, low-toxicity pseudocapacitive materials such as MnO_2 can be used as cathode materials to create a low-cost aqueous asymmetric ultracapacitor with improved energy density that readily scales to system-relevant voltages through a bipolar stack configuration. Unfortunately, low electronic conductivity and the limited solid-state diffusion inherent in pseudocapacitive result in poor utilization with similarly limited energy and power densities.

3DN Asymmetric UCAP Cell



Strategy

We create a film of Mn/Ni oxide less than 50nm thick as a conformal coating on a 3-dimensional carbon structure. This approach preserves the benefits while compensating for the weaknesses of the electroactive oxides.

When combined with an activated carbon anode in pH neutral electrolytes, the system manages HER/OER over-potentials to permit 2.2V cells become possible. This, combined with large normalized capacitance, provides the large energy.

Milestones

Phase II DOE STTR w/FSU; FY11/12; Applied Research and Cell Development

Task	Component	Details	% Complete
Matl's Optimization	Cathode Carbon Cathode Oxide Anode Carbon Electrolyte	features, aerogel/support ratio loading, distribution, phase, ratio increase density, power, reduce cost rate, stability, capacitance, temperature potential window	90% 90% 80% 90%
Synth. Optimization	Cathode Carbon Cathode Oxide	precursors, processing time processing time vs. phase/distribution	90% 90%
Cell Design	Model Electrodes Electrolyte Current Collectors Electrode Adhesive Separator Pouch	capacitance, voltage, energy density, power density, electrode balance, electrolyte conc., inactive components/packaging from model from model stability, strength, density, conductivity, cost stability, conductivity, manufacturability polypropylene vs. glass fiber pouch material, sealer and tab seal	100% 80% 80% 50% 80% 50% 100%
Cell Package Design	W/Yardney	design, fabricate and characterize for ESR, EIS, voltage/capacitance vs. rate, cycle life	10%
Bipolar Stack Proof	W/Nilar	fabricate and characterize per cell	10%
USABC Testing		per protocol	0%

Previous Accomplishments

Previous CRADAs w/NRL; Basic Research

- NiMnOx 3DN for UCAP and ultra high rate LIB; preliminary static cell model
- Preliminary electrode and cell level; aerogel carbon, aqueous and organic Li electrolytes
- Current collector study: Ni, Al
- Preliminary anode AC study

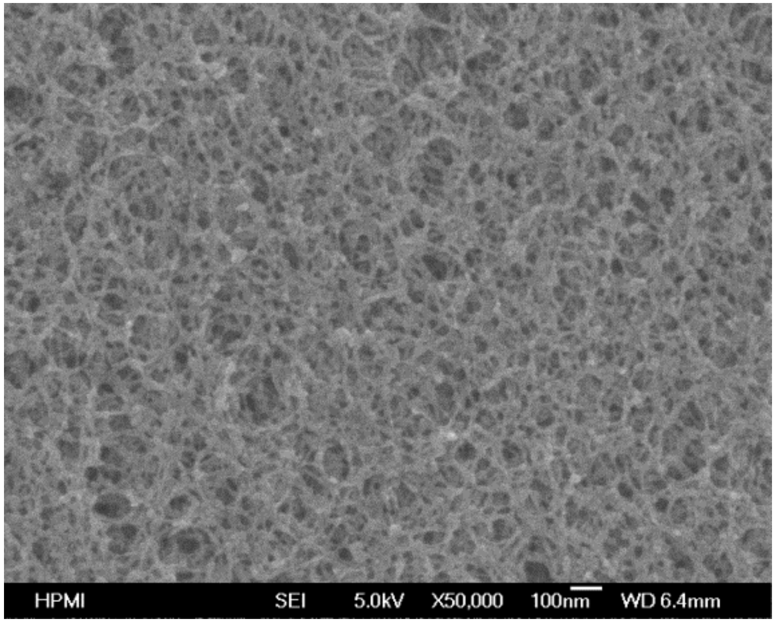
Phase I DOE STTR w/FSU; Applied Research

