Power for Pulse Power Applications

Purdue University
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Topics to be Covered

- **Current Primary and Rechargeable Batteries**
- **New Pulse Power Needs**
- **Capacitors and Ultracapacitors**
- **New Hybrid Systems**

CURRENT PRIMARY AND RECHARGEABLE BATTERIES

Primary Batteries

Maximizing safe energy densities

High rate performance

Digital cameras, etc.

Types	***Wh/kg***
Zn-Alkaline	**50-100**
Li-SO_2	**175-250**
Li-$SOCl_2$	**250-350**
Li-MnO_2	**300-350**
Li-CFx	**400-500**
Zn-Air	**300-350**
Li-Air (future)	**600+**

What other types of primary batteries are used in military Applications ?

Military Primary Batteries

Applications and Types

Use	*Type*	*System*	*Wh/kg*
Missiles	**Thermal**	**$Li-FeS_2$**	**40**
Sonobuoys	**Water Act.**	**Mg-AgCl**	**150**
Torpedoes	**Same**	**Mg-AgCl**	**150**
Life Vests	**Same**	**$Mg-Cu_2Cl_2$**	**80**
Torpedoes	**NaOH**	**Al-AgO**	**160**
Sensors	**Long-life**	**Zn-Air**	**270**

Military Primary Batteries

-- **What is on the Horizon - 1**

-- **Higher energy density primary batteries**

- **Zn-Air**

  300+ Wh/kg energy density, but rate and temperature limitations

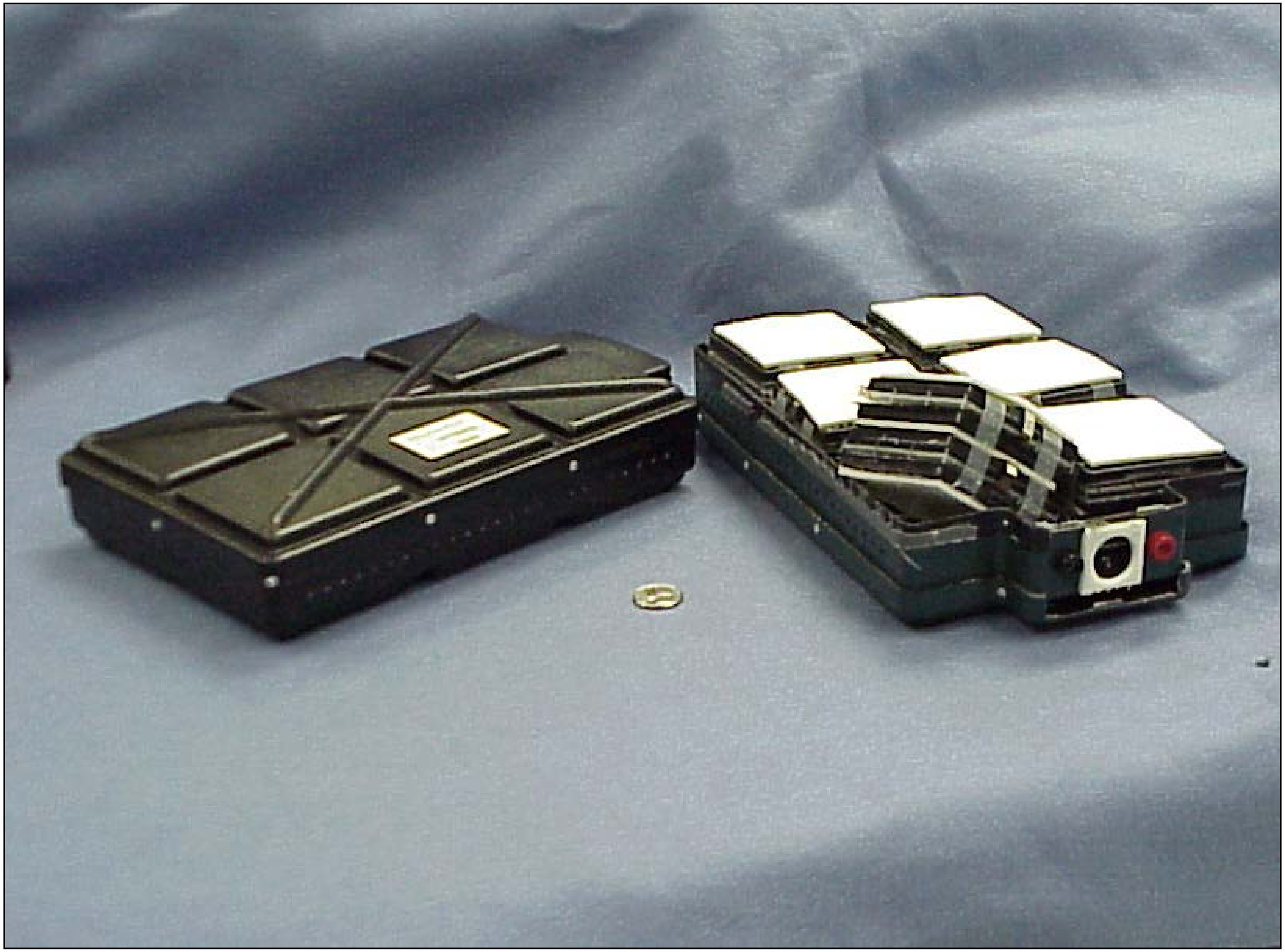
- **Li-CFx**

  500-600 Wh/kg, but poor low temperature performance

  Mixtures with MnO_2

Zinc-Air Power Source   BA-8180/U

800 Wh, 2.3 kg, Recharge batteries or power ASIP radio



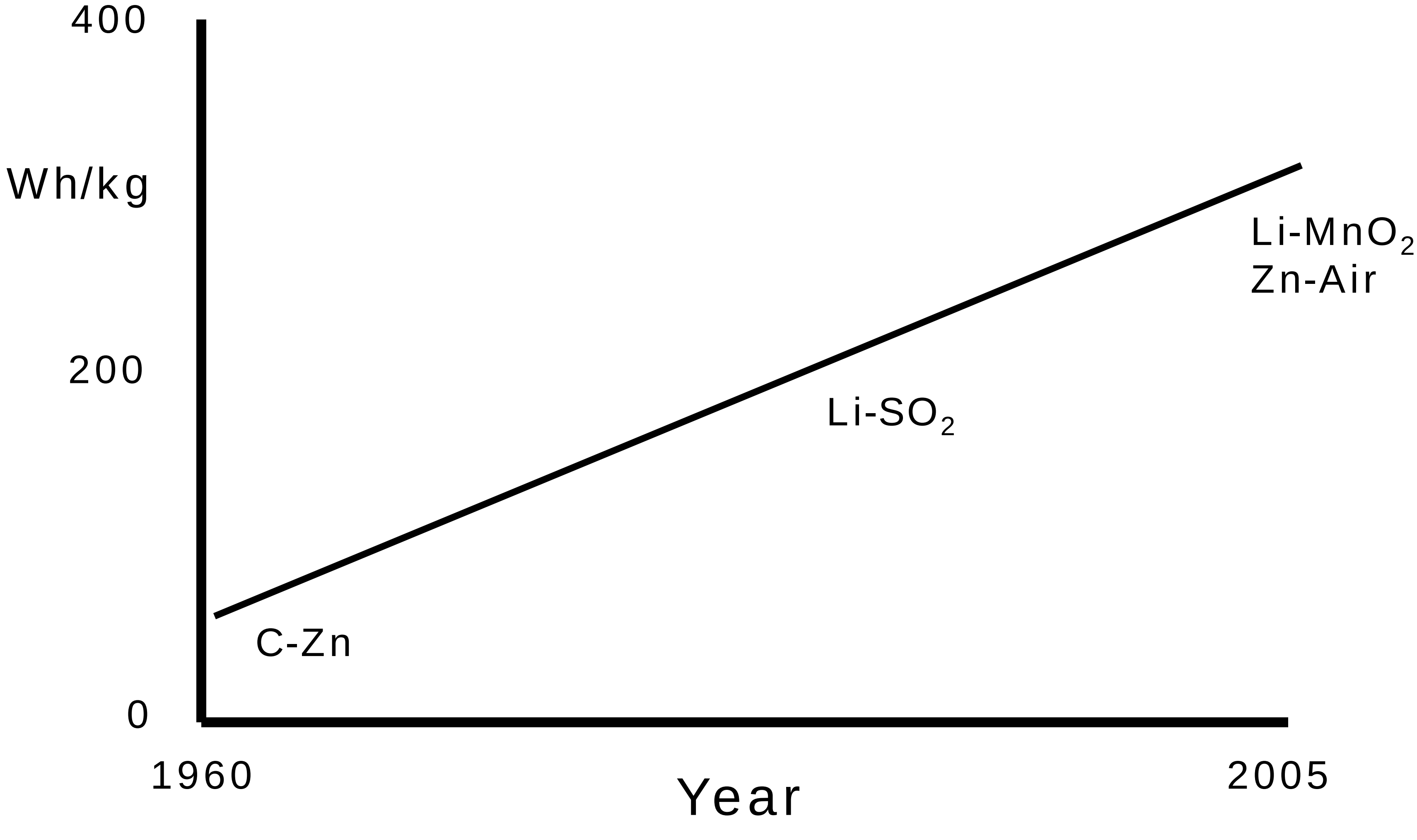
Military Primary Batteries

-- <u>What is on the Horizon - 2</u>

- ***<u>Li-Air</u>***
  Potential for 600+ Wh/kg
  Suited for low rate applications
- ***<u>Li-Water</u>***
  Potential for 1000 Wh/kg
  Ideally suited for low rate applications in the ocean
- ***<u>What primary battery was a focus of the DOE Electric Vehicle program in the 1980's?</u>***


New!
COMPLETELY DIFFERENT SCIENCE KIT
Aluminum + Air + Saltwater → Electricity
ALUPOWER
Aluminum-Air Power Cell Kit
IMAGINE!
Create Electrical Energy From Aluminum + Air + Saltwater
