

Presentation for the Nanotechnology Speaker Series, McLean, VA

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Supercapacitors and Other Nano-Enabled Energy Systems

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MITRE Nanosystems Group

10 May 2006

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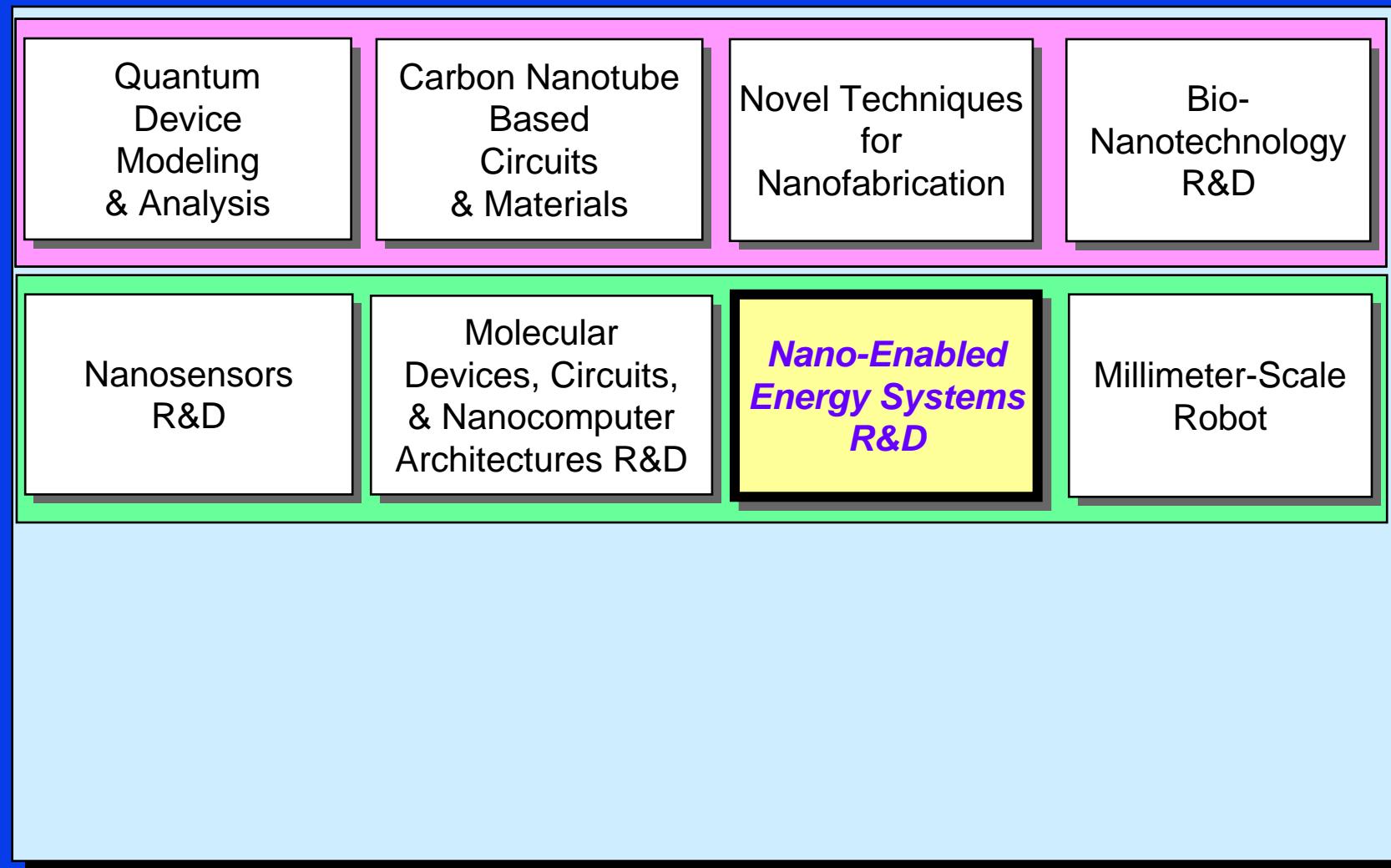
Basis for this Presentation: 14 Years of Nanotechnology R&D at MITRE

Targeted Basic Science and Technology

Applications Focused on the National Need

MITRE

Basis for this Presentation: 14 Years of Nanotechnology R&D at MITRE

**MITRE**

Recently Published A Paper Reviewing Research on Supercapacitors

- Discusses
 - Types of supercapacitors and operational principles
 - Strengths and weaknesses
 - R&D survey and prospectus
- Hardcopies available here today
- Also, a pdf softcopy is in my transfer folder

Supercapacitors: A Brief Overview

Marin S. Halper
James C. Ellenbogen

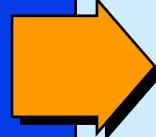
March 2006
MP 05W0000272

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McLean, Virginia

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Outline of this Presentation

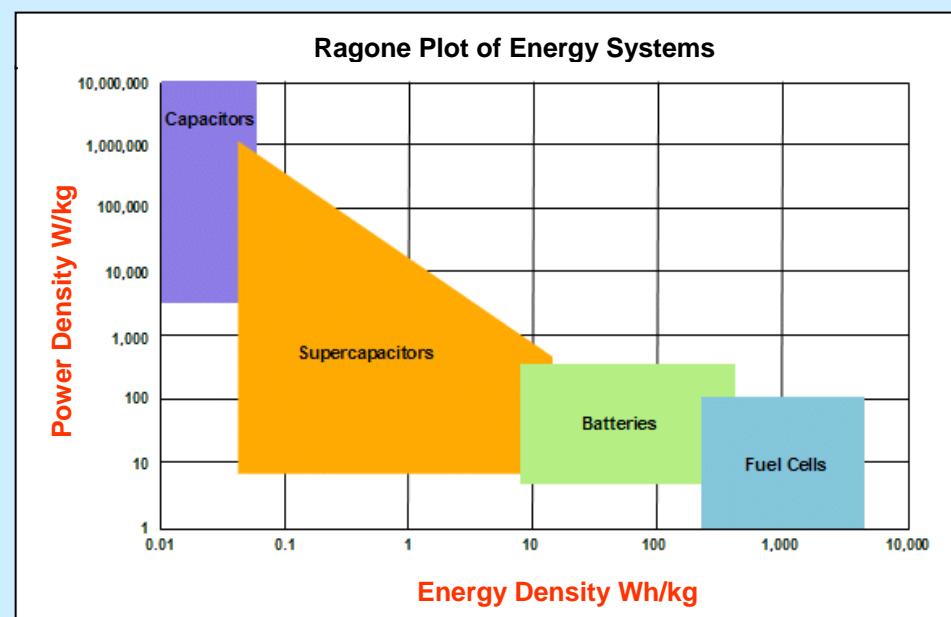
- Introduction



- Background & Motivation for Nano-Enabled Energy Systems
- The Landscape of Nano-Enabled Energy Systems
- Supercapacitors, a Particularly Promising Energy System
 - What is a Supercapacitor?
 - Types of Supercapacitors
 - Applications for Supercapacitors
 - The Future of Supercapacitor R&D