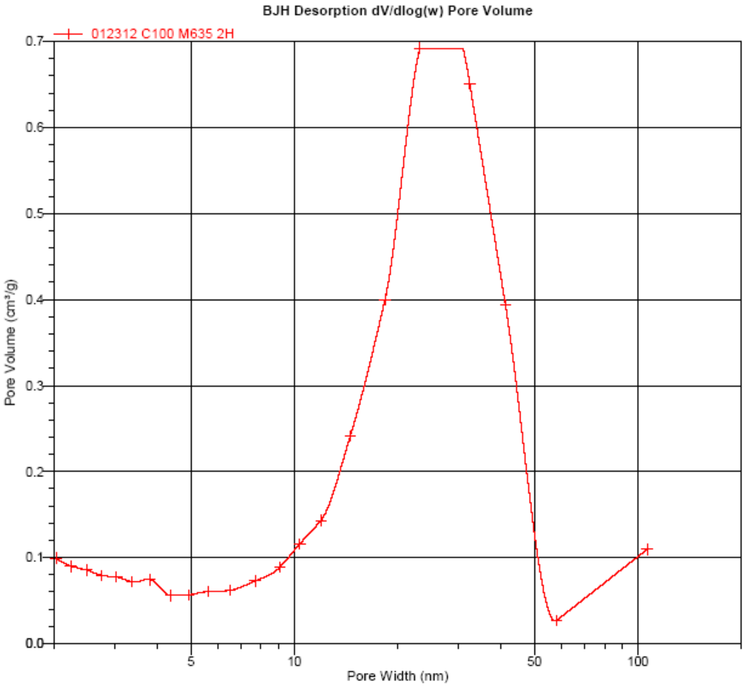
- Cathode: applied research w/3DN on CNT and aerogel, SEM, EDS, BET/BJH, CV, EIS, elect. cond.
- Electrolytes: Li, K and Sn as sulfates, nitrates and hydroxides; pH, ionic conductivity vs. conc.
- Anode: 4 grades AC from two suppliers (Kuraray, Mead Westvaco), sp. cap., CV, EIS, elect. cond.
- Separator, current collector and electrode adhesive: conductivity and stability
- Cell: 8Wh/kg, 15Wh/L obtained, preliminary power, self discharge and cycle characterization

Accomplishments: 3-D Carbon (1)

Polymer-Derived Aerogel 3-D Carbon

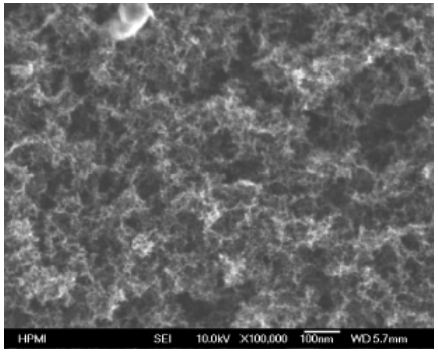
- Through-connected, tunable carbon features (50nm)
- Tunable pore size/volume (30% mesopore@15-50nm, 70% macropores, 2.25cm^3/g, no micropores)
- Surface area from 400-800m^2/g
- Ability to be used as binder-free monolith or "metastructure" powder
- Low cost precursors, orders of magnitude lower vs. CNT and graphene

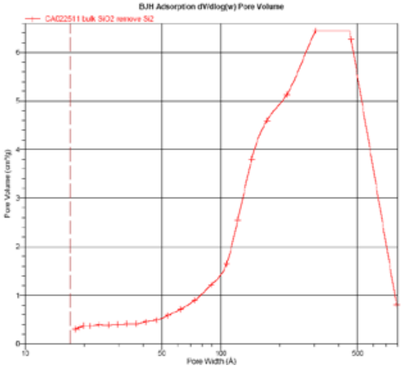




Accomplishments: 3-D Carbon (2)