The ALUMINUM-AIR POWER CELL KIT is easy to assemble and safe to use. It teaches the principles of electrochemistry through a series of simple experiments using illustrated, educational instructions. Additional experiments are proposed to challenge the user's creative imagination.
Aluminum-Air Power Cell Kit
IMAGINE! Create Electrical Energy From Aluminum + Air + Saltwater

PRIMARY BATTERY PROGRESSION



Rechargeable Batteries

Maximize safe energy densities

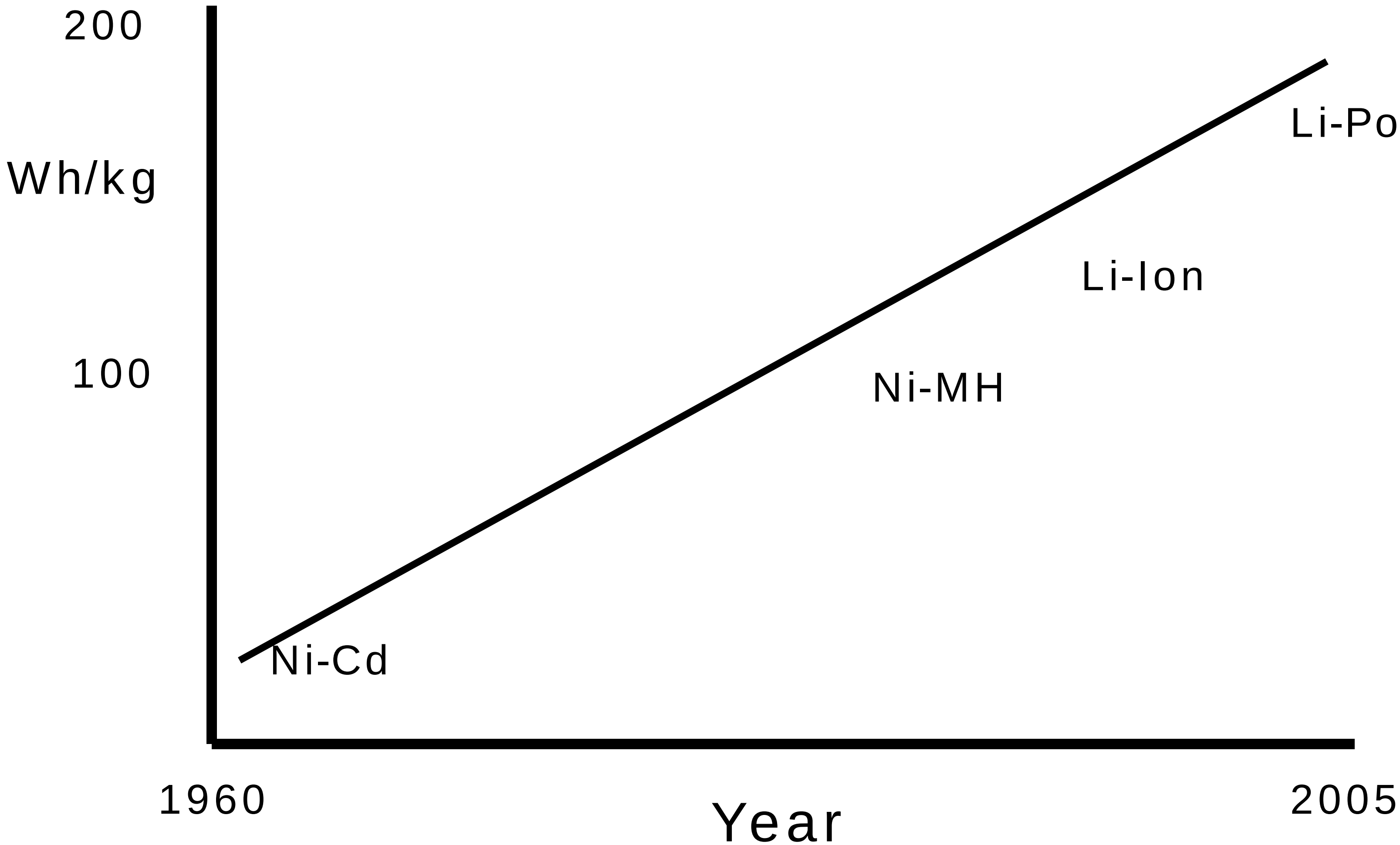
High rate performance

Electric vehicles, Power tools

Types	Wh/kg
Ni-Cd	30
Ni-MH	60
Ni-Zn	60-70
Ag-Zn	60-100
Li-Ion - CoO_2	100-120
Li-Ion polymer	150-200
Li-Fe Phosphate	70-80

FAMILY OF RECHARGEABLE BATTERIES

RECHARGEABLE BATTERY PROGRESSION



<u>What causes batteries to become explosive?</u>

Failure Modes in Li-Rechargeable Batteries

-- ***When energy density exceeds about 300 wh/kg*****, batteries can become inherently explosive, depending on volume. In addition, electrolytes are generally flammable.**

-- ***Most accidents occur on charging***

- **Fire in Swimmer Deliver Vehicle battery in Hawaii**
- **Fire at Ft. Monmouth re fuel cell recharging system**

Relative Energy Densities

Batteries and Explosive Materials

Material	Wh/kg
Ag-Zn battery	130
Li-Ion	130-200
Li-MnO_2 Battery	220-290
Li-S Battery	530
NH_4NO_3	390
TNT	1300

What happened with Samsung batteries?

Areas for Futue Emphasis

Primary batteries

-- Li - FeS_2

-- Li - Air

-- Li - Water

Rechargeable Batteries

-- Li – S

-- High voltage cathodes and electrolytes

New Techologies

-- Ionic liquids

-- Graphene

Start-Up Considerations

- ***What is unique technology?***
- ***Potential markets, product volume goals***
- ***Where to obtain financing***

  Angel investors, Venture capital

  Friends
- ***WHAT ARE EXPECTATIONS OF INVESTORS?***
- ***Management***

Manufacturing Considerations

- ***Li-Ion manufacturing in US***
  A123 – New modern large plant now sold
  Dow-Kokam America, also sold

- ***Domestic manufacturing desired by military***
  Should our military depend on foreign batteries?