Background on Energy & Power

- The terms “energy” and “power” often are used interchangeably, but mean different things
 - Energy is the capacity for a device to do work
 - Power is how fast energy can be delivered from the device, i.e. work per unit time
- These measurements are often divided by device mass to yield a “density”
- A Ragone plot can be used to visualize the trade-off between the energy and power density for energy systems



Plot adapted from www.cap-xx.com

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Motivation for Nano-Enabled Energy Systems: Energy & Power Requirements are Changing

- Applications for and number of conventional electronic systems are growing rapidly
 - Energy and power required for these systems is outpacing the current technology supply
 - Size and weight are becoming significant issues
- Applications under development that require novel, smaller and lighter energy systems
- New, revolutionary fabrication makes possible these applications, but development is limited by available energy systems

Applications with Expanding Energy & Power Needs

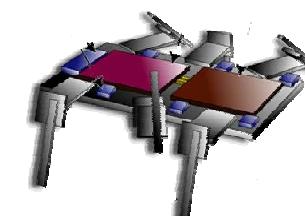
Personal Electronics



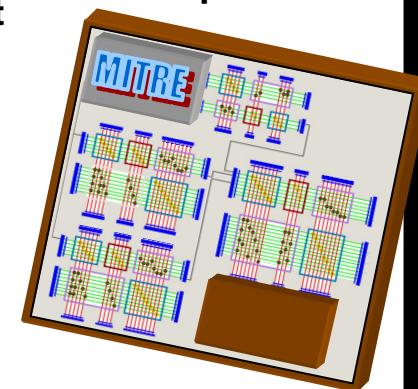
Electric Vehicles



MITRE Millirobot



MITRE Design for Nanoprocessor



Top Left Graphic from www.wintouch.com/websphere-pda.htm

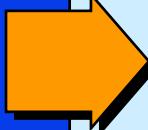
Top Right Graphic from world.honda.com/fuelcell/fcx

Nanotechnology Can Improve Energy Systems

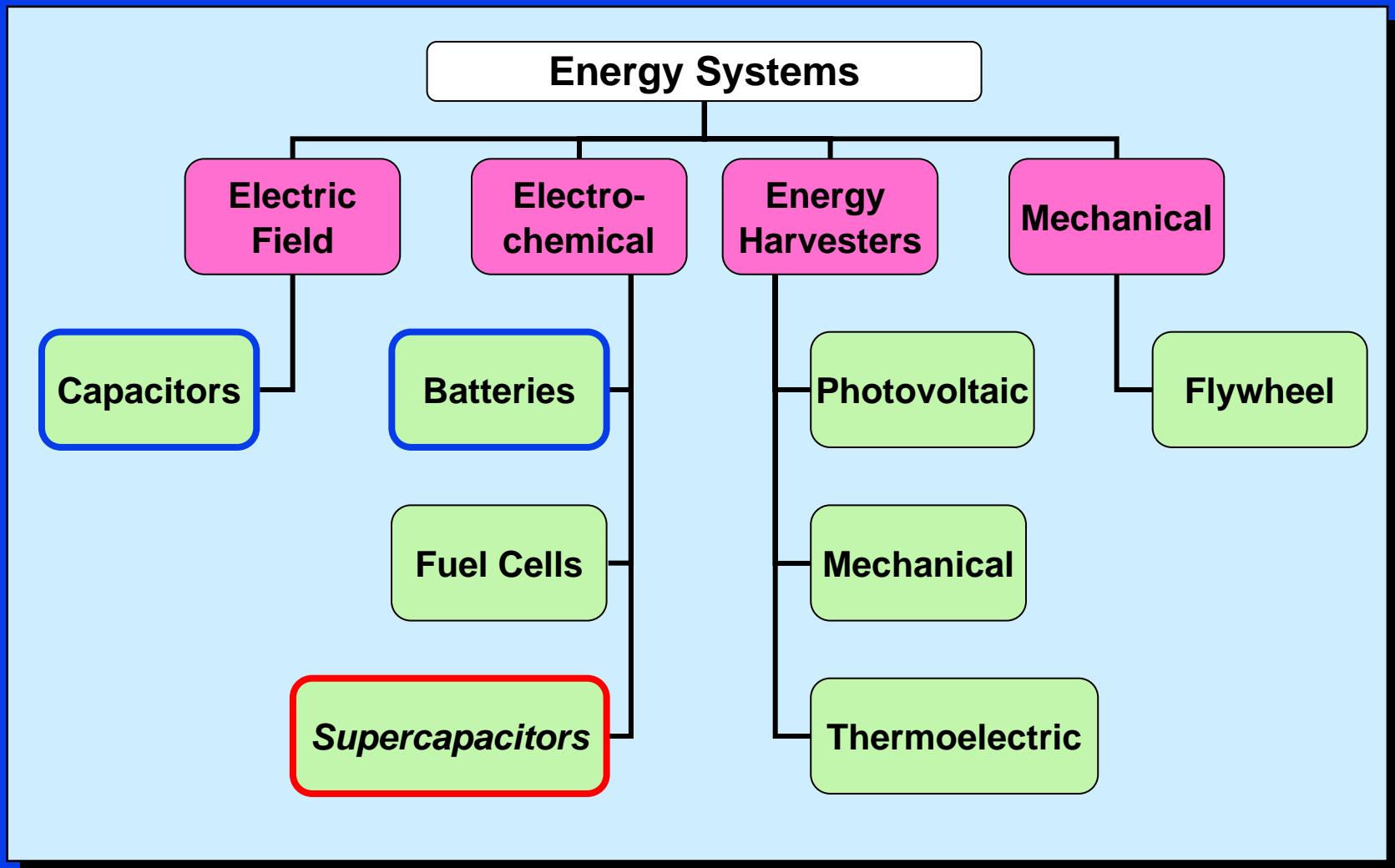
Nanomaterials (e.g. nanotubes and nanowires) have many superior properties and behaviors, such as high surface area, conductivity, and structural strength

- **Large surface area of nanostructured components**
--can increase energy and power densities
- **High degree of order in materials used in components**
--can channel energy more efficiently throughout the device
- **Size, weight, & performance of systems can be tailored**
--to fit the requirements for a wide range of applications

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General Types of Energy Systems



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Two Thrusts for Nano-Enabled Energy Systems

Ultra-small energy systems

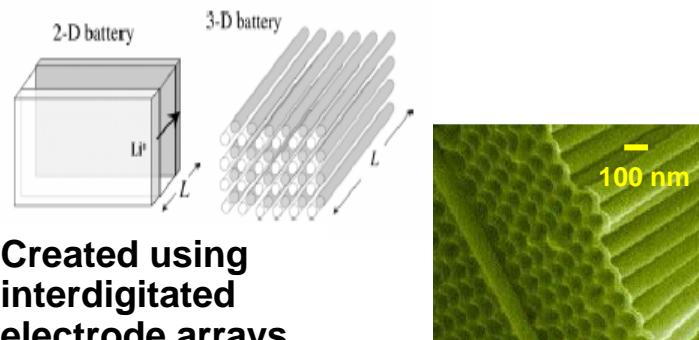
- Nanotechnology is used to shrink the size and weight of energy systems
- Energy & power densities are preserved with scale, with careful design and fabrication

● Macroscale energy systems

- Larger systems are enhanced with nanoscale structures
- Nanotechnology is used to increase energy and power densities, improve efficiency, decrease weight, etc.