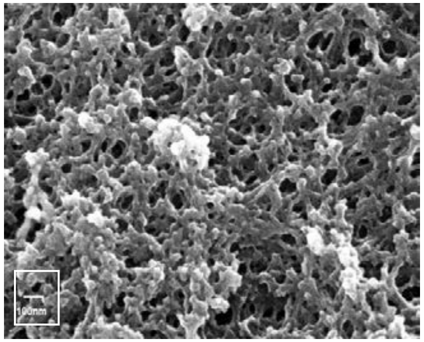
- Performance
  - Increase aerogel/support ratio from 1:1 to 4:1 increases capacitance
  - Increase electronic conductivity to improve power density
  - Modify carbon feature size to optimize surface area for capacitance
- Manufacturing scalability
  - New precursors decrease aerogel synthesis time by 80%, oxide synthesis time by 20-80%
  - Reduced precursor cost to <$10/kg
  - Improved electrode thickness uniformity/repeatability
  - Decreased support carbon costs by 98%
- Lessons learned
  - Activation counterproductive due to creation of micropores
  - Si templating (below) provides mesoporosity, but manufacturing scalability is a challenge



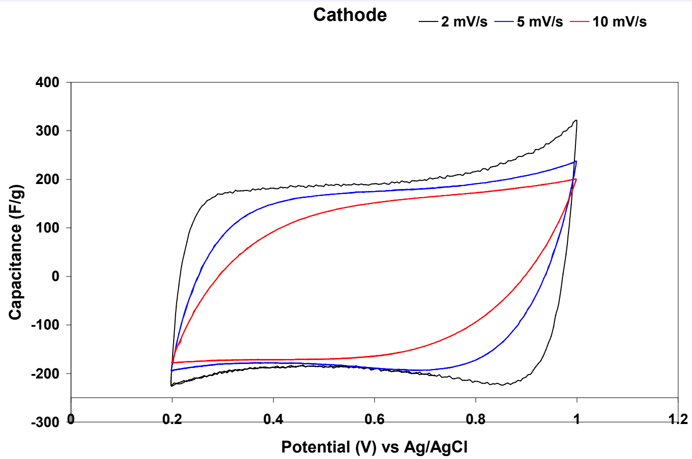


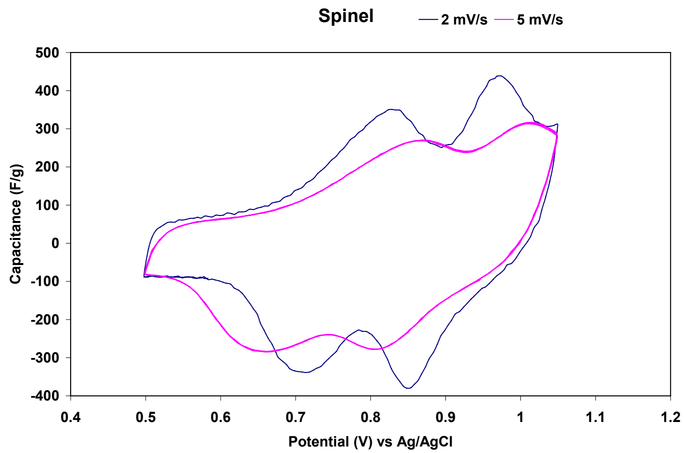
Technical Accomplishments: 3-D Oxide

- Manufacturing scalability
  - Decrease oxide synthesis time by a further 80%
  - Overall materials cost to $10/kg, per DOE target
  - Increased oxide loading above target 60%
  - Control of pore volume 30% increase vs. target 10% increase



