3-D Nanofilm
Asymmetric Ultracapacitor

Annual Merit Review, DOE Vehicle Technologies Program

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Ionova Technologies, Inc.

May 16, 2012

Project ID: ES141
## 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
- Long Cycle Life
- Low Temp Operation
- Charge Acceptance/Delivery (Ch. Sustaining)
- Last The Full Life Of The Vehicle
- Broad Market Geography

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

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#### System Attributes

<table>
<thead>
<tr>
<th>Discharge Power</th>
<th>12V Start-Stop</th>
<th>42V Start-Stop</th>
<th>42V Transient Power Assist (TPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 kW</td>
<td>60 Wh</td>
<td>30 Wh</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cold Cranking Pulse @ -36°C</th>
<th>4.2 kW</th>
<th>7 V Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Available Energy (CP @ VDC)</td>
<td>15 Wh</td>
<td>30 Wh</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Recharge Rate (kWh)</th>
<th>0.4 kW</th>
<th>2.4 kW</th>
</tr>
</thead>
</table>

| Cycle Life | 750k / 150,000 miles |
| Cycle Life (%) | UC10 |
| Calendar Life (%) | UC10 |
| Energy Efficiency (UC10 Load Profile) (%) | 10% |

| Self Discharge (72hr from Max. V) | 4% |

| Maximum Operating Voltage (Vdc) | 42 V |

| Minimum Operating Voltage (Vdc) | 9 |

| Operating Temp. Range (°C) | -30 to +52 |
| Survival Temp. Range (°C) | -46 to +66 |

| Maximum System Weight (kg) | 10 |

| Maximum System Volume (Liters) | 16 |

| Selling Price (System @ 100k/yr) | 2.17 $/Wh |

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

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

* 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**
- Electric Current

**Feature**
- Single vs. Multi-Step Mfg Process
- Scaleable Small To Large Format Devices
- Lower Inductance/Resistance

**Benefit**
- Reduces System Cost, Increase Reliability*
- Enables New (Large Volume) Applications
- Increase Power Density, Reduce Heat

* Main challenge: seal.
Problem

The use of low-cost, low-toxicity pseudocapacitive materials such as MnO₂ 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.

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

<table>
<thead>
<tr>
<th>Task</th>
<th>Component</th>
<th>Details</th>
<th>% Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Matl’s Optimization</strong></td>
<td>Cathode Carbon</td>
<td>features, aerogel/support ratio</td>
<td>90%</td>
</tr>
<tr>
<td></td>
<td>Cathode Oxide</td>
<td>loading, distribution, phase, ratio</td>
<td>90%</td>
</tr>
<tr>
<td></td>
<td>Anode Carbon</td>
<td>increase density, power, reduce cost</td>
<td>80%</td>
</tr>
<tr>
<td></td>
<td>Electrolyte</td>
<td>rate, stability, capacitance, temperature potential window</td>
<td>90%</td>
</tr>
<tr>
<td><strong>Synth. Optimization</strong></td>
<td>Cathode Carbon</td>
<td>precursors, processing time</td>
<td>90%</td>
</tr>
<tr>
<td></td>
<td>Cathode Oxide</td>
<td>processing time vs. phase/distribution</td>
<td>90%</td>
</tr>
<tr>
<td><strong>Cell Design</strong></td>
<td>Model</td>
<td>capacitance, voltage, energy density, power</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>Electrodes</td>
<td>density, electrode balance, electrolyte conc., inactive components/packaging</td>
<td>80%</td>
</tr>
<tr>
<td></td>
<td>Electrolyte</td>
<td>from model</td>
<td>80%</td>
</tr>
<tr>
<td></td>
<td>Current Collectors</td>
<td>stability, strength, density, conductivity, cost</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>Electrode Adhesive</td>
<td>stability, conductivity, manufacturability</td>
<td>80%</td>
</tr>
<tr>
<td></td>
<td>Separator</td>
<td>polypropylene vs. glass fiber</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>Pouch</td>
<td>pouch material, sealer and tab seal</td>
<td>100%</td>
</tr>
<tr>
<td><strong>Cell Package Design</strong></td>
<td>W/Yardney</td>
<td>design, fabricate and characterize for ESR, EIS, voltage/capacitance vs. rate, cycle life</td>
<td>10%</td>
</tr>
<tr>
<td><strong>Bipolar Stack Proof</strong></td>
<td>W/Nilar</td>
<td>fabricate and characterize per cell</td>
<td>10%</td>
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<tr>
<td><strong>USABC Testing</strong></td>
<td></td>
<td>per protocol</td>
<td>0%</td>
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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, 2.25cm³/g, no micropores)
- Surface area from 400-800m²/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

![AC Anode Graph]

- 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 H₂O at cathode
  - In AC micropores H is trapped, combines to H₂, 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 ~$15/kg
  - Excellent rate, capacitance 165F/g @ 1.67A/g, target 180F/g and 140F/cm³ (0.77g/cm³)
  - Good performance to -1.1V vs. Ag/AgCl enables 2.1V cell
  - No micropores to trap evolved nascent H means no capacitance degradation @partial DOD
Neutral electrolytes pursued for widest possible voltage window ($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
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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