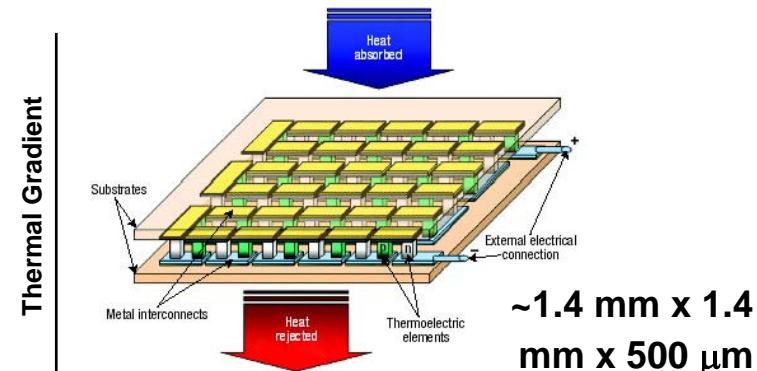
Examples of Nano-Enabled, Ultra-Small Energy Systems

3-D Nanobattery



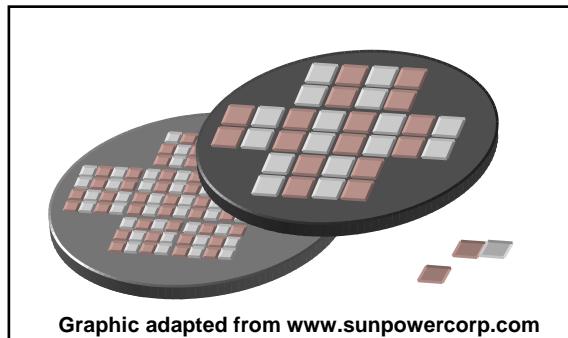
Graphics from Long, et al., *Chem. Rev.*, 104, 4463, 2004 and *C&EN*, 79, 29, 2001

JPL-Caltech Thermoelectric Device



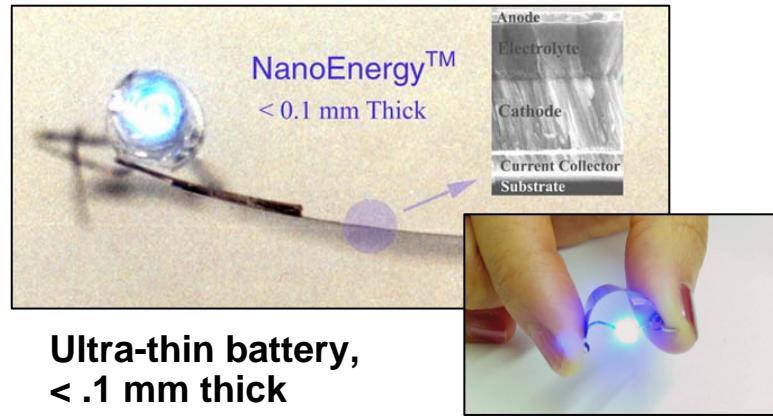
Graphic from Fleurial, et. al., *NatureMaterials* Aug 2003

SunPower Photovoltaic Device



Customizable solar cells, ~2.3 x 2.3 mm

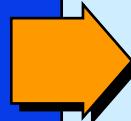
NanoEnergy Thin Film Battery



Two Thrusts for Nano-Enabled Energy Systems

- Ultra-small energy systems

- Nanotechnology is used to shrink the size and weight of energy systems
- Energy & power densities are preserved with scale, with careful design and fabrication



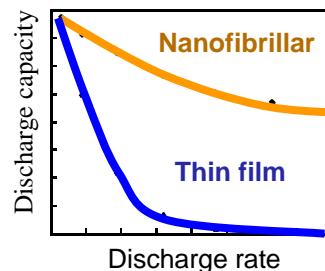
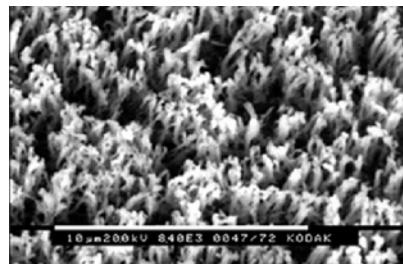
Macroscale energy systems

- Larger systems are enhanced with nanoscale structures
- Nanotechnology is used to increase energy and power densities, improve efficiency, decrease weight, etc.

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Examples of Nano-Enabled, Macroscale Energy Systems

Improved Li-Ion Batteries

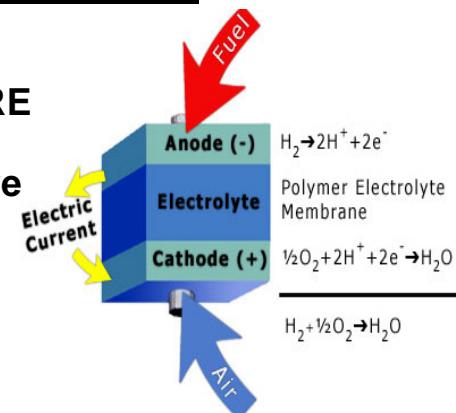


Nanostructured electrode

Graphics from Singhal et al., *J. Power Sources*, 129, 38, 2004

PEM Fuel Cells

Research at MITRE has shown how CNTs can improve PEM Fuel Cell performance



Graphic from <http://www.savett.com/about/research.php>

Thin-film Photovoltaic Fabric



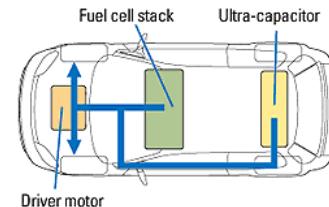
Roll to roll processing yields photoactive "fabrics"...



