NEW APPROACHES TO INCREASE ULTRACAPACITOR ENERGY, POWER AND EFFICIENCY

EESAT, October 11-13, 2017
NEED FOR ENERGY STORAGE AND HARVESTING

- No electric vehicles possible without storage
- No CO₂ emission reduction possible without hybridizing ICE
- No renewables possible without storage
- No smart grids possible without storage
CHALLENGES FOR BATTERIES – OPPORTUNITY FOR ULTRACAPACITORS

- Low charge / discharge rate (not quick enough for frequency regulation in grids, slow charge of EV battery)
- Safety concerns (fire hazard)
- Short lifetime (expensive to change)
- Low and high temperatures intolerance
- Low efficiency (heat generation requires expensive thermal management systems)
BATTERY vs ULTRACAPACITOR

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>BATTERY</th>
<th>ULTRACAPACITOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Density</td>
<td>&gt;100Wh/kg</td>
<td>&lt;10Wh/kg</td>
</tr>
<tr>
<td>Power Density</td>
<td>1kW/kg</td>
<td>10kW/kg</td>
</tr>
<tr>
<td>Efficiency</td>
<td>~80%</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>Cyclability</td>
<td>400 – 2500</td>
<td>1,000,000</td>
</tr>
<tr>
<td>Calendar life</td>
<td>Short (4.6 years)</td>
<td>Long (15+ years)</td>
</tr>
<tr>
<td>Low Temperature</td>
<td>-20°C</td>
<td>-40°C</td>
</tr>
<tr>
<td>High Temperature</td>
<td>+60°C</td>
<td>+85°C</td>
</tr>
<tr>
<td>Death</td>
<td>Sudden</td>
<td>Predictable</td>
</tr>
<tr>
<td>Principle</td>
<td>Electrochemical</td>
<td>Electrostatic</td>
</tr>
<tr>
<td>Cost</td>
<td>0.07 - 0.2 $/kWh/cycle</td>
<td>$0.006 $/kWh/cycle</td>
</tr>
</tbody>
</table>

Ultracapacitors are all about power, unlimited cycling, safety and predictable life. Ultracapacitors are less expensive than batteries for frequent cycling applications.
ULTRACAPACITOR PRINCIPLE AND BASIC DESIGN

Ultracapacitor (UC) comprises two electrodes soaked in electrolyte. UC stores energy due to charge separation in the electric double layer of about 1 nm thick that forms at the electrode-electrolyte interface when the potential is applied.

UC electrodes are made of nano-structured carbon applied on aluminum foil as a current collector. The electrodes are interleaved with an insulating porous film, impregnated with electrolyte and sealed in a cylindrical or prismatic case.
MAIN APPLICATIONS

- Start / stop systems for cars
- Energy recovery in hybrid cars
- Light trains
- Wind and solar power
- Large engine (diesel) cold cranking
- Frequency and peak shaving in electrical grids
- Emergency backup power
- Aerospace applications (“more electric aircraft”)
- Military applications
ULTRACAPACITORS IN GRIDS

- Peak shaving

Without ultracapacitor

Example of input wave

Output wave is not fixed

With ultracapacitor (UC)

Charge energy

Discharge energy

UC energy wave type

Output wave is higher and fixed
MOST IMPORTANT METRICS FOR ENERGY STORAGE

- **ENERGY** – “how far we can drive”. Practically no difference in energy density among ultracapacitor manufacturers. Lots of hype around graphene, but no actual applications in energy storage.

- **POWER / EFFICIENCY** – how fast we can use the energy and how much energy we lose due to non-ideal system.

- **COST** – Units: $/Wh/cycle or better “cost of ownership”.

- **SAFETY** – no issues for ultracapacitors or hybrid devices.
WHY LOW INNER RESISTANCE (ESR) IS OUR MANTRA?

- Low ESR results in high power density: $P \sim 1/R$
  (hence, less UC mass $\rightarrow$ lower cost)

- Low ESR results in small voltage drop: $\Delta U \sim R$
  (since $P$ and $E \sim U^2$, less UC cells can provide the power and energy needed $\rightarrow$ lower cost)

- Low ESR results in low heat generation: $Q \sim R$
  (hence, no active cooling is needed $\rightarrow$ safety and low cost)
Total resistance of ultracapacitor

\[ R_{in} = R_1 + R_2 + R_3 + R_4 + R_5, \]

ULTRACAPACITOR (UC) resistivity \((in \ \Omega cm^2)\)

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>(~0.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R_1+R_2</td>
<td>(~0.01)</td>
</tr>
<tr>
<td></td>
<td>R_3</td>
<td>(~0.05)</td>
</tr>
</tbody>
</table>

Thus: \( R_4 + R_5 \) \(~0.64\)

Though: \( R_5 \) \(~0.14\)

\( R_4 \) “in-pore resistance” \(~0.5\)

UC resistance is mostly due to low electrolyte mobility in nanopores
ELECTROLYTE IN-PORE MOBILITY CAN BE MEASURED

Typical plot of ultracapacitor resistivity vs electrolyte in-pore mobility:

$D_{\text{eff}}, \text{m}^2\text{s}^{-1}$

$R_{UC}, \text{Ohm}\cdot\text{cm}^2$

Carbon with highest cation mobility can be selected for negative electrode, and that with highest anion mobility can be selected for positive electrode.