- ***Simpler manufacturing processes desired***

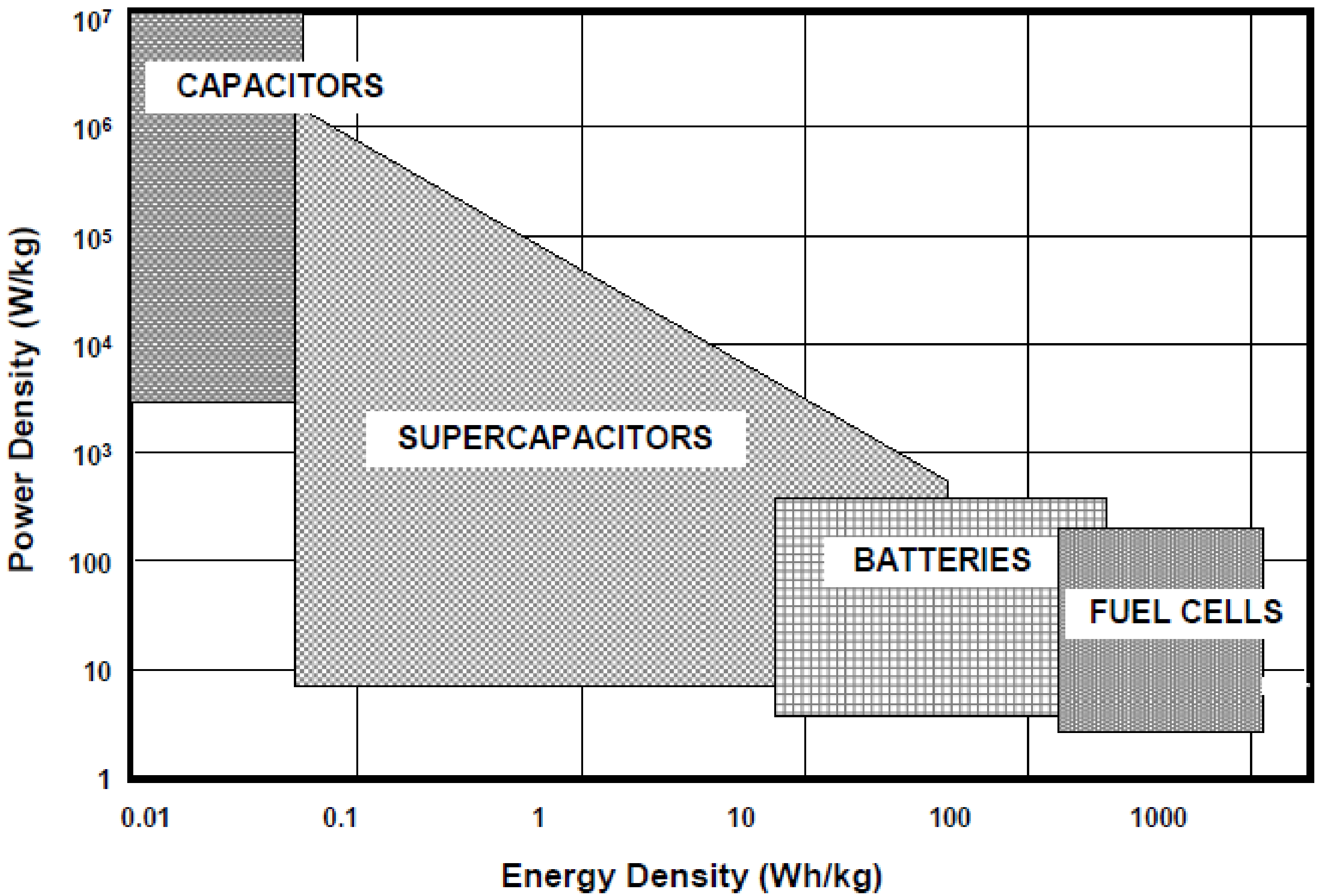
- ***Need domestic source of battery scientists and engineers***

- ***Type of battery is designed in by product manufacturer*, in country where design originates**

ADVANCES IN ELECTROCHEMICAL CAPACITORS AND HYBRIDS

by
Dr. Robert P. Hamlen
Dr. Peter J. Cygan

RAGONE PLOT OF ENERGY STORAGE DEVICES



* R. Kotz and M. Carlen , "Principles and Applications of Electrochemical Capacitors." Electrochimica Acta 45(15-16): 2483-2498,

Marin S. Halper and James C. Ellenbogen, "Supercapacitors: A Brief Overview", March 2006, MITRE Nanosystems

COMPARISON OF PROPERTIES OF SECONDARY BATTERIES AND ELECTROCHEMICAL CAPACITORS

PROPERTY	BATTERY	CAPACITOR
Storage Mechanism	**Chemical**	**Physical**
Power Limitations	**Electrochemical reaction kinetics, active materials conductivity, mass transport**	**Electrolyte conductivity in separator and electrode pores**
Energy Limitation	**Electrode mass (bulk)**	**Electrode surface area**
Output Voltage	**Approximately constant value**	**Sloping value – state of charge known precisely**
Charge Rate	**Reaction kinetics, mass transport**	**Very high, same as discharge rate**
Cycle Life/Life Limitations	**Mechanical stability, chemical reversibility / Thermodynamic stability**	**Side reactions**

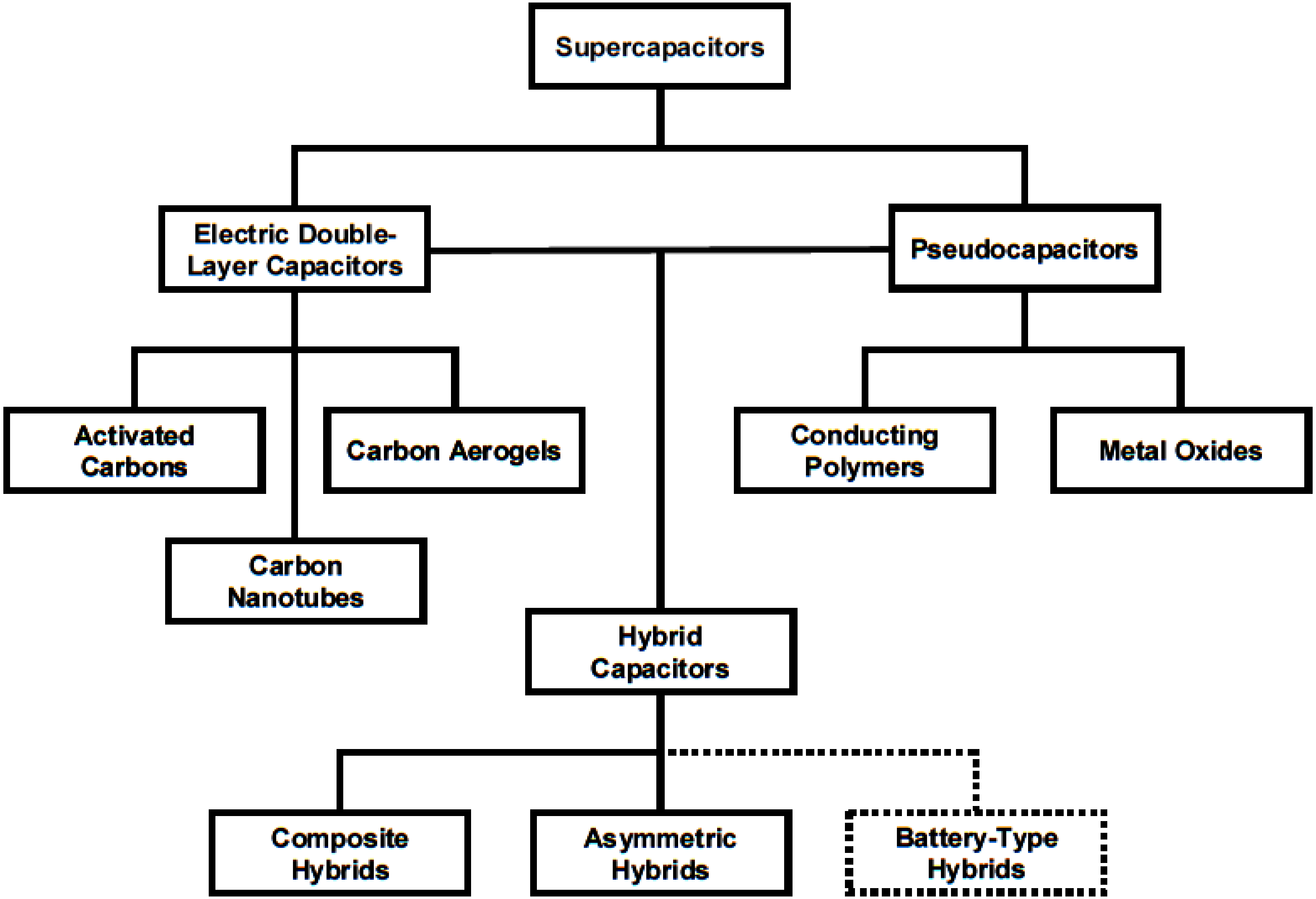
* *John R. Miller and Patrice Simon, "Fundamentals Of Electrochemical Capacitor Design And Operation, The Electrochemical Society Interface, Spring 2008*