...which can be printed in a range of patterns or colors

Graphics from www.konarka.com

Supercapacitors for Electric Vehicles



Provides power boosts needed for startup and acceleration

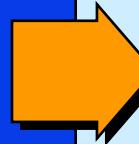


Graphics from world.honda.com/fuelcell/fcx

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- Background & Motivation for Nano-Enabled Energy Systems
- The Landscape of Nano-Enabled Energy Systems



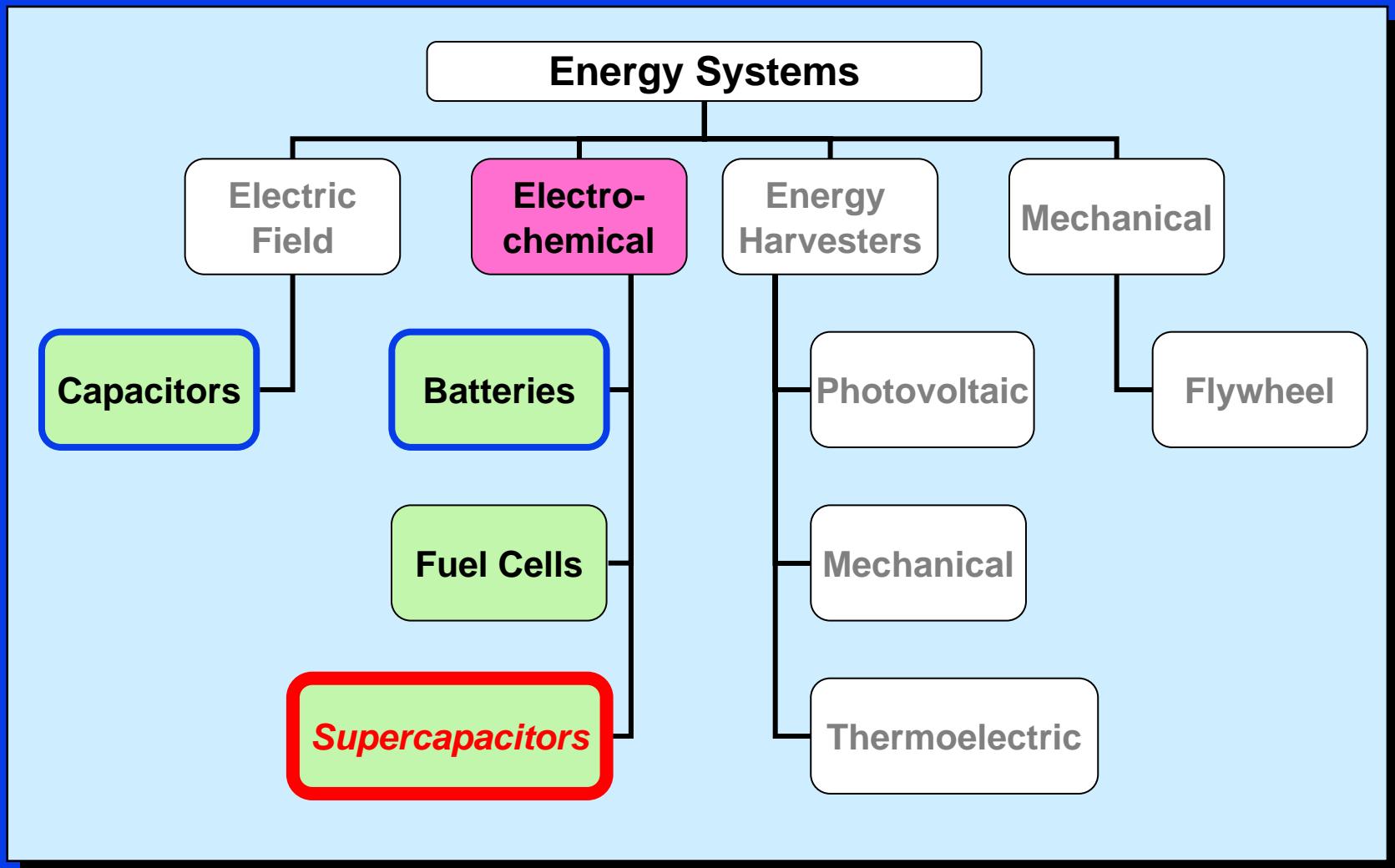
Supercapacitors, a Particularly Promising Energy System

- What is a Supercapacitor?
- Types of Supercapacitors
- Applications for Supercapacitors
- The Future of Supercapacitor R&D

Supercapacitors, both small and large, may facilitate major advances in energy storage

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General Types of Energy Systems



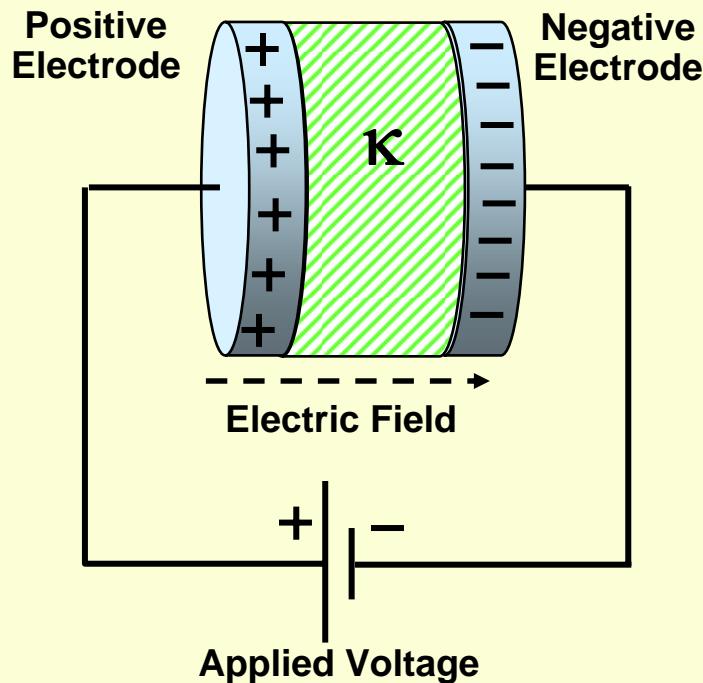
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Why Supercapacitors?

- **Nanotechnology is enabling ultra-small supercapacitors, as well as macroscale supercapacitors**
 - Supercapacitors are very scalable--performance scales well with size and weight
 - Supercaps can be designed to fit virtually any form factor
- **Supercapacitors can achieve a wide range of energy and power densities--have the largest area on a Ragone plot**
- **Also, have many other desirable characteristics, e.g. rapid charging times, high cycling stability, temperature stability**
- **Thus, supercapacitors can be designed to address a wide range of applications**

Background on Conventional Capacitors

Schematic of Essential Components of Conventional Capacitor



Fundamental Equations

$$C = \kappa \epsilon_0 \frac{A}{D}$$

$$E = \frac{1}{2} CV^2$$

$$P_{\max} = \frac{V^2}{4 \times ESR}$$

κ : Dielectric Constant

ϵ_0 : Permittivity of Vacuum

A: Surface Area

d: Electrode Distance

V: Voltage

ESR: Equivalent Series Resistance

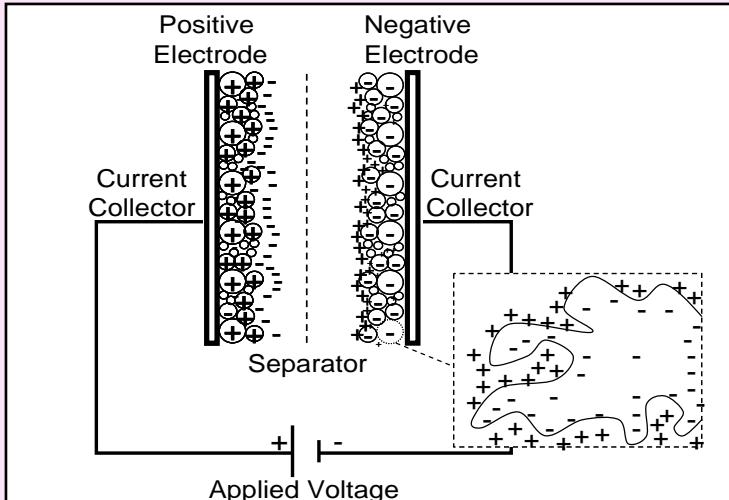
- Capacitance is proportional to electrode surface area (A)
- Energy is proportional to capacitance (C)
- Maximum power is limited by the internal resistances (ESR) of a capacitor

What is a Supercapacitor?