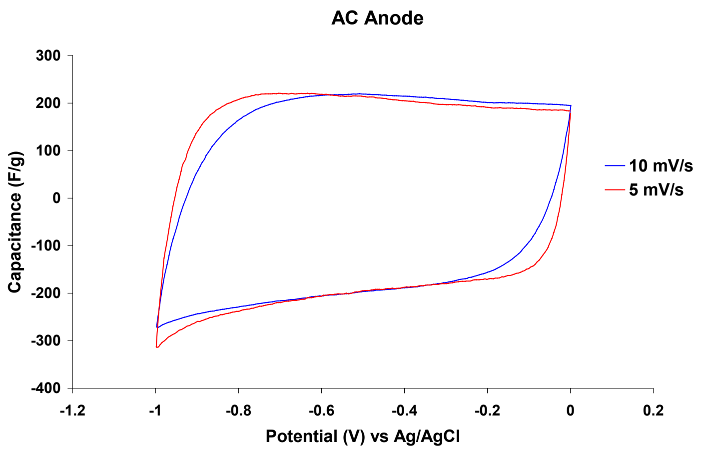
- Performance
  - Peak capacitance occurs at high potentials benefit usable energy I=C(dV/dt)+V(dC/dt)
  - Electrode normalized 220F/g (layered birnessite) and 300F/g (spinel)

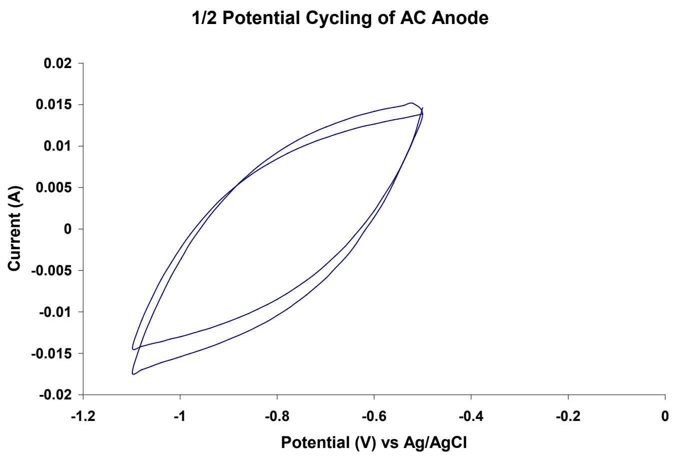




Technical Accomplishments: Anode (1)

- Performance (cellulose derived AC)
  - Two sample materials each from Kuraray and Mead Westvaco
  - One from each was low-cost, the other was high-capacitance ($50-100/kg)
  - High capacitance MWV shown below left is 190F/g @2A/g, but rate constricted above 2.5A/g