PERFORMANCE COMPARISON BETWEEN SUPERCAPACITOR AND LI-ION

Function	Supercapacitor	Lithium-ion (general)
Charge time	**1–10 seconds**	**10–60 minutes**
Cycle life	**1 million or 30,000 h**	**500 and higher**
Cell voltage	**2.3 to 2.75V**	**3.6 to 3.7V**
Specific energy (Wh/kg)	**5 (typical)**	**100–200**
Specific power (W/kg)	**Up to 10,000**	**1,000 to 3,000**
Cost per Wh	**$20 (typical)**	**$0.50-$1.00 (large system)**
Service life (in vehicle)	**10 to 15 years**	**5 to 10 years**
Charge temperature	**–40 to 65 C (–40 to 149 F)**	**0 to 45 C (32 to 113 F)**
Discharge temperature	**–40 to 65 C (–40 to 149 F)**	**–20 to 60 C (–4 to 140 F**

* *Maxwell Technologies, Inc.*

TYPES OF SUPERCAPACITORS



* *Marin S. Halper and James C. Ellenbogen, "Supercapacitors: A Brief Overview", March 2006, MITRE Nanosystems Gro*

CAPACITOR ELECTRODES

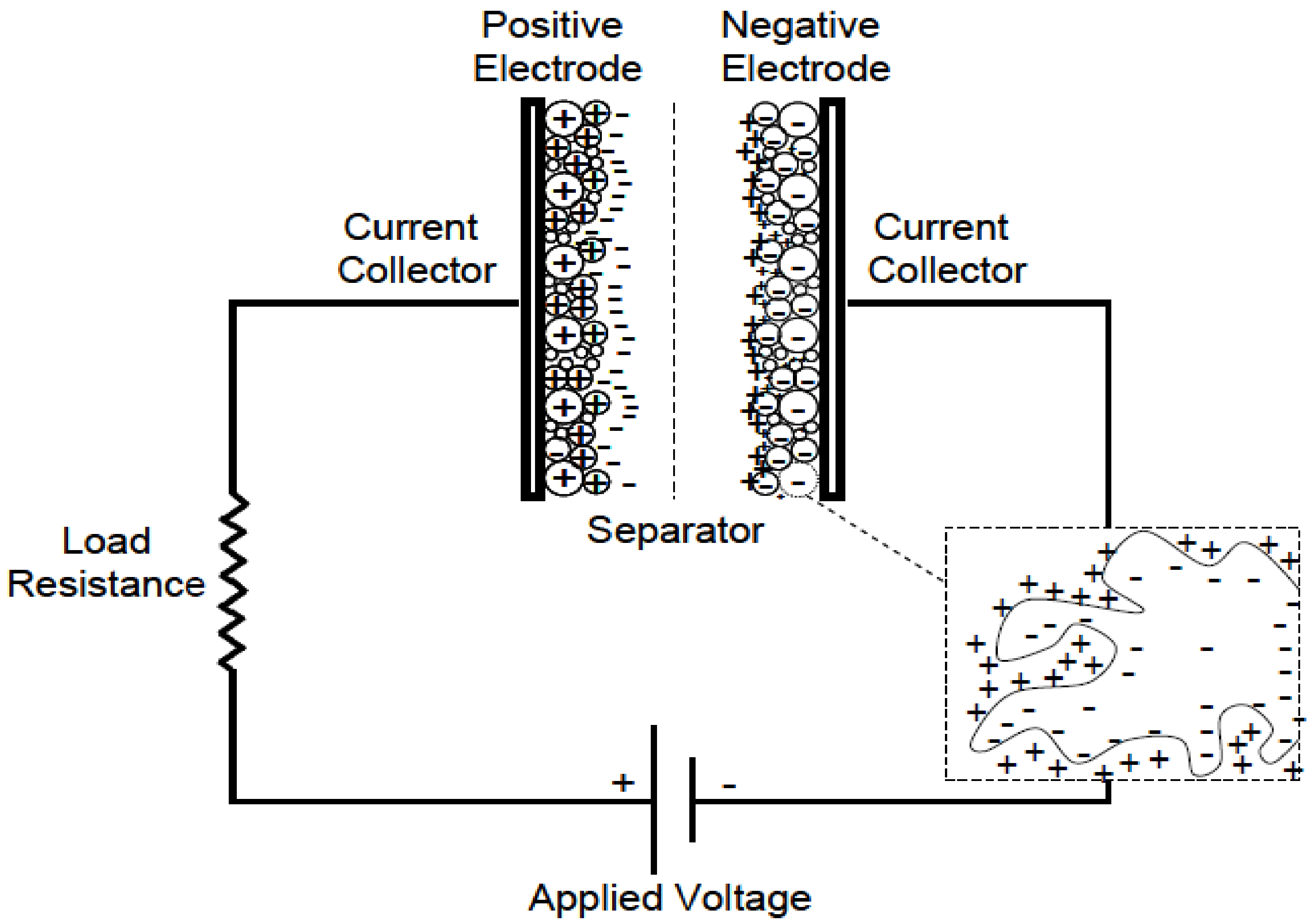
- CAPACITIVE – conventional capacitor - electrostatic electrode
- ELECTRIC DOUBLE LAYER CAPACITOR (EDLC)
- SURFACE FARADAIC REACTIONS
- COMPOSITE: C-based materials + conducting polymers or metal oxides. Physical and chemical storage in same electrode
- FARADAIC – Battery electrode – High capacity, limited cycle life

ELECTROLYTE PROPERTIES

Electrolyte	Density g/cc	Resistivity Ohm-cm	Cell Voltage
KOH	1.29	1.9	1.0
Sulfuric acid	1.2	1.35	1.0
Propylene Carbonate	1.2	52	2.5-3.0
Acetonitrile	0.78	18	2.5-3.0
Ionic liquid	1.3-1.5	125 (25^oC) 28 (100^oC)	4.0 3.25

** A. Burke, "R&D considerations for the performance and application of electrochemical capacitors", Electrochimica Acta 53*

ELECTROCHEMICAL DOUBLE LAYER CAPACITOR



* Marin S. Halper and James C. Ellenbogen, “Supercapacitors: A Brief Overview”, March 2006, MITRE Nanosystems Group

RELATIVE MERITS – ELECTRIC DOUBLE-LAYER CAPACITORS

ADVANTAGES :

- Established technology and markets
- High power

DISADVANTAGES:

- Cost of electrode materials
- Low energy storage capacity

R&D DIRECTION:

- New or improved activated carbons
- Research ionic liquid electrolytes for higher operating voltage
- Lower the cost of precursor carbon electrode materials

MAIN APPLICATIONS FOR ELECTRIC DOUBLE-LAYER CAPACITORS

- TRANSPORTATION – hybrid/electric cars, trucks, buses, diesel and electric trains. Engine starting, capturing breaking energy and providing burst power for rapid acceleration.

- FREQUENCY REGULATION and other power-conditioning grid applications.