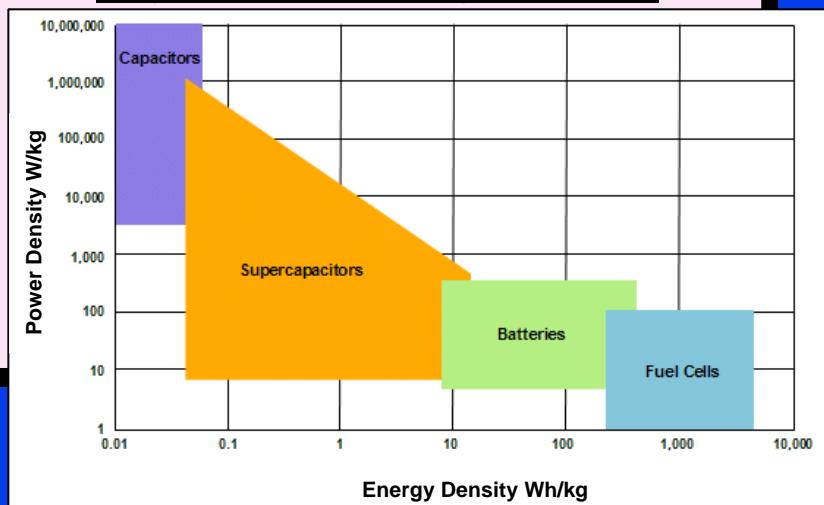
- Also known as ultracapacitor, electrochemical capacitor
- Distinguished by its great capacitance derived from
 - Molecule-thin dielectrics
 - High surface area, nanostructured electrodes
 - In some cases, charge transfer reactions similar to those in batteries
- In between conventional capacitors and batteries in design and performance