Typical plot of ultracapacitor resistivity vs electrolyte in-pore mobility:

$D$ measured by NMR “Pulse Gradient Stimulated Echo” method or CV “Rotatory Disc Electrode” method

US Pat. 9524830 publ. 2016
Low inner resistance:
- 2 times more energy under high load;
- high power density that can not be reached by other ultracapacitors.
LOW INNER RESISTANCE (ESR) INCREASES EFFICIENCY
(as tested by Dr. Dennis Corrigan, Wayne State Univ., Detroit, 2014)

<table>
<thead>
<tr>
<th>Company</th>
<th>Mass, kg</th>
<th>Capacitance, F</th>
<th>Voltage, V</th>
<th>ESR, mΩ</th>
<th>Eff.% @ CP* 10 s discharge</th>
<th>Eff. % @ CP* 5 s discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell Tech.</td>
<td>0.26</td>
<td>1200</td>
<td>2.7</td>
<td>0.50</td>
<td>95.6</td>
<td>92.0</td>
</tr>
<tr>
<td>Ioxus</td>
<td>0.29</td>
<td>1200</td>
<td>2.7</td>
<td>0.40</td>
<td>96.7</td>
<td>93.9</td>
</tr>
<tr>
<td>Yunasko</td>
<td>0.25</td>
<td>1200</td>
<td>2.7</td>
<td>0.09</td>
<td>99.2</td>
<td>98.3</td>
</tr>
<tr>
<td>Yunasko</td>
<td>2.5</td>
<td>200</td>
<td>16</td>
<td>1.07</td>
<td>98.5</td>
<td>97.2</td>
</tr>
</tbody>
</table>

*CP – constant power

Low resistance results in 3… 5 times less heat generation
BATTERY vs ULTRACAPACITOR

HOW TO CREATE A MÉLANGE OF LARGE ENERGY AND HIGH POWER?
Effect of low inner resistance of Yunasko ultracapacitor module (A) as compared with the best competing devices (B):

1 – current flowing through battery; 2 – current flowing through ultracapacitor; 3 – total current

Yunasko UC effectively unloads the battery and enhances total current
TYPES OF CAPACITOR SYSTEMS

EDLC
(C-C supercapacitor, ultracapacitor)

Asymmetric hybrid
(internal serial, LIC)

Symmetric hybrid
(parallel LIC (\//LIC) or enhanced LIB)
PARALLEL HYBRID SOLUTION

OUR APPROACH: electrode level hybridization - both positive and negative electrodes comprise Li-ion and activated carbon components with thoroughly matched potential ranges: “parallel hybrid” //LIC, patent pending

RESULT: energy storage system with battery-type charge-discharge curve and energy density up to 40 Wh/kg (also confirmed by tests in ITS, Davis, USA and VW Group, Germany)
PARALLEL HYBRID: SIMPLE MODEL

Nanoporous carbon particles loosen oxide particles spatially while connecting them electrically. This results in:

- oxide particles become more accessible to electrolyte, and nanoporous carbon provides a reservoir of electrolyte;
- fast discharge of nanoporous carbon particles is then accompanied and supported by discharging the intercalated oxide particles.

**General result:** large energy density along with low inner resistance and high power density.
HYBRIDIZATION RESULTS

<table>
<thead>
<tr>
<th></th>
<th>HIGH POWER Li-ion</th>
<th>ULTRACAPACITOR</th>
<th>YUNASKO //LIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power, kW/kg</td>
<td>1…3</td>
<td>10…50</td>
<td>3…5</td>
</tr>
<tr>
<td>Energy, Wh/kg</td>
<td>60…100</td>
<td>5…7</td>
<td>30…40</td>
</tr>
<tr>
<td>Charge / discharge time</td>
<td>15…90 minutes</td>
<td>10…30 seconds</td>
<td>2…3 minutes</td>
</tr>
<tr>
<td>Cycle life</td>
<td>&lt;10,000</td>
<td>&gt;1,000,000</td>
<td>&gt;30,000</td>
</tr>
<tr>
<td>Temperature window</td>
<td>-20 °C…+60 °C</td>
<td>-40 °C…+85 °C</td>
<td>-40 °C…+60 °C</td>
</tr>
</tbody>
</table>
TECHNOLOGY COMPARISON