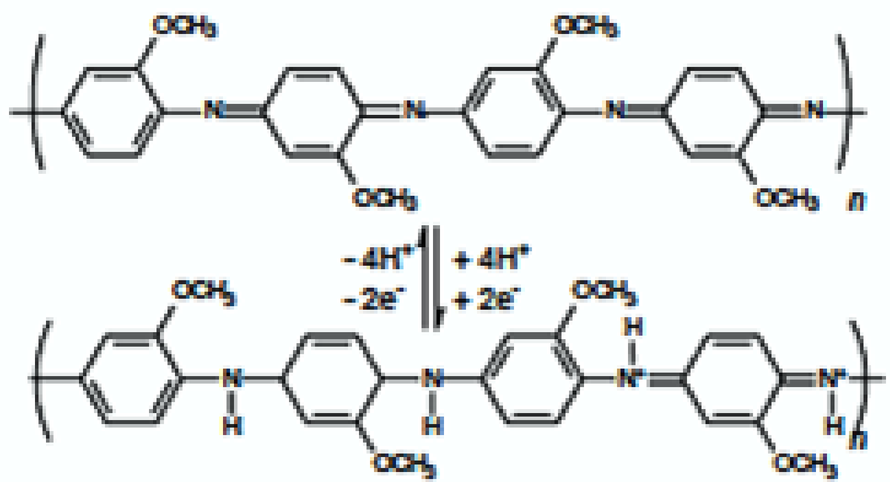
- ENERGY RECAPTURE in industrial applications, including forklifts and cranes.

PSEUDOCAPACITORS

- Electric double layer and thin layer faradaic processes
- Faradaic - chemical reaction - reduction or oxidation (the addition or subtraction of electrons)
- Transition metal oxides or conducting polymers
- Reaction occurs within a nanometer or two of the electrode surface
- higher charge storage capacities than electric double-layer capacitors
- best performing - rare metal oxide (ruthenium) electrode materials - cost prohibitive for mass production

EXAMPLE OF PSEUDOCAPACITIVE CHARGE-STORAGE MECHANISM

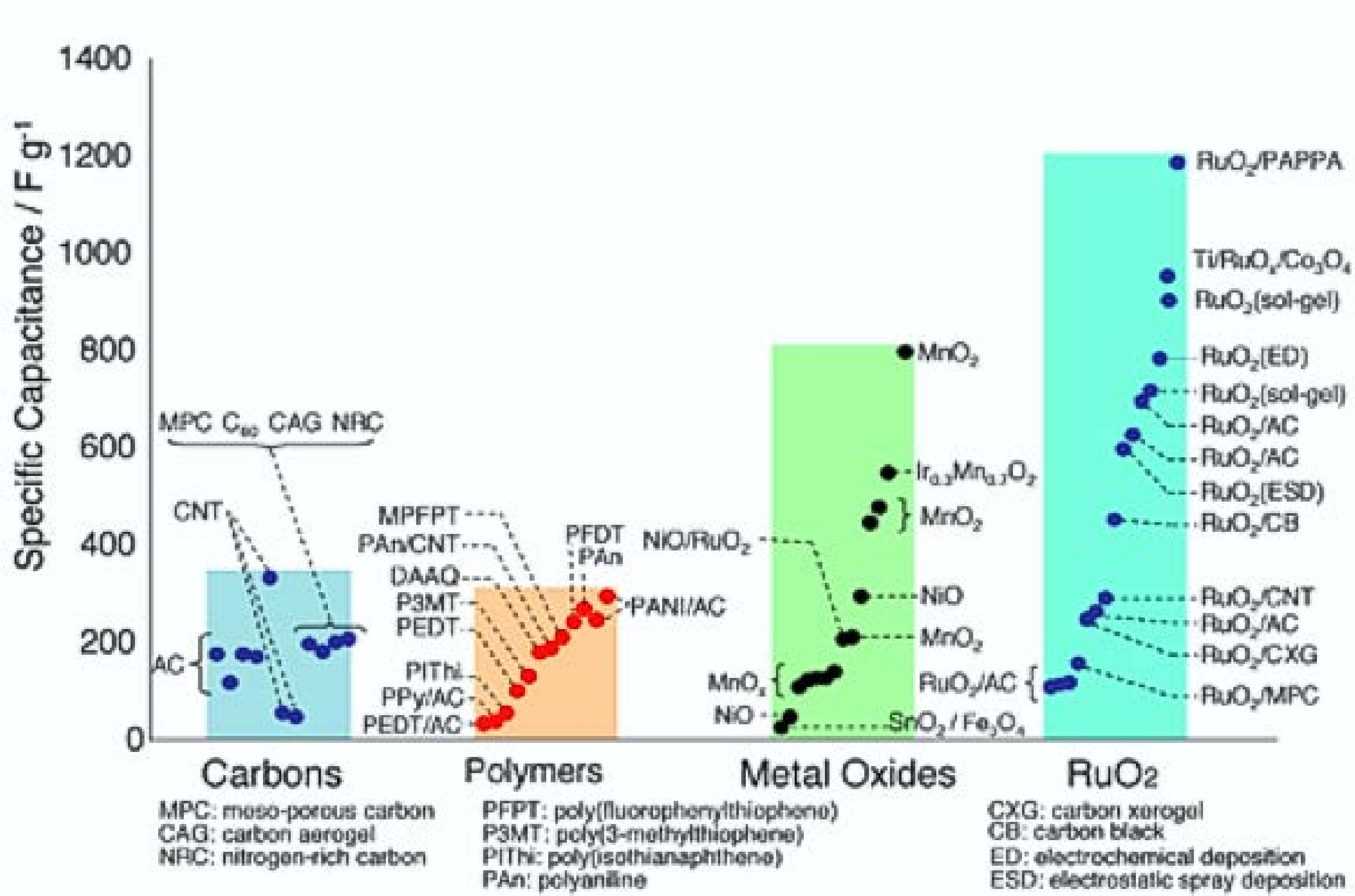
Poly(o-methoxyaniline) - *POMA*



$$Ru^{IV}O_2 + xH^+ + xe^- \rightleftharpoons Ru^{IV}_{1-x}Ru^{III}_{x}O_2H_x$$

* *Eric Smalley, "Ultracapacitors: Emerging Technologies for High-Power Energy Storage", Emerging Technologies Report, Energy Research News*

PROPOSED PSEUDOCAPACITOR MATERIALS AND SPECIFIC CAPACITANCE



* *Katsuhiko Naoi and Patrice Simon, "New Materials and New Configurations for Advanced Electrochemical Capacitors", The Electrochemical Society Interface, Spring 2008*

RELATIVE MERITS OF PSEUDOCAPACITORS

- *ADVANTAGES*:
- Larger capacity than electric double-layer capacitors
- Can bridge gap between ultracapacitors and batteries

- *DISADVANTAGES*:
- Lower power
- Electrode instability, particularly for polymers, which leads to shorter lifetimes
- Cost, particularly for higher-performance, scarce transition metal oxides like ruthenium

PSEUDOCAPACITORS

R&D DIRECTIONS:

- Non-carbon electrode materials, especially high-surface-area nanostructured metal oxides
- Nanostructured carbon including carbon nanotubes as supports for pseudocapacitive nanoparticles

APPLICATIONS:

- Could replace batteries for high-power applications, such as in renewable energy storage.

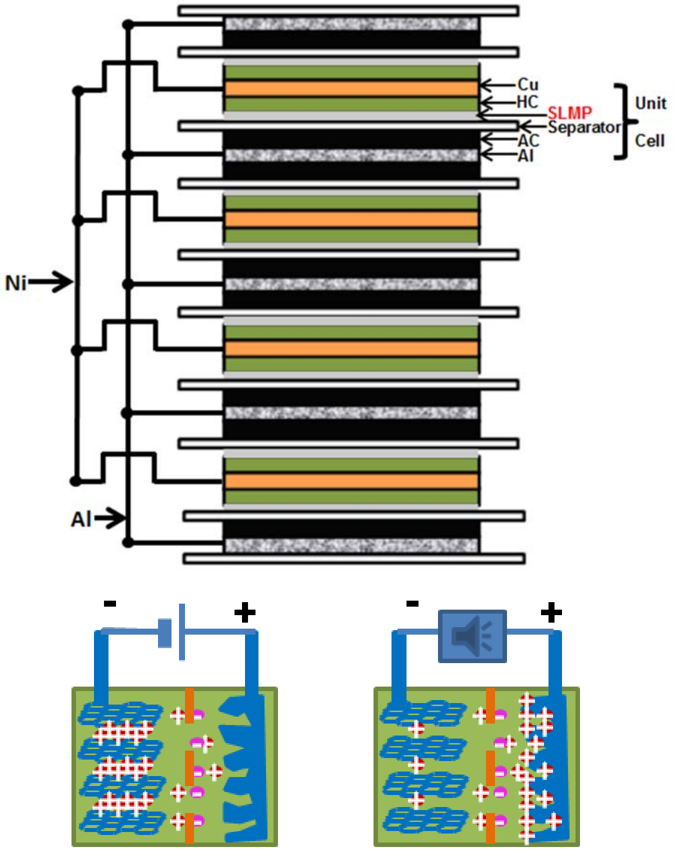
ASYMMETRIC / HYBRID CAPACITORS

- Two different types of electrodes
- Increased overall capacitance
- Several variations of these types of capacitors

R&D APPROACHES FOR ASYMMETRIC ECS

Lithium Capacitors Using Carbon-Carbon Electrodes at Florida State University - FSU

- Similar to battery – **Ions are consumed**
- **22 Wh/kg** - 3 times higher than traditional supercapacitors.
- **Limit - 30-35 Wh/kg** – higher than lead acid battery.
- Time constant about **10 sec**.
- Power greater than **2.5 kW/kg**.
- **Operational voltage** greater than **3.9 V**.