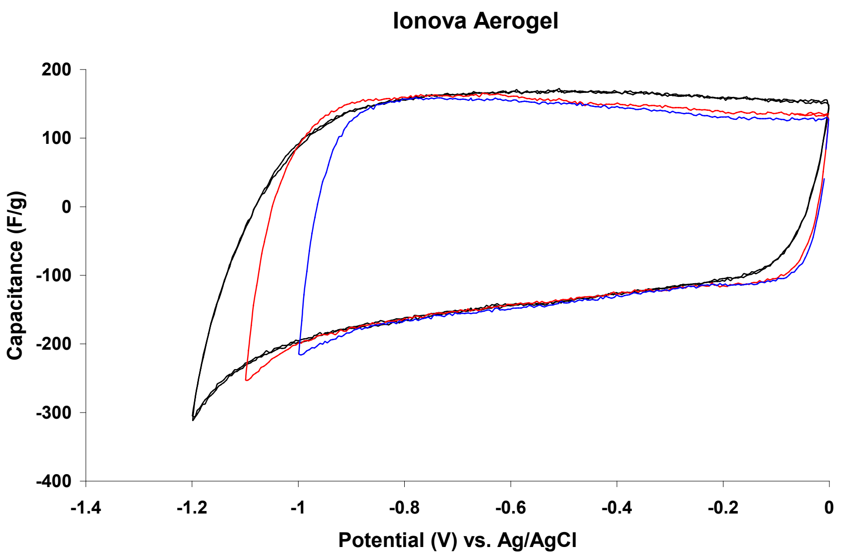




- Capacitance degradation
  - **Previously unreported issue;** AC as anode in aqueous cells >1.2V (utilizing –ve overpotential)
  - Nascent H evolved at low anode potentials should be recombined to H_2O at cathode
  - In AC micropores H is trapped, combines to H_2, decreases available surface for DL capacitance
  - When DOD is limited, capacitance decreases (until H is oxidized in a deeper DOD cycle)
  - Above right shows AC capacitance decrease of 12% over 200 cycles to ½ DOD, 20mV/s

Technical Accomplishments: Anode (2)

- Alternate carbons (purchased aerogel and carbide derived)
  - Density increase from .5 to .75 increases electrode volumetric capacitance 50%
  - But still a device cost driver at $50-100/kg and H trapping remains (carbide derived C)
- Ionova mesoporous aerogel-derived carbon
  - Decrease cost to ~$15/kg
  - Excellent rate, capacitance 165F/g @ 1.67A/g, target 180F/g and 140F/cm^3 (0.77g/cm^3)
  - Good performance to –1.1V vs. Ag/AgCl enables 2.1V cell
  - No micropores to trap evolved nascent H means no capacitance degradation @partial DOD