EDLC = Electrochemical Double Layer Capacitor
 Plot adapted from www.cap-xx.com

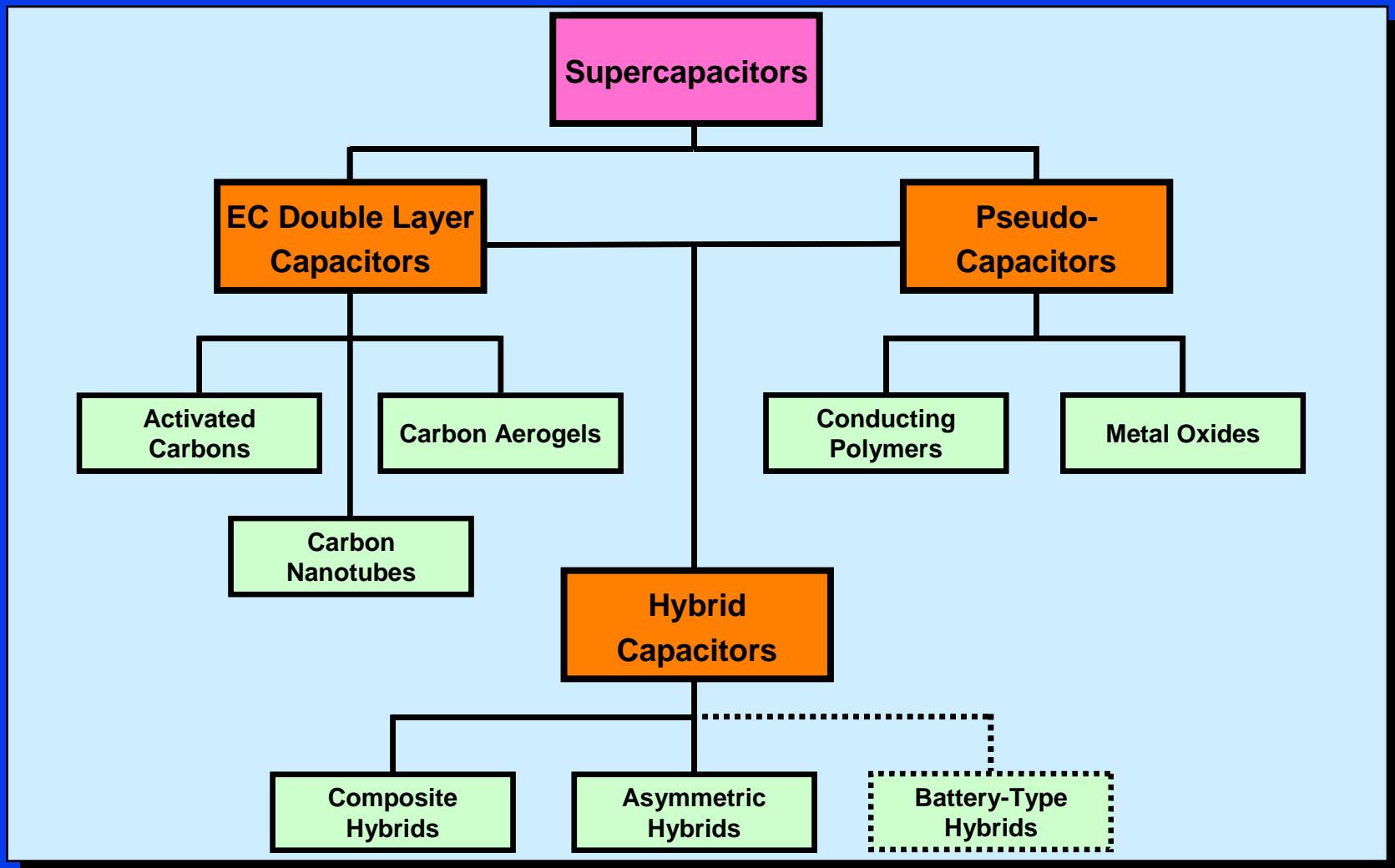
Schematic of an EDLC Supercapacitor



Ragone Plot of Energy Systems



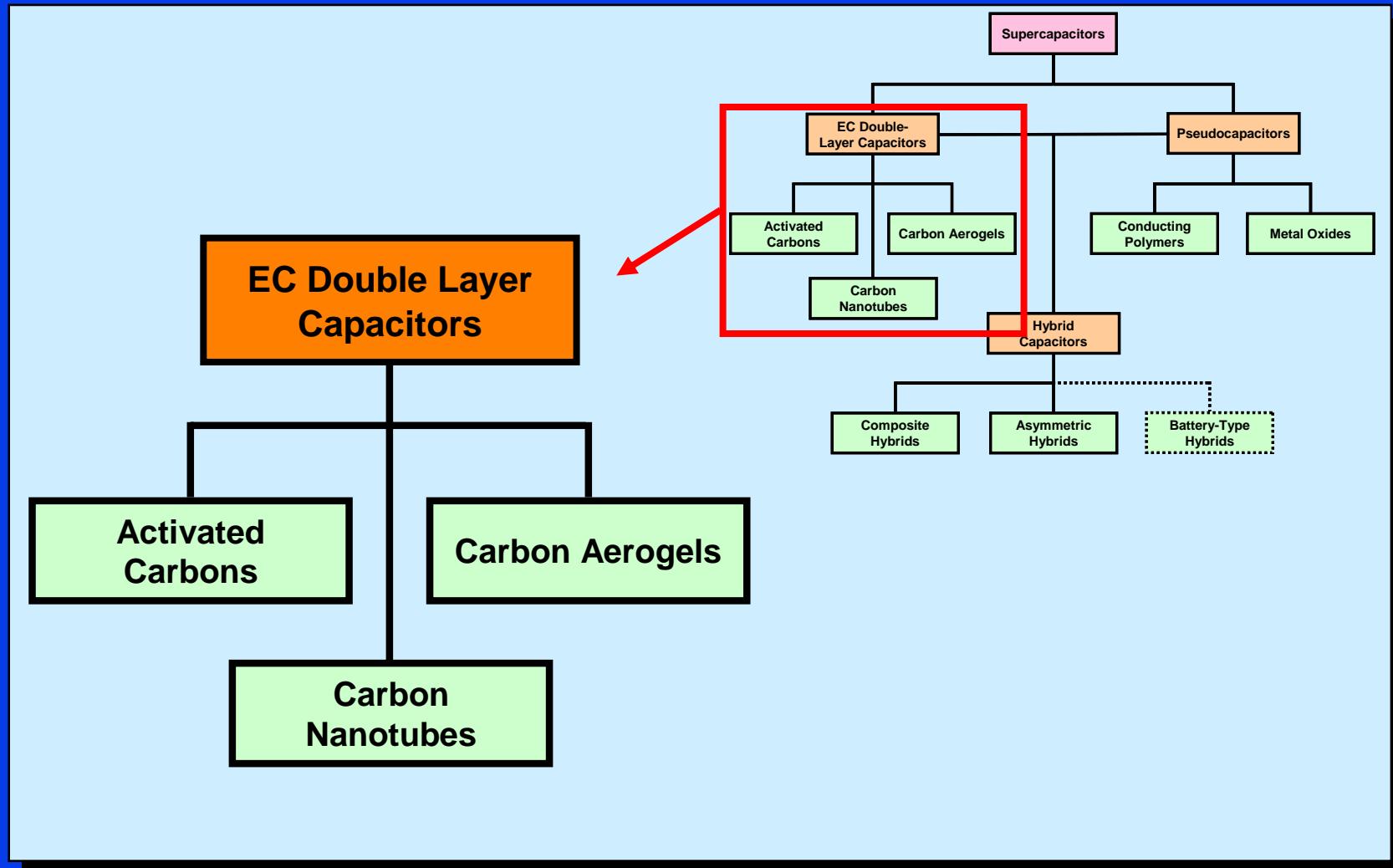
Taxonomy of Supercapacitors



EC = Electrochemical

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Focus on Electrochemical (EC) Double Layer Capacitors

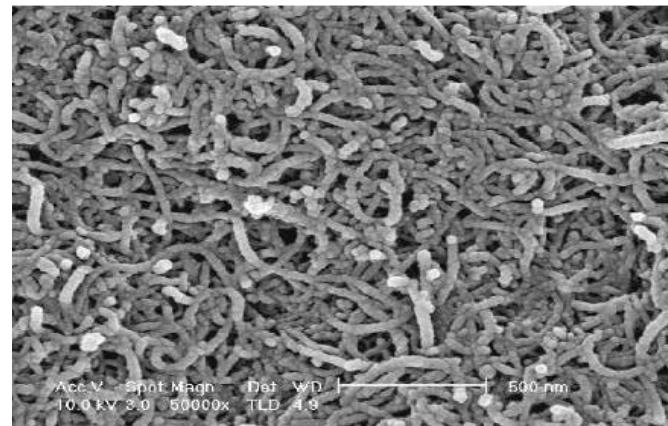


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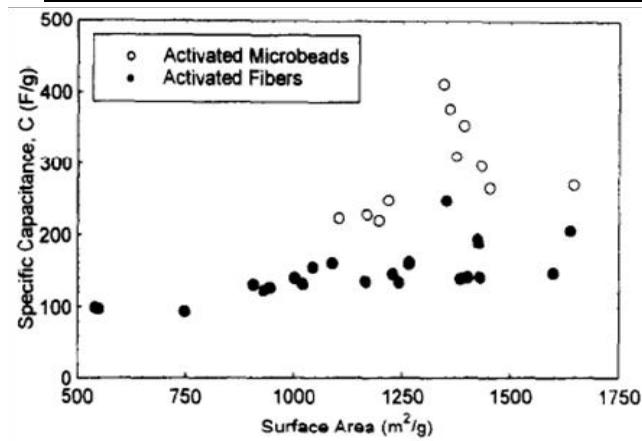
Overview of Electrochemical Double Layer Capacitors

- There is no transfer of charge, *non-Faradaic*
- Two carbon-based electrodes, aqueous or organic electrolyte
- Electrode is made from porous nanostructures-- activated carbon, nanotubes, aerogels
 - Trade-off between pore size, energy, power
 - Small pores have large surface areas, but restrict electrolyte ions
 - Also, small pores increase ESR and lower max power

SEM Image of CNT Electrode



Capacitance vs. Surface Area



Top SEM Image from Kim, et al., ESSL 2005.

Bottom Plot from Shi, EA 1996.

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Advantages & Disadvantages of Electrochemical Double Layer Capacitors