Two-electrode lithium Capacitors

* *W. Cao and J.P Zheng, "High Energy Density Lithium Capacitors Using Carbon-Carbon Electrodes", Department of Electrical and Computer Engineering, Florida State University (FSU), Tallahassee, FL*

Maxwell family of electrochemical capacitors and modules

Maxwell Technologies, Inc.,
http://www.maxwell.com/ultracapacitors/

Ioxus family of electrochemical capacitors and modules [*]

Ioxus, Inc., *http://www.ioxus.com/*

General Capacitor LLC

132-1 Hamilton Park Dr,
Tallahassee, FL 32304, USA

American Lithium Energy Corp.

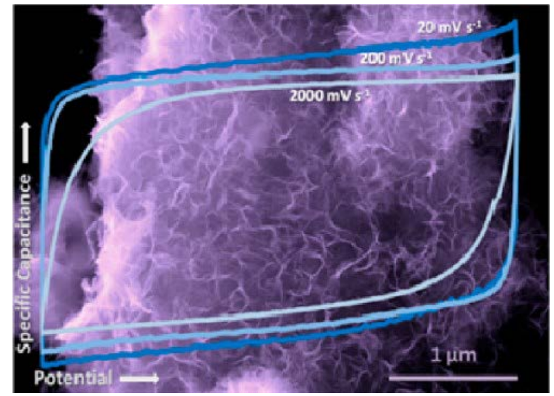
1485 Poinsettia Avenue STE 118
Vista, CA 92081

R&D APPROACHES FOR ASYMMETRIC ECS

Sponge-like Graphene Nanoarchitectures with Ultrahigh Power Density*

- **<u>Ionic liquid-based electrochemical capacitor</u> electrodes that operate at very high scan rates**
- **<u>Microwave synthesis process</u> of cobalt phthalocyanine molecules templated by acid-functionalized multiwalled carbon nanotubes to create electrode materials**
- **Sequential molecular synthesis and carbonization process <u>complete in less than 20 min</u>**
- **In aqueous electrolyte, <u>specific capacitance of 3D electrode fades significantly slower than that of 2D platelets</u> with higher current density**
- **<u>Stable in both ionic liquids and 1 M H2SO4</u>, retaining 90 and 98% capacitance after 10 000 cycles**
- **Delivers an energy density of <u>7.1 Wh/kg</u> at an extra high power density of <u>48 kW/kg</u>**

a.



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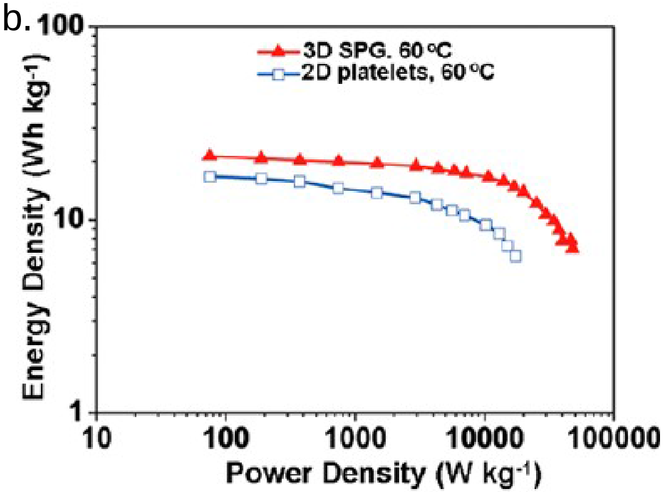


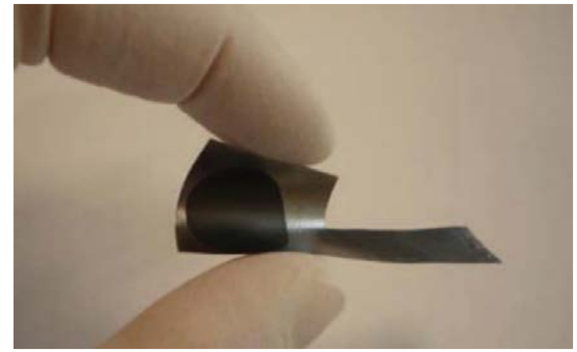
(a) Electrochemical performance of SPG in IL
(b) Ragone plots of 3D SPG and 2D platelets)

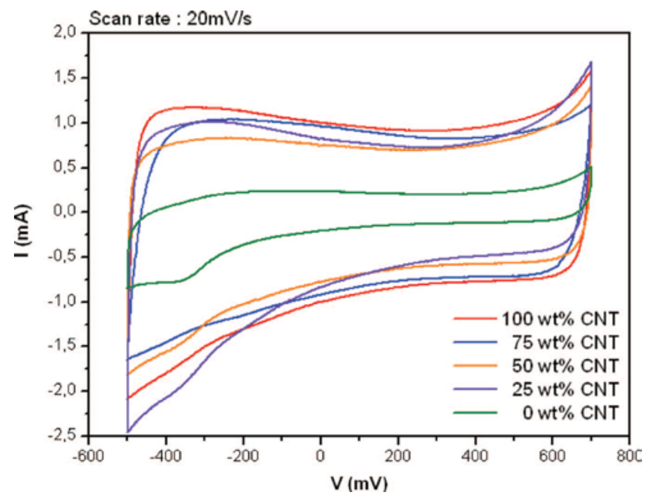
* *Zhanwei Xu, et al., Chemical and Materials Engineering, University of Alberta, National Institute for Nanotechnology (NINT), National Research Council of Canada, Edmonton, Alberta, J. Phys. Chem. Lett. 2012, 3, 2928−2933*

R&D APPROACHES FOR ASYMMETRIC ECS

Mixtures of Graphite and Carbon Nanotubes Deposited Using a Dynamic Air-Brush Deposition Technique *

- **<u>suitable for industrial fabrication</u>**
- **<u>highly uniform and reproducible mats</u>**
- **mixture of 75% of graphite and 25% of CNTs increases the <u>power by a factor 2.5</u> compared to bare CNT-based electrodes**
- **Electrodes made of 50% of CNTs and graphite mixture and organic electrolyte ($TEABF_4$) gives specific energy of <u>30 Wh/kg</u> (5.5 W/kg for 3M $LiNO_3$) and a specific power of <u>265 kW/kg</u> (53 kW/kg for 3M $LiNO_3$).**





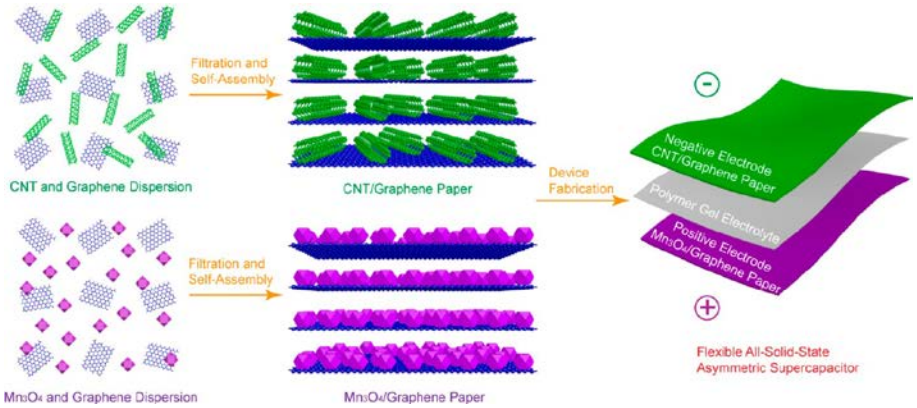
Three-electrodes based measurements, of the electrodes fabricated using different CNTs and Graphite/Graphene Concentrations - aqueous electrolyte used 3M LiNO3.