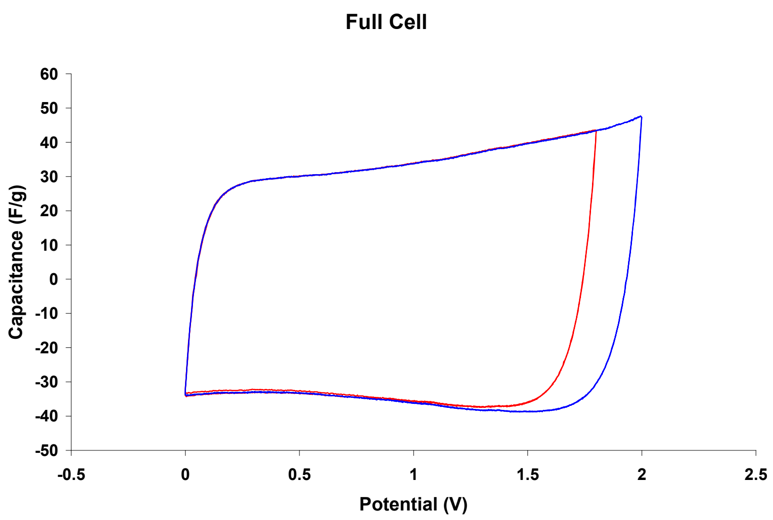
Technical Accomplishments: Electrolyte

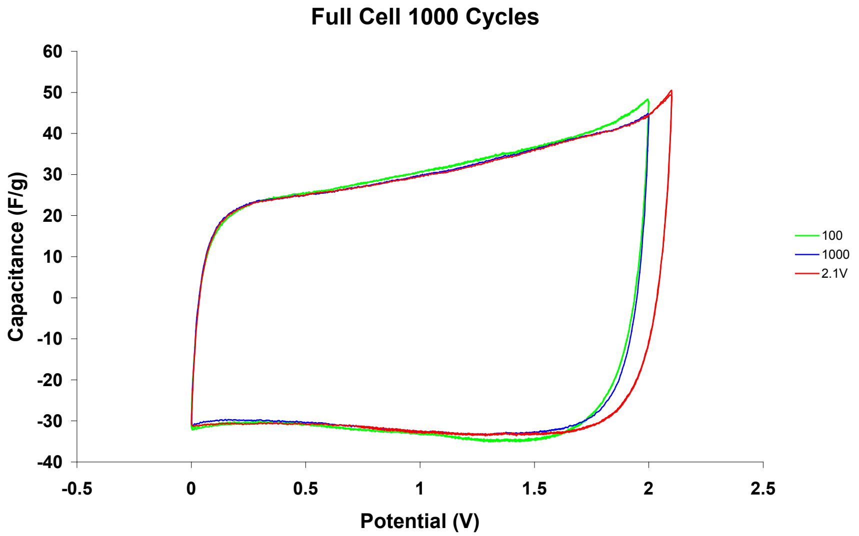
- Neutral electrolytes pursued for widest possible voltage window (V^2 energy advantage)
- Electrolyte salts investigated
  - Nitrates and/or sulfates of lithium, sodium, potassium, magnesium and calcium
- Performance findings
  - Highest rate (related to ionic conductivity, concentration and hydration energy)
  - Highest capacitance (related to ionic radius, concentration)
  - Potential at which max capacitance occurs
  - Low temperature solubility
  - OER/HER potentials vs. pH
- Manufacturing implications
  - Na, K possible low-cost alternatives to Li (2x, 4x lower respectively)
  - Bivalent cations Ca and Mg too slow, AC capacitance and 3DN potentials not ideal
  - Li cost impact of anticipated changes in supply/demand
- Other considerations
  - Use of Li-based electrolytes enables redox functionality in spinel phase cathode

- Bottom line
  - Electrolytes selected for devices using layered and for spinel cathode materials

Technical Accomplishments: Cell (1)

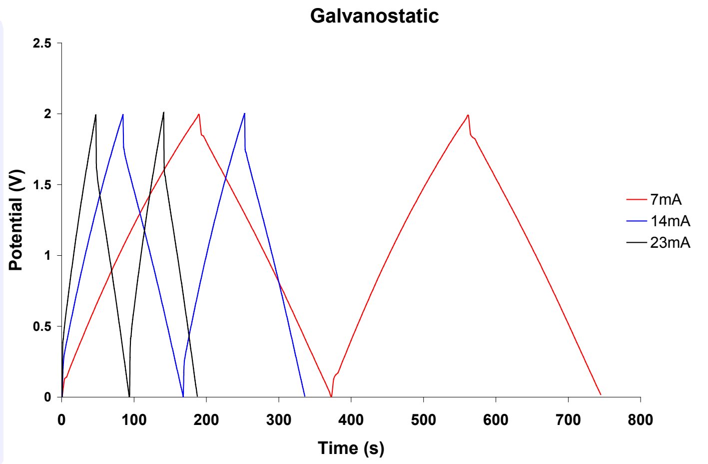
- Preliminary 1000 cycles (pouch cell right)
  - Voltage range 700 cycles at 0-2V, 300 cycles at 0-2.1V (below right)
  - Capacitance constant (<0.5% change) and ESR improvement
  - 0-1.8V tracks 2V cycle (below left)
- Model of packaged 10 cell module, full DOD using our data
  - 10Wh/kg, 15.5Wh/L (MWV)
  - 10.5Wh/kg, 18Wh/L (new anode)
- Due to limitations of power electronics, half voltage is usable (~75% energy)