We can charge energy of lead-acid battery within 2-3 minutes and discharge up to 150C* rate with efficiency >80%

* NOTE: C-Rate is a measure of the rate (time or current) at which a battery is charged or discharged relative to the capacity of the battery. A 1C rate means that the discharge current will discharge the entire battery in 1 hour.
SAFETY OF PARALLEL HYBRID

Nail penetration test

No fire or thermal runaway
CONCLUSIONS

1. The ultracapacitor power output and efficiency are due to its low internal resistance, which in its turn is mostly determined by the electrolyte mobility in carbon electrode nanopores.

2. A new approach with both positive and negative electrodes being hybridized (///LIC) gives a chance to increase the ultracapacitor energy density up to 30-40 Wh/kg while maintaining the power output of 3-5 kW/kg at the efficiency above 80%.

3. Ultracapacitors are most efficient if the high power pulses of short duration (from fractions of a second to ca. 20 seconds) are needed, while longer pulses (from 20 s to 10 min) can be best covered by ///LIC devices.
# YUNASKO BACKGROUND AND DOMAIN

<table>
<thead>
<tr>
<th>COMPANY</th>
<th>MANUFACTURING</th>
<th>PRODUCT</th>
<th>TECHNOLOGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Founded in 2010, in energy storage projects since 1989</td>
<td>Pilot plant in the West of Ukraine</td>
<td>Ultra high power heavy duty ultracapacitor cells from 200F to 3,000F. 3-5 times more power than competitors.</td>
<td>Carbon / carbon ultracapacitors and lithium–ion capacitors with organic electrolytes and proprietary design</td>
</tr>
<tr>
<td>51 employees, 17 of them in R&amp;D and Design Bureau (7 PhD level)</td>
<td>Ready to build large scale manufacture with the capacity over 4 million large cells / year</td>
<td>16V, 48V or 90V stacks and module building blocks</td>
<td>Proprietary dry electrode manufacture technology</td>
</tr>
<tr>
<td>Ukraine: R&amp;D, Design Bureau and Pilot Plant</td>
<td></td>
<td>Lithium capacitors with high energy (up to 40 Wh/kg) and power (up to 5 kW/kg)</td>
<td>Power fusion treatment of current collector foil</td>
</tr>
<tr>
<td>London: financial and IP harbour</td>
<td></td>
<td>High temperature ultracapacitors with -25°C…+110°C operating temperature range</td>
<td>8 patents granted and 8 patent applications filled</td>
</tr>
<tr>
<td>Registering company in the US</td>
<td></td>
<td></td>
<td>Commercially available, low cost components only</td>
</tr>
</tbody>
</table>
YUNASKO TRACTION

Materials performance: simplest lithium capacitor built to show performance

Prototype performance: large cells (>1 Wh) that maps to modules

Device performance: pilot plant production rate reached 200 large cells/year with yield over 90%

2010-2012

Product performance: lithium capacitors cells sold and tested by the customers

2015-2016

Device performance: pilot plant production rate reached 200 large cells/year with yield over 90%

2012-2014

Product performance: lithium capacitors cells sold and tested by the customers

2015-2016

Unit economics: large scale production

2017

Test results verified by independent experts:
Institute of Transportation Studies, Davis, USA; Wayne State University, Detroit, USA; JME, Cleveland, USA.

and customers:

(reports available upon request)

Seeking for an investor or a strategic partner in the US

STEPS COMPLETED

2010

2010

2010-2012

2012-2014

2015-2016

2017
Dr. Natalia Stryzhakova, Laboratory Head: over 25 year experience of research in the field of ultracapacitors. Co-author in 60+ scientific papers and a co-inventor of over 15 patents.

Dr. Yurii Maletin, Chief Scientist: over 25 year experience of research in the field of ultracapacitors, 30+ patents, 80+ papers. Yurii is responsible for IP and R&D activities.

Dr. Dmitriy Tretyakov, Senior Researcher: 14 year experience of research in the energy storage area, a co-author of 40+ scientific papers.

Dr. Sergii Tychina, New Business Development Manager. Master degree from the National Technical University of Ukraine, PhD in Physical Chemistry from the National Academy of Science of Ukraine.

Vitaliy Shuster, Pilot Factory Manager. Master Degree in Electronic Engineering from Lviv Polytechnic Institute, 35+ year experience in development and production of capacitors.

Vadim Utkin, CEO. Master degree in engineering from the National Technical University of Ukraine ‘Kyiv Polytechnic Institute’. Executive MBA graduated.