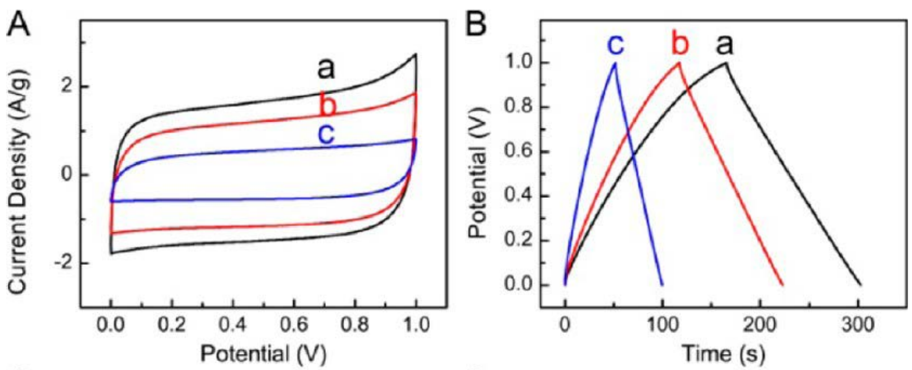
* Paolo Bondavalli, *et al., Thales Research and Technology, Palaiseau, France, Department of Energy Science, Sun Kyun Kwan University, Suwon, South Korea, Journal of The Electrochemical Society, 160 (4) A601-A606 (2013)*

R&D APPROACHES FOR ASYMMETRIC ECS

Free-Standing Carbon Nanotube/Graphene and Mn_3O_4 Nanoparticle/Graphene Paper Electrodes*

- **polymer gel electrolyte of potassium polyacrylate/KCl.**
- **composite paper electrodes with carbon nanotubes or Mn_3O_4 nanoparticles uniformly intercalated between graphene nanosheets**
- **enhanced ion transport**
- **increased cell voltage of 1.8 V,**
- **stable cycling performance (capacitance retention of <u>86.0% after 10 000 cycles</u>**
- **2-fold increase of energy density (<u>32.7 Wh/kg @ 0.5A/g)</u>**





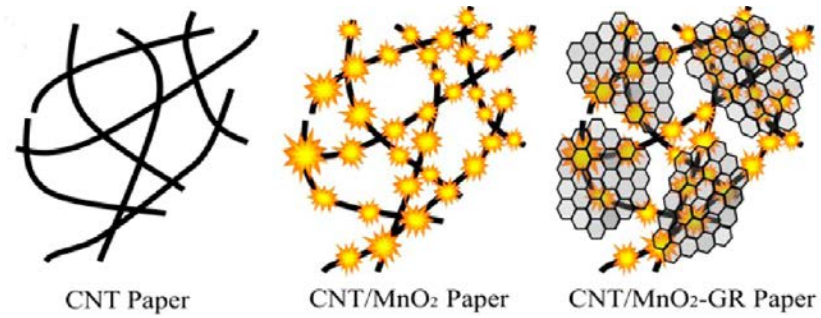
(A) Cyclic voltammograms of CNTG-40 (a), CNTG-20 (b), and rGO (c) papers at a scan rate of 20 mV/s.
(B) (B) Galvanostatic charge/discharge curves of CNTG-40 (a), CNTG-20 (b), and rGO (c) papers at a current density of 0.5 A/g.

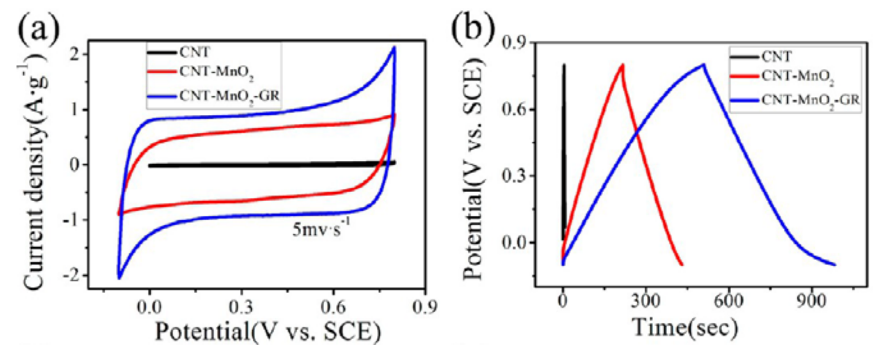
* *Hongcai Gao et al., School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore*
ACS Appl. Mater. Interfaces 2012, 4, 7020−7026

R&D APPROACHES FOR ASYMMETRIC ECS

Graphene-Patched CNT/MnO2 Nanocomposite Paper Electrodes

- **ternary composite paper prepared by electrochemical deposition of MnO_2 on a flexible CNT paper and adsorption of GR on its surface to enhance the surface conductivity of the electrode and prohibit MnO_2 nanospheres from detaching from the electrode**
- **GR enhances capacitance of the composite from 280 F/g to 486.6 F/g**
- **prepared CNT/polyaniline/CNT/MnO_2/GR asymmetric supercapacitor with composite paper as electrode and aqueous electrolyte gel**
- **operating cell voltage of 1.6 V with energy density of 24.8 Wh/kg (9.7 Wh/kg @ 1V) based on weight of composite paper**





Electrochemical tests: (a) CV curves (5 mV/s); (b) charge/discharge curves (500 mA/g)

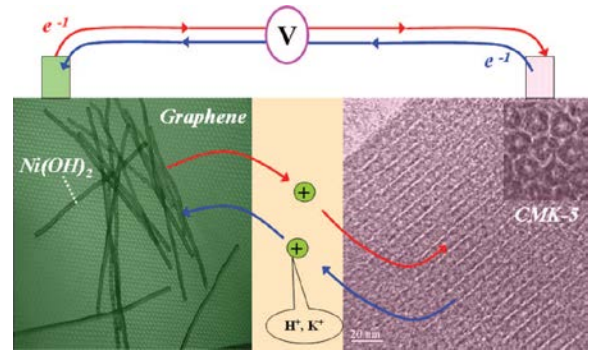
** Yu Jin et al., Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, Suzhou*
ACS Appl. Mater. Interfaces 2013, 5, 3408−3416

R&D APPROACHES FOR ASYMMETRIC ECS

Graphene-Supported Ni(OH)2-Nanowires and Ordered Mesoporous Carbon CMK-5 *

- **graphene-supported Ni(OH)2-nanowires and CMK-5 were used as the positive and negative electrode, respectively, to form hybrid supercapacitor**
- **alkaline electrolyte (6 M KOH)**
- **cell voltage (V) of the hybrid supercapacitor is 1.4 V**
- **Ni(OH)2-nanowires display ultrafast charge-discharge rate**
- **Maximum specific power density of <u>40840 W/kg</u> with a high energy density of about <u>17.3 Wh/kg</u>**

a.