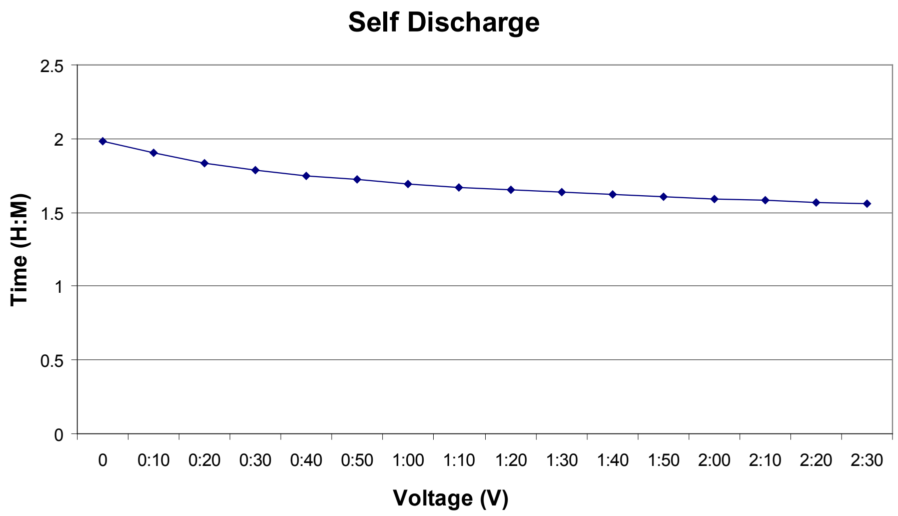


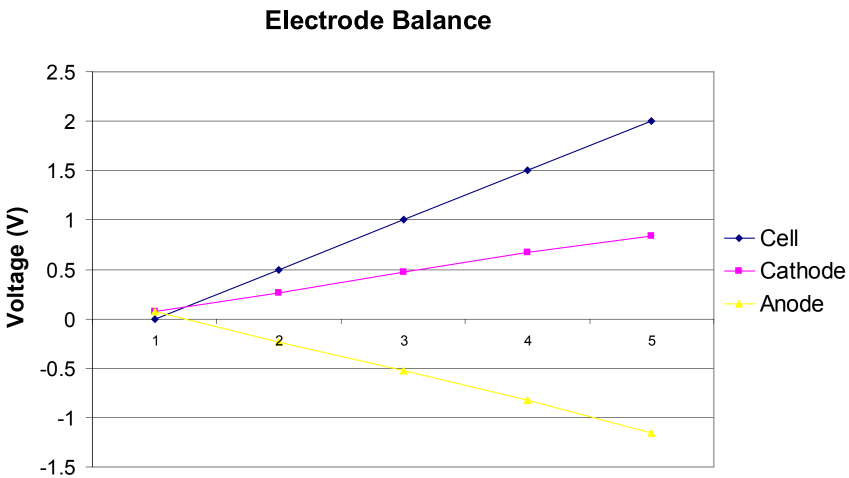


Technical Accomplishments: Cell (2)

- 23mA (right) correlates to 1kW/kg and 1.7kW/L (packaged cell)
  - IR drop ~20ohms (obtained similar value at current collector I/F)
- Electrode balance below right is 1.6:1
  - Cathode 760mV swing to 840mV vs. Ag/AgCl
  - Anode 1.24V swing to –1.16V vs. Ag/AgCl
- Self discharge (from 2V)
  - 22% over 2.5hrs
  - 2.8%/hr at 2.5hrs







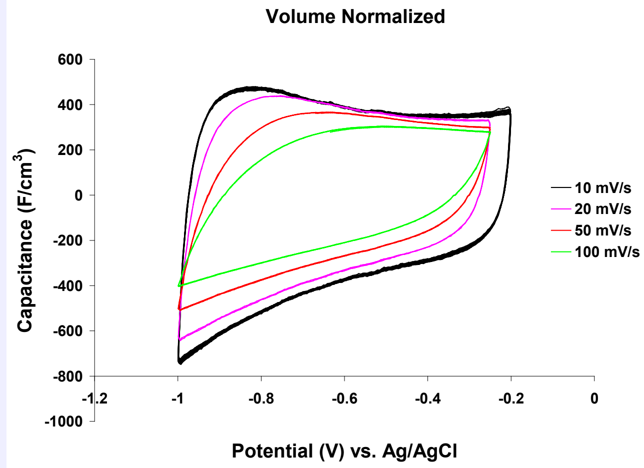
Future Work (Proposed)