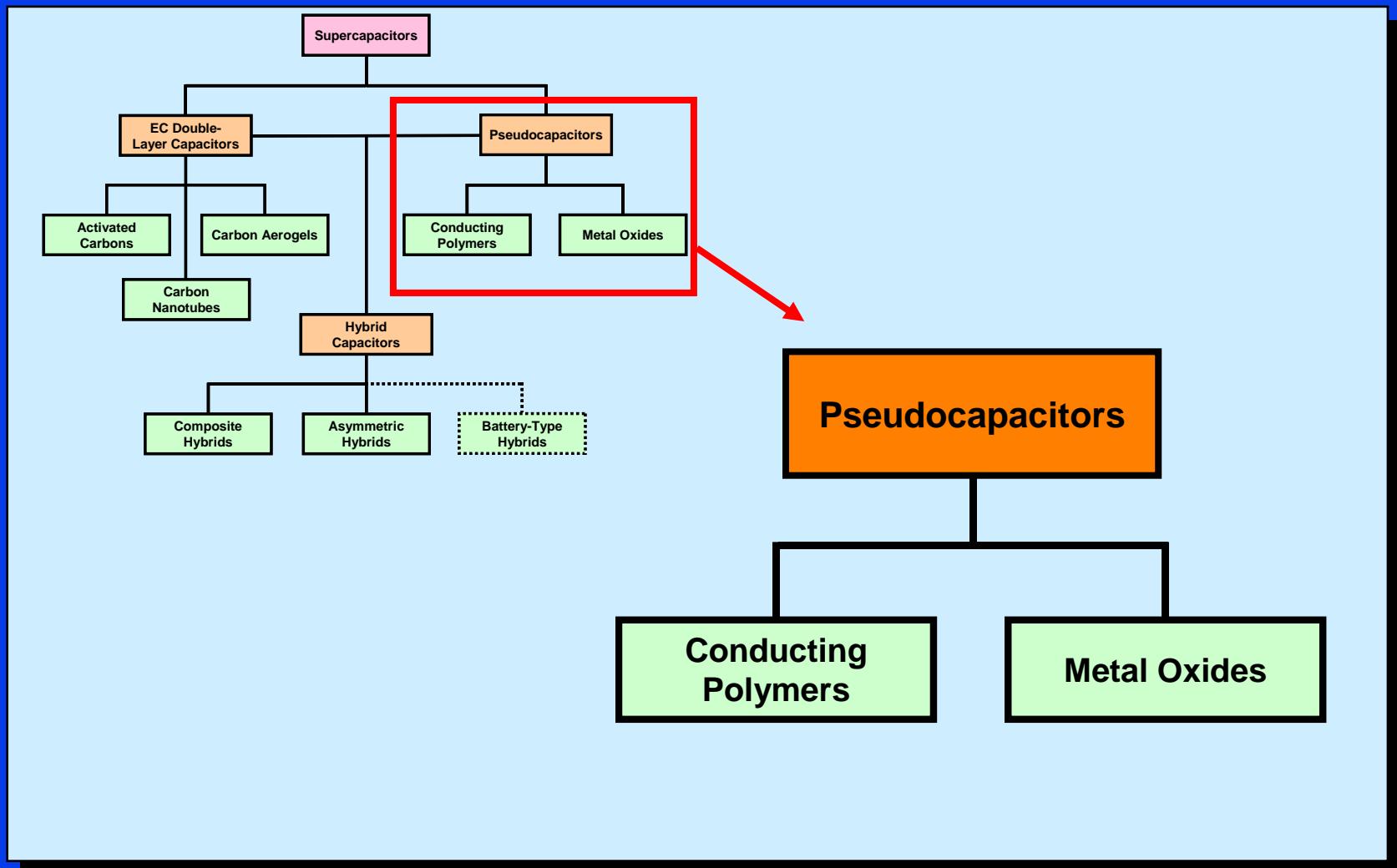
- Advantages:

- High surface area and double layer of charge allows for much higher energy densities than conventional capacitors, comparable power densities
- No chemical or structural change during charge storage -- 10^6 cycles for supercaps compared to 10^3 for batteries
- Work in extreme temperatures and are very safe
- Nanostructured carbon materials are relatively cheap and have well developed fabrication techniques--can achieve wide range of pore distributions, thus energies & powers

- Disadvantage:

Cannot match energy densities of mid-level batteries

Focus on Pseudocapacitors

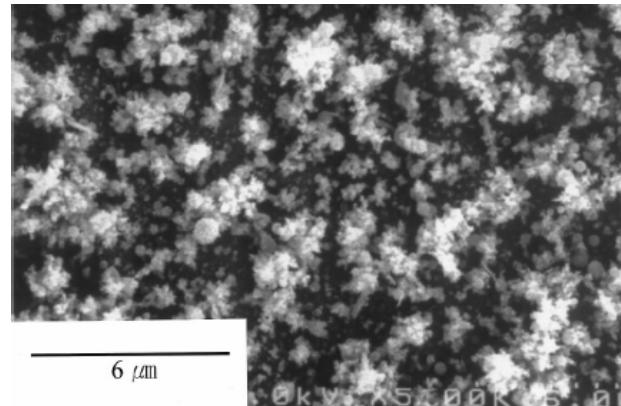


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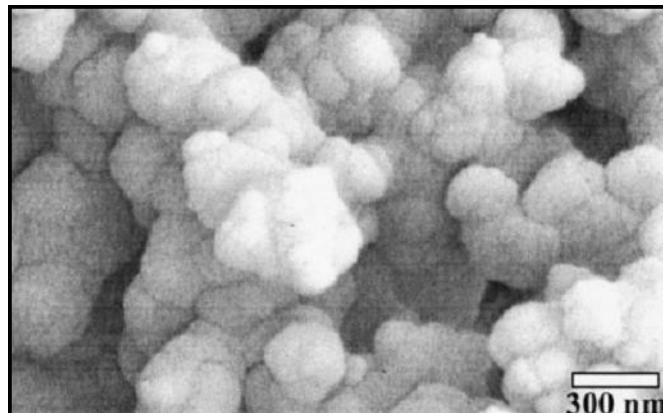
Overview of Pseudocapacitors

- Charge transfer through surface Faradaic, redox reactions
- Similar to EDLCs, but electrodes are made from metal-oxides or conducting polymers
 - Electrolyte ions diffuse into pores and undergo fast, reversible surface reactions
 - Relationship between charge and potential gives rise to a *pseudocapacitance*
 - Can achieve very high capacitances, energies

SEM of Metal-Oxide Electrode



Conducting Polymer Electrode



Top SEM Image from Kim, et al. ESSL 2001.