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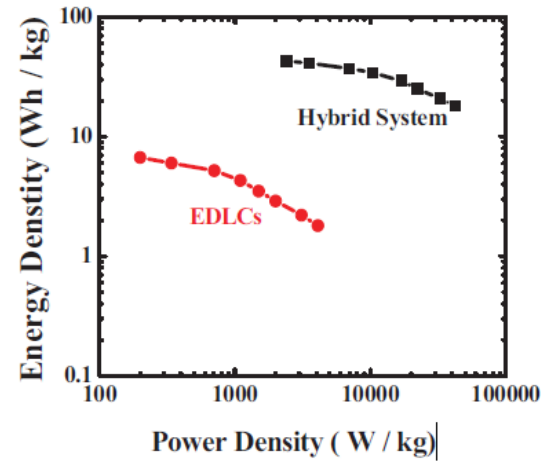


**a.) Schematic representation of operating principle of the developed
hybrid supercapacitor based on graphene-supported Ni(OH)2-nanowires (positive electrode) and CMK-5 (negative electrode).
b.) Ragone plot of Hybrid System and EDLC**

* *Yonggang Wang, et al., Institute of New Energy, Fudan University, Shanghai, China, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang, Journal of The Electrochemical Society, 160 (1) A98-A104 (2013)*

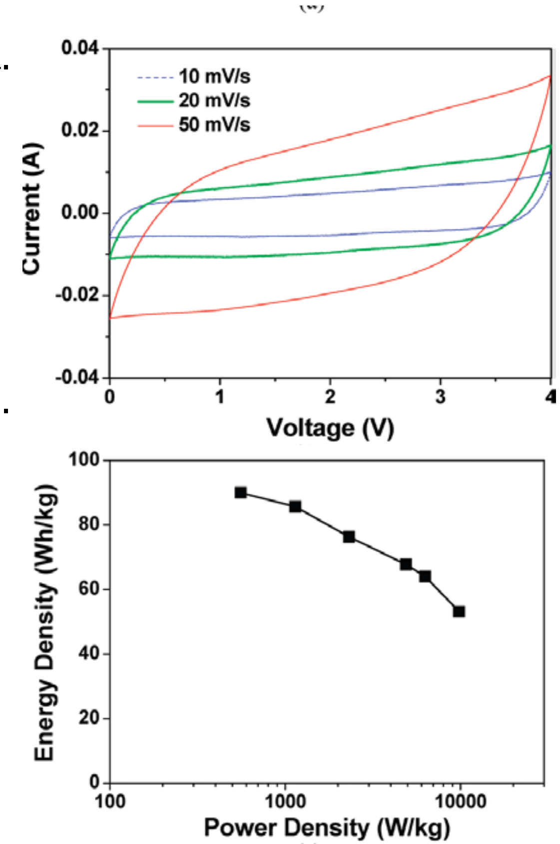
R&D APPROACHES FOR ASYMMETRIC ECS

Graphene-Based Supercapacitor with an Ultrahigh Energy Density *

- **full utilization of the highest intrinsic surface capacitance and specific surface area of single-layer graphene by preparing curved graphene sheets that will not restack face-to-face**
- **electrodes contained 5 wt % Super-P and 10 wt % polytetrafluoroethylene (PTFE) binder**
- **ionic liquid electrolyte was 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4)**
- **4V operating voltage**
- **Celguard-3501 porous membrane separator**
- **specific energy of 21.4-42.8 Wh/kg (derated from 85.6 Wh/kg for total electrode weight only)**

a.

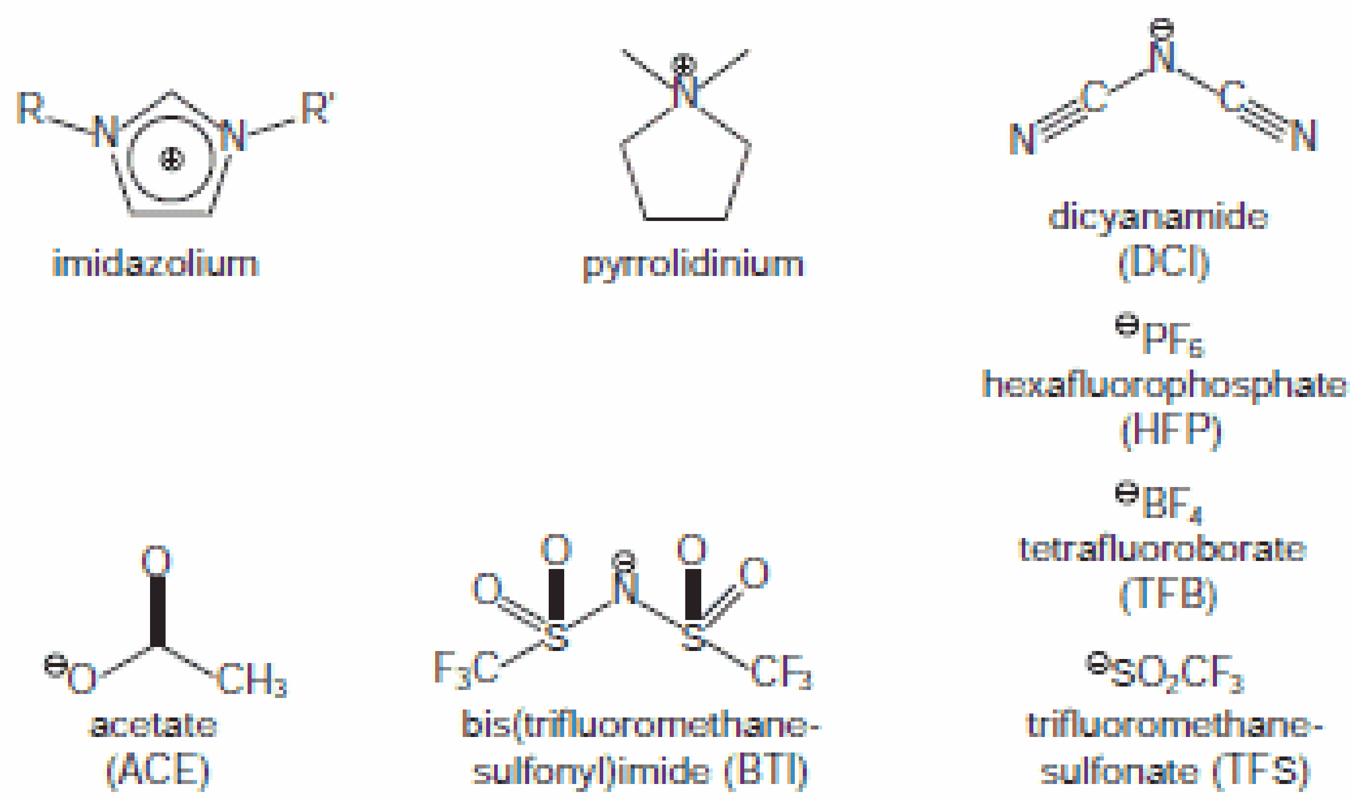
b.



a. **cyclic voltammograms for graphene electrode at different scan rates using EMIMBF4 ionic liquid electrolyte**
b. **Ragone plot of graphene supercapacitor**

* *Chenguang Liu, et al., Nanotek Instruments, Inc. and Angstron Materials, Inc., Dayton, Ohio, Dalian University of Technology, China, Nano Lett. 2010, 10, 4863-–4868*

COMMON CATIONS AND ANIONS FOUND IN IONIC LIQUIDS



* ***John D. Stenger-Smith, Jennifer A. Irvin****, Material Matters* ***2009****, 4.4, 103*

ULTRACAPACITOR APPLICATION AREAS

(from Maxwell)

TRANSPORTATION:

- Regenerative braking and acceleration on hybrid buses.
- Truck starting in cold climates.
- Start-stop automotive systems, and absorbing energy in hybrid vehicles.
- Capture and provide power for electric trains.
- Open aircraft doors in event of power failure.

UTILITY LOAD LEVELING, POWER CONDITIONING:

- Immediate back-up power for computer centers and other systems before diesels start.
- Large scale utility power grids.

GREEN ENERGY:

- Blade pitch systems for wind turbines.

MILITARY APPLICATIONS

- *COMMUNICATIONS*, since many transmissions are in energy bursts
- *POWER INTERRUPTION BUFFER*, power back-ups in avionics
- *LASER TARGETING*
- *SENSORS*, involving long low power listening periods, and short bursts of data transmission
- *DIESEL ENGINE COLD START*
- *TACTICAL LED FLASHLIGHT E2-D*
- *PHASED ARRAY RADAR*

POTENTIAL MODES OF FAILURE

- *ELECTROLYTE AND ELECTRODE BREAKDOWN*, especially at high charging voltages
- *CELL REVERSAL*, especially after long cycling and unbalanced cell decay
- *GAS GENERATION* and subsequent loss of electrolyte
- *SEPARATOR BREAKDOWN*

FUTURE R&D AREAS

- NEW ELECTRODE MATERIALS:
  nanomaterials, carbon nanotubes, graphene
- NOVEL ELECTRODES
- IONIC LIQUIDS
- HYBRID CAPACITORS