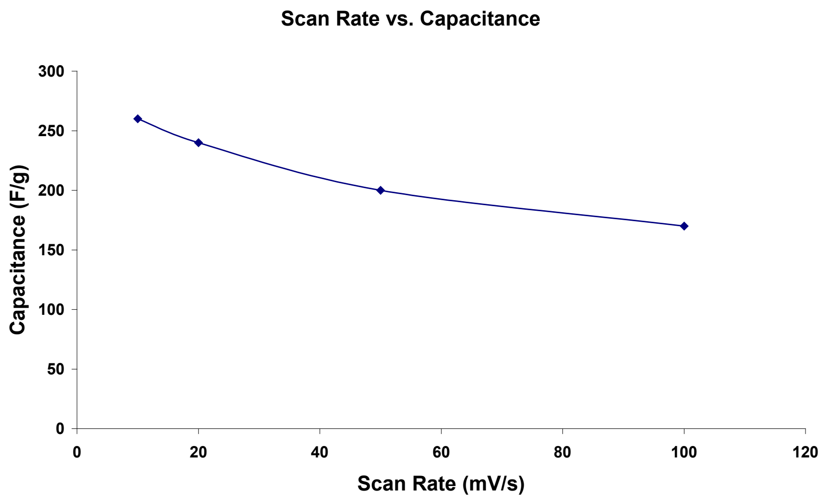
Task	Component	Details
Matl's Optimization	Cathode Carbon	features, aerogel/support ratio
	Cathode Oxide	spinel
	Anode Carbon	increase density, power, reduce cost
Cell Design	Current Collectors	stability, strength, density, conductivity, cost
	Electrode Adhesive	stability, **conductivity**, manufacturability
	Separator	polypropylene vs. glass fiber
Cell Package Design	W/Yardney	design, fabricate and characterize for ESR, EIS, voltage/capacitance vs. rate, cycle life
Bipolar Stack Proof	W/Nilar	fabricate and characterize per cell
USABC Testing		per protocol

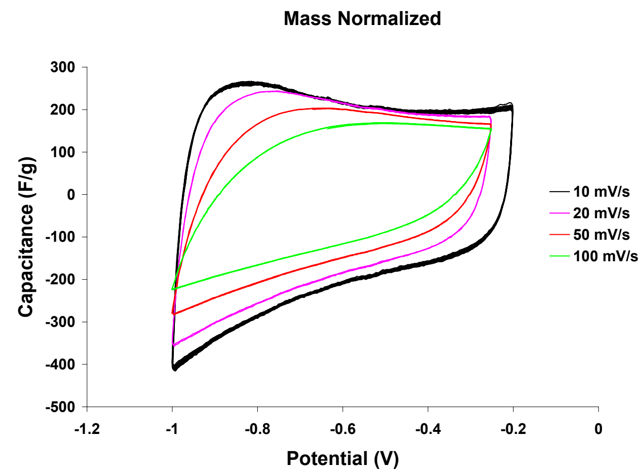
Future Work (Related)

Pseudocapacitive Alternate To AC Anode*

- Potential to increase volumetric energy to ca. **30Wh/L**
- Useful above 10A/g may enable ca. **5KW/kg, 10KW/L**
- ~500% increase in volumetric capacitance
- ~50% increase in gravimetric capacitance
- Appears to be H^+ insertion
- Preliminary data shows no degradation (150 cycles tested)
- Permit 2.2V cell used with 3DN or carbon cathode







* Beyond project scope but prospective product enhancement; proposal currently pending.

Summary

- Objectives are achievable with carbon anode
  - Simple multi-cell module
  - 5x energy improvement vs. EDLC
    - 2.1V cell, 18Wh/L
  - 10x cost improvement
    - $10/kg 3DN cathode
    - $15/kg new anode
    - Low cost electrolyte and manufacturing
  - Safe, environmentally benign materials
- Improvements possible with pseudocapacitive anode
  - ~30Wh/L, 15Wh/kg
  - Li-Ion capacitor energy with but much lower cost
- Work continues
  - Current collector is major focus