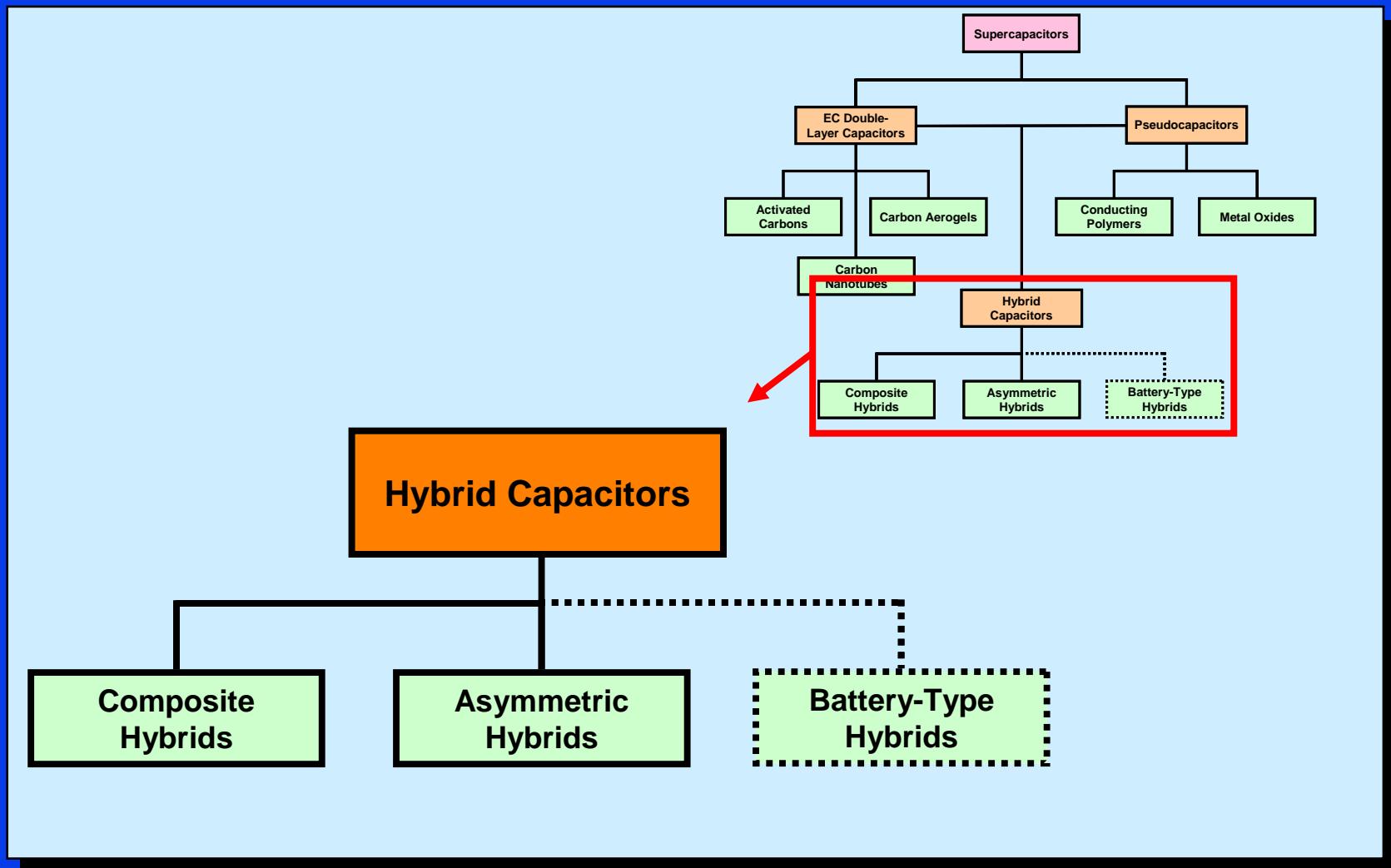
Bottom SEM Image from An et al., JES 2002.

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Advantages & Disadvantages of Pseudocapacitors

- **Advantage:**
High surface area and fast Faradaic reactions allow for higher energy densities than EDLCs--hydrous ruthenium oxide can achieve extraordinary capacitances
- **Disadvantages:**
 - Generally, lower power densities than EDLCs
 - Cycle life can be limited by mechanical stress caused during reduction-oxidation reactions
 - Negatively charged conducting polymer electrodes are not very efficient
 - The best metal-oxide electrodes are very expensive and require aqueous electrolytes, which means lower voltage

Focus on Hybrid Capacitors



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Overview of Hybrid Capacitors

- Charge transfer through a combination of Faradaic and non-Faradaic processes
 - Combine the advantages and mitigate the disadvantages of EDLCs and pseudocapacitors
 - Three types of hybrids
 - Composites integrate carbon and pseudocapacitor materials on each electrode
 - Asymmetrics couple carbon and pseudocap. electrodes
 - Battery-Types couple battery and supercap. electrodes

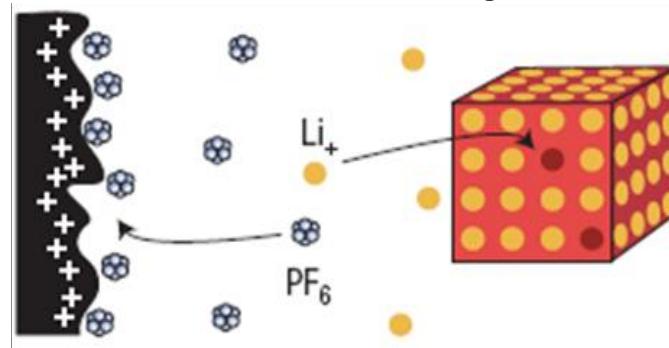
Composite CNT+Polymer Electrode



Battery-Type Configuration

Activated Carbon: Positive Electrode

Nano-Li₄Ti₅O₁₂ Negative Electrode



Top SEM Image from An et al., JES 2002.

Bottom Graphic adapted from Amatucci et al. JES 2001.

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Advantages & Disadvantages of Hybrid Capacitors

- **Advantages:**

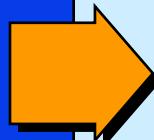
- Most flexible performance characteristics of any supercapacitor--fits the widest range of applications
- Can achieve very high energy and power densities without the sacrifices in cycling stability and affordability

- **Disadvantages:**

- Relatively new and unproven technology
- More research is needed to better understand the full potential of hybrid capacitors

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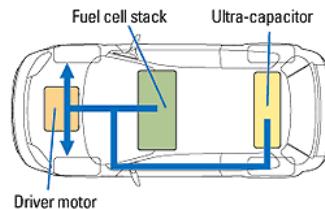
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Potential Applications for Supercapacitors

- | | |
|--|--|
| <ul style="list-style-type: none">● Pulse power systems<ul style="list-style-type: none">– Commercial, e.g. vehicles, cell phones– Medical, e.g. defibrillators– Military & space, e.g. detonators, launchers, lasers, satellites● Load leveling, smoothing, and uninterruptible systems● Quick charge applications, e.g. wireless power tools | <ul style="list-style-type: none">● High cycle life & long lifetime systems--especially when coupled with energy harvesters<ul style="list-style-type: none">– Remote and maintenance free locations, e.g. sensors– Metro buses that start and stop frequently● All-weather applications, e.g. to power Siberian trains● Complement to high energy devices--reduce size and weight, improve performance |
|--|--|

Examples of Existing Supercapacitor Applications

Honda FCX Electric Vehicle



SC charged by braking, provides pulse power for startup & acceleration



Graphics from world.honda.com/fuelcell/fcx

Boeing Radio: Combat Survivor Evader Locator

SC provides backup power for downed pilot locator radio



Graphic from <http://www.boeing.com/defense-space/ic/csel/userequip.html>

SmartSynch Smart Meter System

SC powers wireless meter that transmits data about utility usage



Graphic from <http://www.smartsynch.com/>

High-Res LED Flash Camera Phones



SC allows pulse power needed for camera flash



Graphics from <http://www.cap-xx.com/news/photogallery.htm>

SC = Supercapacitor

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The Future of Supercapacitor R&D

- Reduce the impurities of materials-- *self-discharge* is the biggest problem for commercial supercapacitors
- Improve fabrication & packaging methods, decrease costs
- Reduce the ESR for all components to increase power
- Optimize electrolytes--often limiting factor for supercaps
- Optimize electrodes by understanding the relationship between pore size and ion accessibility, e.g. work at Skeleton NanoLabs
- Further explore hybrid capacitors--the most promising, but least developed supercapacitor technology

Supercapacitors may not replace batteries,
but they have great potential for many applications